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Miscibility and crystallinity of poly(3-hydroxybutyrate)/poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) blends

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Abstract

With the objective of developing new biodegradable materials, the miscibility and the crystallinity of blends of poly(3-hydroxybutyrate), P(3HB), and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), P(3HB-*co*-3HV), have been studied. P(3HB) (300 kg mol^{-1})/P(3HB-*co*-3HV)–10% 3HV (340 kg mol^{-1}) blends were prepared by casting in a wide range of proportions, and characterized by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR). The experimental values for the glass transition temperatures (T_g) are in good agreement with the values provided by the Fox equation, showing that the blends are miscible. It was observed that the T_g and the melting temperature (T_m) decreases with the increase in the P(3HB-*co*-3HV)–10% 3HV content, while the crystallization temperature (T_c) increases. FT-IR analyses confirmed the decrease on the crystallinity of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends with higher copolymer contents. Bands related to the crystallinity were changed, due to the copolymer content that produced miscible and less crystalline blends.

Keywords: Poly(3-hydroxybutyrate); Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); Blends; Miscibility; DSC; FT-IR

1. Introduction

Polyhydroxyalkanoates (PHAs) are a class of naturally occurring biodegradable and biocompatible polyesters that are produced by a wide variety of different microorganisms [1,2]. Since the conventional synthetic polymers have the disadvantage of low microbial decomposition rate and the lifetime of hundreds of years when discarded into the environment, the PHAs have been receiving keen interest, among all natural biodegradable polymers, due to its mechanical properties similar to those of synthetic polymers [3,4].

Poly(3-hydroxybutyrate), P(3HB), discovered by Lemoigne in 1925, is one of the most studied bacterial polyesters in the PHA family [5–7]. P(3HB) is a highly crystalline thermoplastic polymer with a relatively high melting temperature (170–180 °C) and a glass transition temperature in the range from 0 to 5 °C. Mechanically, P(3HB) is a brittle material with a large elastic modulus and high tensile strength [5,6].

The copolymer P(3HB-*co*-3HV), released by ICI in 1983 as Biopol® [8], is more ductile and flexible than P(3HB) due to the presence of 3-hydroxyvalerate (3HV) units in its molecular structure [4,9]. The increase of the 3HV content in the copolymer reduces the melting temperature and crystallinity, however, P(3HB-*co*-3HV) with low 3HV contents (<15 mol%) is quite fragile [10]. Nevertheless, P(3HB) and P(3HB-*co*-3HV) are promising candidates to be widely applied in many areas, including medicine, pharmacology, packaging and agriculture [5,11].

There are many references attempting to blend P(3HB) with other polymers, with the aim of improving its mechanical properties and its utility in daily applications [8]. However, blends of P(3HB) and P(3HB-*co*-3HV) have been barely studied in the literature.

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Differential scanning calorimetry (DSC) is the method of choice to study the phase behavior of polymer blends [5], by the determination of the glass transition (T_g), crystallization (T_c), and melting temperatures (T_m) [12–15,18,19]. In the same way, Fourier transform infrared spectroscopy (FT-IR) has been successfully applied to the studies of crystalline/amorphous phase transition process of polymers, due to the fact that IR absorption bands are very sensitive to changes in intermolecular and intramolecular interactions and conformational changes of polymers [7,10,14,16,18,29,30,31].

The objective of this work was to study the miscibility and the crystallinity of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends by DSC and FT-IR.

2. Experimental

2.1. Sample preparation

The biopolymers were supplied by PHB Industrial (Brazil) with the trade name Biocycle®, in the form of a white fine powder. P(3HB) and P(3HB-*co*-3HV)–10% 3HV used in this work are isotactic configuration (99.5%) and optically actives with “R” form. The specifications of these materials are summarized in Table 1.

P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends were prepared as films by casting. The biopolymers were dissolved in chloroform (1%, w/v for DSC analyses and 0.3%, w/v for FT-IR analyses) and kept under constant agitation. The solvent was then slowly evaporated in saturated atmosphere. The films were dried in a vacuum oven (24 h at 45 °C) and stored in a desiccator. The ratios (w/w) of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends were: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100.

