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Thermal characterization of the interaction of poly(3-hydroxybutyrate) with maleic anhydride

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Abstract Poly(3-hydroxybutyrate), PHB, has been structurally modified with maleic anhydride, MA, in the presence of triethylamine, TEA. Glass transition, melting, and crystallization temperature, obtained from DSC curves, and thermal degradation temperatures obtained from TG ones, were employed to evaluate the influence of the MA proportion on the modification in the PHB chain. According to the results, most of chain modification reactions are the 80/20 and 90/10 proportions. Observations suggest that most chain modification reactions occur when the ratio of PHB/MA is 80/20 or 90/10. This suggests that modifications of PHB in the presence of MA involve main chain scission.

Keywords Transesterification reaction · Poly(3-hydroxybutyrate) · Maleic anhydride

Introduction

Poly(3-hydroxybutyrate) (PHB) is a biopolymer produced and accumulated intracellular by a wide variety of bacteria during unbalanced growth from renewable carbon sources in a controlled biotechnological process [1–3]. *Ralstonia eutropha* has been used to produce the polymer with the PHB content nearly 70% of dry weight [4]. The prospective market for PHB is the general packages, injected products, disposable materials in cosmetic industries [5], and it is also a highly potential biomaterial in biomedical applications such as scaffolds for bone reconstruction, sutures surgical fibers [6], and capsules for drug delivery [7], due to its biocompatibility and absorption in the organism [8–10]. Nevertheless, PHB is thermal unstable, brittle, and presents high melting crystalline temperature (e.g., 165 °C). In order to improve these disadvantages, some alkanoates monomers have been introduced in the polymer chain during the biosynthesis, as an example the 3-hydroxyvalerate, thus obtaining a random copolymer [11, 12]. The transesterification reaction conditions were carried out at 110 °C, during 1 h and with triethylamine (TEA) concentration in 5% v/v [13, 14]. The main purposes of this article are to evaluate the thermal behavior of the PHB homopolymer and PHB structurally modified with maleic anhydride (MA) in different proportions (w/w of PHB/MA) by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG).

Experimental

Film preparation

Pre-treating

PHB homopolymer (PHB Industrial, Serrana, Brazil) with average molecular weight 300848 Dalton [15, 16] were added in 2 mL of chloroform (J T Baker) in sealed vials (8 mL). MA (MERCK) was prepared in the same way. The sealed vials were kept at 100 °C during 10 min and stirred (90 RPM) during 20 h for complete dissolution of the polymer. After the stirring period, the MA solution was completely transferred to PHB solution to obtain a different ratio (w/w) of PHB/MA, according to Table 1.

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Table 1 Composition of PHB/MA films

Film (PHB/MA)/%	PHB/% (w/w)	MA/% (w/w)
1 (80/20)	80	20
2 (90/10)	90	10
3 (93/07)	93	07
4 (95/05)	95	05
5 (97/03)	97	03
6 (99/01)	99	01

Transesterification reaction

The solutions were heated at 110 °C during 1 h, and the triethylamine TEA concentration (5% (v/v) was introduced in the vials. The vials were cooled to 25 °C, and films were obtained from open vials by slow evaporation of the solvent. The films were then dried inside a desiccator at 40 °C during 12 h.

The same way, films of PHB homopolymer were prepared, PHB only with catalyst TEA, PHB/TEA (concentration of 5% v/v), MA pure and MA only with catalyst, MA/TEA (concentration of 5% v/v).

Thermal analysis

PHB homopolymer, PHB/TEA, MA, MA/TEA, and PHB/MA samples were evaluated by DSC and TG–DTA. Samples about 6 mg were first-heated in a DSC (2910-TA Instruments) from 40 to 195 °C with 5 min of isothermal in the highest temperature. Immediately, the DSC cell supports were filled with liquid nitrogen to cool the samples from 195 to −50 °C. Again the same samples were heated from −50 to 200 °C to obtain some thermal parameters: glass transition (T_g), crystallization temperature (T_c), melting temperature (T_m), and enthalpy of melting (H_f). The heating rate in the first and second analysis was 20 °C min^{-1} with a sealed aluminum reference and sample crucibles under dynamic nitrogen atmosphere (50 mL min^{-1}).

The TG was carried out with samples about 6 mg using an SDT 2960-TA Instruments. Samples were heated from 