Table 1
Specification of biopolymers

Biopolymer	Identification number	3HV content (mol%)	Molar mass (M_w) (kg mol^{-1})
P(3HB)	57-2	0	300
P(3HB-*co*-3HV)	58-2	10	340

2.2. Differential scanning calorimetry (DSC)

DSC analyses of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends were performed to identify the transition temperatures (T_g, T_c and T_m), the enthalpies of these transitions and the degree of crystallinity. The analyses were carried out in a Shimadzu DSC50 equipment at a heating rate of 10 °C min^{-1} in helium atmosphere. The samples (about 4 mg) were placed in a aluminum vessel, heated from −120 to 200 °C (first heating), cooled quickly to −140 °C and heated again to 200 °C (second heating). The experimental values of T_g were compared with the T_g calculated by Fox equation (1) [20]. In this equation: T_{gAB} is the calculated value of T_g of the blend, W_A and W_B are the mass ratios of components in the mixture, T_{gA} and T_{gB} are the values of T_g of the pure components determined by DSC:

$$\frac{1}{T_{gAB}} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \tag{1}$$

The degree of crystallinity (X_c) of the blends was calculated by Eq. (2) [21], where ΔHm° is the variation of the melting enthalpy for PHB 100% crystalline (142 J/g) [22] and ΔHm is the variation of melting enthalpy of the blend during the first heating determined by DSC (J/g).

$$X_c = \frac{\Delta Hm}{\Delta Hm^\circ} \times 100 \tag{2}$$

2.3. Fourier transform infrared spectroscopy (FT-IR)

FT-IR analyses of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends were carried out to identify characteristic bands related to amorphous and crystalline phases of the biopolymers, as well as alterations in these bands (displacement and/or widening) in function of the interactions between the components in the blend. The analyses were done in a Perkin-Elmer Spectrum One equipment, in the transmission mode, from 4000 to 450 cm^{-1}. The spectra were normalized with zero point at 629 cm^{-1} and ordinate limit at 1.5 A.U.

Table 2
DSC results of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends

Composition	T_g experimental (°C)	T_g calculated by Fox equation (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔHm (J g^{-1})	X_c (%)
100/0	0.90	0.90	–	156.4	167.3	73.7	51.9
90/10	–	–	–	155.6	167.1	77.8	54.8
80/20	−0.12	−0.07	–	152.7	165.2	69.6	49.0
70/30	–	–	45.0	153.1	165.7	73.3	51.6
60/40	–	–	44.0	150.8	166.4	61.9	43.6
50/50	–	–	–	150.8	166.5	67.7	47.7
40/60	−1.88	−1.99	47.5	150.3	167.5	61.8	43.5
30/70	–	–	45.0	148.7	166.0	56.0	39.4
20/80	−2.32	−2.94	47.0	148.2	167.2	48.7	34.3
10/90	−3.01	−3.41	46.9	144.8	166.8	49.4	34.8
0/100	−3.88	−3.88	49.9	–	167.4	45.6	32.1

3. Results and discussion

3.1. Calorimetric analyses

The DSC results for the different P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends are showed in Table 2. The transition temperatures (T_g, T_c and T_m) were determined in the second heating (to eliminate the thermal history of the films), while the enthalpies used to calculate the degree of crystallinity were obtained in the first heating (to determinate the crystallinity of the blends obtained by casting). In some experiments it was not possible to visualize T_g and/or T_c, what is typical for polymers with high degrees of crystallinity [23]. It was not observed any T_g for 90/10, 70/30, 60/40, 50/50 and 30/70 blends, even after quenching in liquid N_2 from the melt. Therefore, for these blends, it is not possible to state a miscibility behavior.

The degree of crystallinity of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends decreased with the increase of copolymer content and this became markedly for 50/50 blends, as one can see in Table 2. This suggests that the increase in the disorganization of the blends was due to the presence of P(3HB-*co*-3HV)–10% 3HV since this copolymer is more amorphous. Similar results were also described by Scandola et al. [14].

It was detected that the T_g of the blends decreased with the increase of copolymer content and that 80/20, 40/60, 20/80 and 10/90 blends presented only one T_g (Fig. 1). In addition, there is a very good agreement between the experimental data and values provided by the Fox Equation (Table 2), that should be an indicative that the blends are miscible in the amorphous phase, as pointed out by Scandola et al. [14].

The second heating of some blends showed exothermic peaks related to a cold crystallization. The increase of the copolymer content in the blend provided an increase in the T_c, as can be seen in Table 2 and Fig. 2. According to DSC results, P(3HB-*co*-3HV)–10% 3HV is less crystalline than P(3HB) and the crystallization peak temperature for P(3HB) is lower than that for P(3HB-*co*-3HV), showing that higher temperatures are needed to disentangle the chains in the amorphous phase and to start a crystallization in the blends with higher copolymer content.

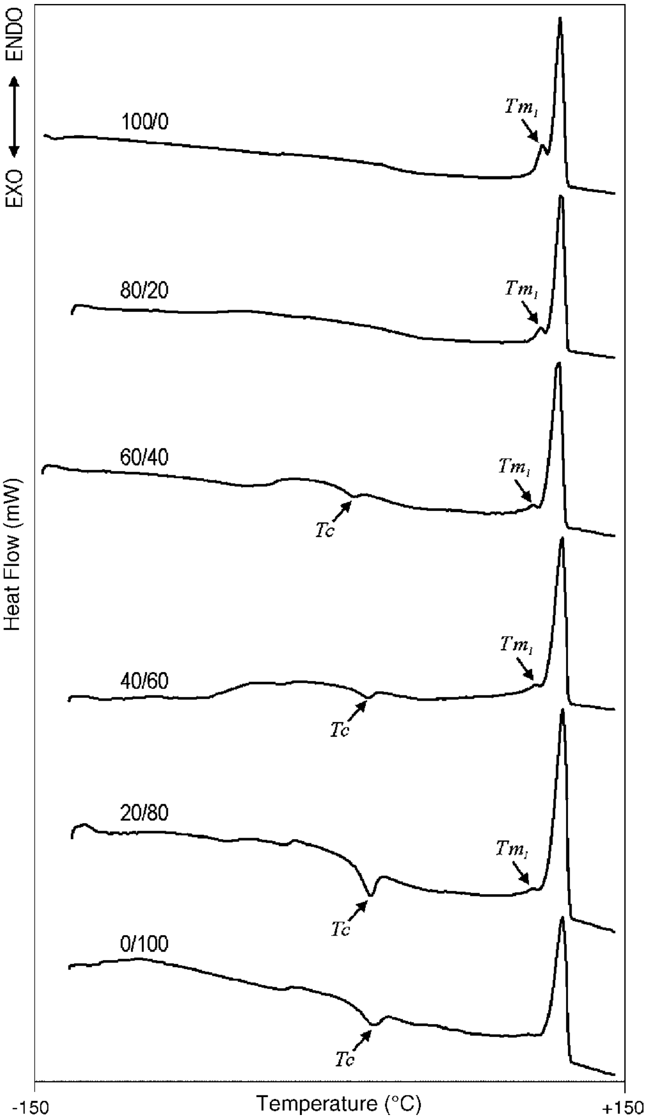

Fig. 2. DSC heat flow melting curves of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends.

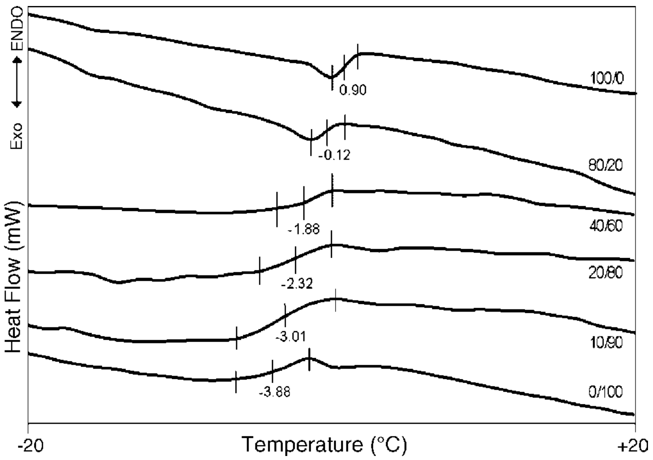

Fig. 1. Glass transition temperatures of P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends.

The second heating for P(3HB) showed an additional small melting peak (T_{m1}) before the principal peak (T_{m2}), as showed in Fig. 2. The presence of multiple melting peaks is typical for P(3HB) and its copolymers [5]. The reasons for this behavior can be: (1) partial melting, recrystallization and remelting; (2) melting of crystals with different lamellar thickness; (3) melting of different crystalline structures. Most of the works, however, suggest that double melting peaks of P(3HB) are due to process of melting, recrystallization and remelting [5,18].

The P(3HB-*co*-3HV)–10% 3HV presented only one melting peak, as shown in Fig. 2. It was expected a reduction in the melting temperature due to the presence of 10 mol% of 3HV in the structure of this copolymer. The 3HV units contain ethyl groups, larger than the methyl groups of 3HB that reduces the ordering of the material causing a reduction in T_m, T_g and crystallinity [4,9]. In this work, however, the T_m of P(3HB-*co*-3HV)–10%

3HV presented essentially the same value of T_{m2} of P(3HB). This is an indicative that 10 mol% of 3HV were not enough to change the melting process. Similar results were obtained by Kunioka et al. [24] which observed a T_m of 178 °C for P(3HB) and a T_m of 176 °C for P(3HB-*co*-3HV)–9% 3HV. In addition it should be noted that the biopolymers used in this work have similar molar masses. This is related to little difference in the melting temperatures of P(3HB) and P(3HB-*co*-3HV), even with 10 mol% of 3HV in the copolymer.

The blends presented the values of main melting peak (T_{m2}) very close to that of the pure biopolymers, while the first melting peaks (T_{m1}) had decreased in area and numerical value with the increase of P(3HB-*co*-3HV)–10% 3HV content in the blends (Table 2 and Fig. 2).

Two melting peaks are commonly observed for blends of semicrystalline polymers. It is important to distinguish melting peaks due to phase separation and those caused by melting/recrystallization [17]. The results showed that P(3HB)/P(3HB-*co*-3HV)–10% 3HV blends presented two melting peaks due to the process of melting/recrystallization of P(3HB), since the temperature and area of the peak T_{m1} decreased clearly with the addition of P(3HB-*co*-3HV)–10% 3HV (Table 2 and Fig. 2).

There is an almost linear relationship between T_{m1} or T_{m2} versus copolymer content, as shown in Fig. 3. According to Organ and Barham [25] this linear relation is an indicative of the miscibility between the components of the blend during the melting without phase separation. In addition these results indicate that P(3HB) and P(3HB-*co*-3HV)–10% 3HV cocrystallized (polymers coexisted in a lamella) as already pointed out by other authors [17,26,27]. The cocrystallization in a lamella is a rare phenomenon observed only when the chemical structures of two component polymers are very similar [16], as occurs with the chemical structures of P(3HB) and P(3HB-*co*-3HV)–10% 3HV.

3.2. FT-IR analyses

Both spectra of P(3HB) and P(3HB-*co*-3HV)–10% HV had similar appearance typical of P(3HB) crystalline spectrum. It was not observed new bands of functional groups neither disappearing nor displacement of bands in the P(3HB-*co*-3HV)–10% HV spectrum. It is possible to conclude that 10 mol% of 3HV in the P(3HB-*co*-3HV) were not enough to cause changes in the molecular structure of this copolymer. Therefore, some spectral regions that have been related to crystalline and amorphous phases of polymers were studied in this work.

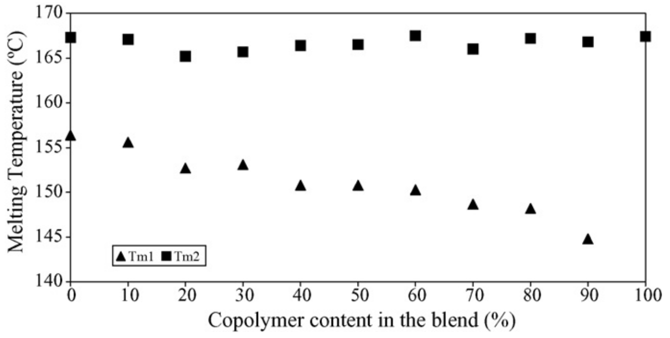

Fig. 3. Influence of P(3HB-*co*-3HV)–10% 3HV content in the melting temperatures of the blends.

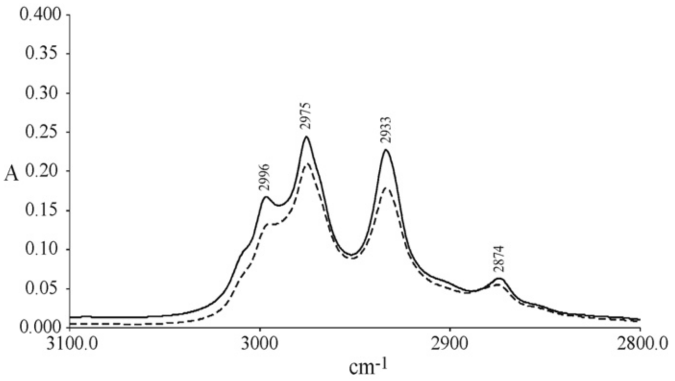

Fig. 4. FT-IR spectra in the 3100–2800 cm^{-1} region of P(3HB) (—) and P(3HB-*co*-3HV)–10% 3HV (- - - - -).

The infrared absorption spectra of the polymers in the crystalline and amorphous states can differ for at least two reasons: first of all, specific intermolecular interactions may exist in the crystalline polymer which lead to the sharpening or the splitting of certain bands; and second, some specific conformations may exist in just one phase, leading to bands which are characteristic exclusively of either crystalline or amorphous material [32].

Fig. 4 shows the FT-IR spectra of P(3HB) and P(3HB-*co*-3HV)–10% HV in the 3100–2800 cm^{-1} region. Bands at 3015–2960, 2945–2925 and 2855–2865 cm^{-1} regions are assigned to CH_3 asymmetric stretching, CH_2 antisymmetric stretching and CH_3 symmetric stretching modes, respectively [29]. The bands at 3009, 2995, 2974 and 2967 cm^{-1} are ascribed to the CH_3 asymmetric stretching modes of the crystalline parts [7,29]. Zhang et al. [28] has observed that the intensity of band at 2935 cm^{-1} increases gradually with the development of the crystalline structure of P(3HB), and that the shift of CH_3 stretching band from 2878 to 2873 cm^{-1} should be correlated to the disordered to ordered conformational transition of P(3HB) in the crystallization process. In this work it was verified that P(3HB) presented the bands at 2996, 2975, 2933 and 2874 cm^{-1} with more intensity than P(3HB-*co*-3HV)–10% 3HV (Fig. 4) suggesting the higher crystallinity of P(3HB), as already presented in DSC results. Comparing the FT-IR spectra of P(3HB) and of a 80/20 blend (Fig. 5) the same behavior is observed, with more intense crystallization bands in P(3HB) spectrum. However, comparing FT-IR spectra of P(3HB-*co*-3HV)–10% HV and of a 80/20 blend (Figs. 4 and 5), it is verified that the bands related to crystallinity are more intense in the 80/20 blend spectrum, suggesting a higher crystallinity for the blend, as already presented in DSC results.

The part of the molecular structure in the repeat unit of P(3HB) is the same as that of polypropylene (PP), and the bands due to the helical forms of isotactic PP appear in the C–C stretching vibration region (1000–800 cm^{-1}). Five crystalline bands at 978, 938, 929, 896 and 825 cm^{-1} of P(3HB) appearing in the range of 1000–800 cm^{-1} are correlated to the formation of the 2_1-helix structure of P(3HB) chain [28]. It was verified that these

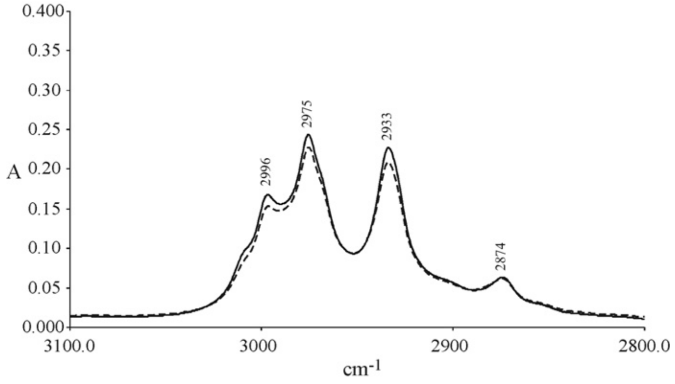

Fig. 5. FT-IR spectra in the 3100–2800 cm^{-1} region of P(3HB) (—) and of a 80/20 blend (- - - - -).

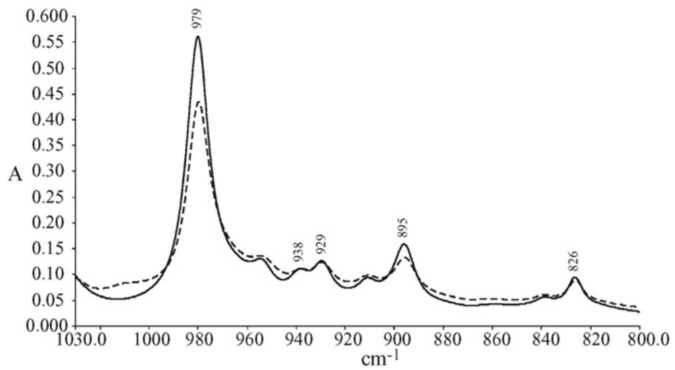

Fig. 6. FT-IR spectra in the 1030–800 cm^{-1} region of P(3HB) (—) and P(3HB-*co*-3HV)–10% 3HV (- - - - -).

bands are relatively more intense for P(3HB) than for P(3HB-*co*-3HV)–10% 3HV (Fig. 6) indicating the more crystalline helical structure of P(3HB). Comparing the FT-IR spectra of P(3HB) and of a 20/80 blend (Fig. 7) it is noted that these bands are more intense for P(3HB) than for a 20/80 blend, confirming a more crystalline structure for P(3HB).

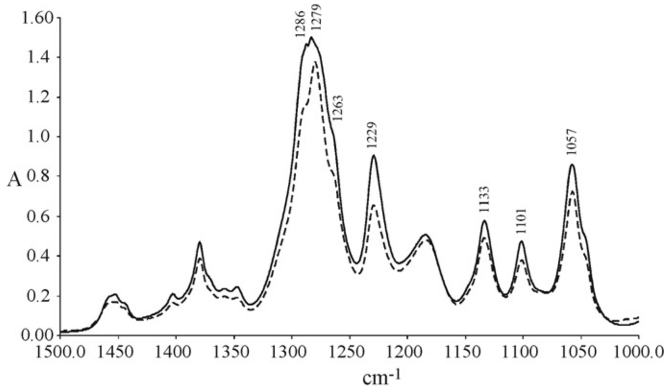

Fig. 8. FT-IR spectra in the 1500–1000 cm^{-1} region of P(3HB) (—) and P(3HB-*co*-3HV)–10% 3HV (- - - - -).

It is well know that the bands of the C–O–C stretching region (1300–1000 cm^{-1}) are very sensitive to the conformation of a polymer [18,29,31]. Four bands at 1289, 1279, 1263 and 1228 cm^{-1} are very sensitive to the degree of crystallinity [31] and reflect the helical structure [7,18,29] whereas two bands at 1302 and 1257 cm^{-1} arise from the random structures [7,29]. The bands at 1134, 1102 and 1060 cm^{-1} are also sensitive to the degree of crystallinity, however, to a lesser extent [31]. Fig. 8 shows the FT-IR spectra in the 1500–1000 cm^{-1} region of P(3HB) and P(3HB-*co*-3HV)–10% 3HV. It was not found bands at 1302 and 1257 cm^{-1}, but it is verified that the P(3HB) presented the bands at 1286, 1279, 1263, 1229, 1133, 1101 and 1057 cm^{-1} more intense than P(3HB-*co*-3HV)–10% 3HV, indicating that P(3HB) has a higher degree of crystallinity than the pure copolymer, in agreement with the previous spectra and the DSC results.

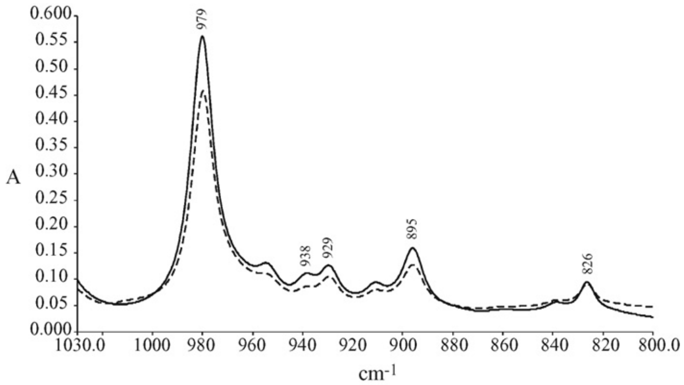

Fig. 7. FT-IR spectra in the 1030–800 cm^{-1} region of P(3HB) (—) and of a 20/80 blend (- - - - -).

In the 1800–1680 cm^{-1} region bands due to C=O stretching modes appear. The C=O stretching band region consists of at least two dominant bands. The sharp band at around 1723 cm^{-1} arises from the crystalline C=O groups, and the broad band at around 1740 cm^{-1} is attributed to the amorphous groups [7,10,14,18,28,29]. The bands at around 1731 and 1722 cm^{-1} arise from the crystalline state. Based on frequency and intensity, the band at 1722 cm^{-1} may be assigned to the C=O stretching mode of the well-ordered crystalline state of P(3HB), and the band at 1731 cm^{-1} may be due to the C=O stretching mode of the less ordered crystalline part of the polymer [7], which may be related to the intermediate state [28,29]. The weak band at 1686 cm^{-1} is very much characteristic of the crystalline state

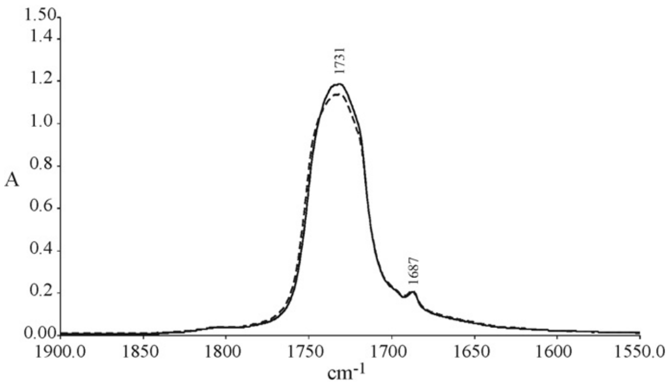

Fig. 9. FT-IR spectra in the 1900–1550 cm^{-1} region of P(3HB) (—) and of a 50/50 blend (- - - - -).

[29]. On the basis of its weak intensity and band position, this band is related to the crystal defect which is caused by the interaction of an OH end group and a C=O group of P(3HB) [28]. Fig. 9 shows that the P(3HB) presented the band at 1731 cm^{-1} with a little more intensity than the 50/50 blend, suggesting the higher crystallinity of P(3HB), although these materials had presented the same intensity in the band at 1687 cm^{-1}.

4. Conclusions

The miscibility and the crystallinity of P(3HB)/P(3HB-*co*-3HV) blends have been studied by DSC and FT-IR analyses. The DSC analyses showed that P(3HB) has a higher crystallinity than P(3HB-*co*-3HV)–10% 3HV and the blends, and that the increase of P(3HB-*co*-3HV)–10% 3HV content in the blend decreased the degree of crystallinity. It was verified by FT-IR that P(3HB) presented some more intense and sharper bands than P(3HB-*co*-3HV)–10% 3HV and the blends. This behavior could be related to a higher degree of crystallinity of P(3HB).

It was observed that most of the blends presented only one T_g that agreed to the T_g calculated by the Fox equation, suggesting that these blends are miscible in the amorphous phase. The increase of P(3HB-*co*-3HV)–10% 3HV content in the blends causes a decrease in the T_g and a increase in the T_c, probably due to the fact that the crystallization occurs in the P(3HB) easier than in P(3HB-*co*-3HV). Nevertheless, it was not observed any T_g for some blends and, therefore, for these blends, it is not possible to state a miscibility behavior.

With regard to the melting process, it was verified that P(3HB) and the blends showed two melting peaks due to processes of melting, recrystallization and remelting. The biopolymers presented essentially the same value of main melting peak, probably due to the small content of 3HV in the copolymer (only 10%) and the similar molar masses of the biopolymers. There was an almost linear relation between the melting peaks versus copolymer content, indicating miscibility in the melting and also a cocrystallization of the components of the blends.

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References

[1] A.J. Anderson, E.A. Dawes, Microbiol. Rev. 54 (1990) 450–472.
[2] A. Steinbüchel, Macromol. Biosci. N1 (2001) 1–24.
[3] Y. Doi, Microbial Polyesters, VCH Publishers, New York, 1990.
[4] D.S. Rosa, R. Pantano Filho, Biodegradação: um ensaio com polímeros, Moara, Itatiba; Universidade São Francisco, Bragança Paulista, 2003.
[5] L.M.W.K. Gunaratne, R.A. Shanks, G. Amarasinghe, Thermochim. Acta 423 (2004) 127–135.
[6] D. Briassoulis, J. Polym. Environ. 12 (2) (2004) 65–81.
[7] A. Padermshoke, Y. Katsumoto, H. Sato, S. Ekgasit, I. Noda, Y. Ozaki, Spectrochim. Acta Part A 61 (2005) 541–550.
[8] A. El-Hadi, R. Schanabel, E. Straube, G. Muller, S. Henning, Polym. Test. 21 (2002) 665–674.
[9] J.A. Brydson, Plastics Materials, 7th ed., Butterworth Heinemann, Oxford, 2000.
[10] B. Fei, C. Chen, H. Wu, S. Peng, X. Wang, L. Dong, Eur. Polym. J. 39 (2003) 1939–1946.
[11] T. Volova, E. Shishatskaya, V. Sevastianov, S. Efremov, O. Mogilnaya, Biochem. Eng. J. 16 (2003) 125–133.
[12] N. Lotti, M. Pizzoli, G. Ceccorulli, M. Scandola, Polymer 34 (23) (1993) 4935–4940.
[13] Y. Kumagai, Y. Doi, Polym. Degrad. Stabil. 36 (1992) 241–248.
[14] M. Scandola, M.L. Focarete, G. Adamus, W. Sikorska, I. Baranowska, S. Swierczek, M. Gnatowski, M. Kowalczuk, Z. Jedlinski, Macromolecules 30 (1997) 2568–2574.
[15] Z. Qiu, S. Fujinami, M. Komura, K. Nakajima, T. Ikehara, T. Nishi, Polymer 45 (2004) 4355–4360.
[16] N. Yoshie, A. Asaka, K. Yazawa, Y. Kuroda, Y. Inoue, Polymer 44 (2003) 7405–7412.
[17] N. Yoshie, M. Saito, Y. Inoue, Polymer 45 (2004) 1903–1911.
[18] T. Furukawa, H. Sato, R. Murakami, J. Zhang, Y.X. Duan, I. Noda, S. Ochiai, Y. Ozaki, Macromolecules 38 (2005) 6445–6454.
[19] N. Vogelsanger, M.C. Formolo, A.P.T. Pezzin, A.L.S. Schneider, S.A. Furlan, H.P. Bernardo, S.H. Pezzin, A.T.N. Pires, E.A.R. Duek, Mater. Res. 6 (3) (2003) 359–365.
[20] E.F. Lucas, B.G. Soares, E. Monteiro, Caracterização de Polímeros: determinação de peso molecular e análise térmica, E-Papers, Rio de Janeiro, 2001.
[21] L. Zhang, C. Xiong, X. Deng, Polymer 37 (1996) 235–241.
[22] H. Tsuji, Y. Ikada, J. Appl. Polym. Sci. 60 (1996) 2367–2375.
[23] S. Bloembergen, D.A. Holden, Macromolecules 22 (1989) 1656–1663.
[24] M. Kunioka, A. Tamaki, Y. Doi, Macromolecules 22 (1989) 694–697.
[25] S.J. Organ, P.J. Barham, Polymer 34 (1993) 459–467.
[26] N. Yoshie, M. Fujiwara, M. Ohmori, Y. Inoue, Polymer 42 (2001) 8557–8563.
[27] M. Saito, Y. Inoue, N. Yoshie, Polymer 42 (2001) 5573–5580.
[28] J. Zhang, H. Sato, I. Noda, Y. Ozaki, Macromolecules 38 (2005) 4274–4281.
[29] H. Sato, J. Dybal, R. Murakami, I. Noda, Y. Ozaki, J. Mol. Struct. 744/747 (2005) 35–46.
[30] N. Yoshie, A. Asaka, Y. Inoue, Macromolecules 37 (2004) 3770–3779.
[31] S. Bloembergen, D.A. Holden, Macromolecules 19 (1986) 2865–2871.
[32] F.W. Billmeyer Jr., Textbook of Polymer Science, 2nd ed., John Wiley & Sons, New York, 1971.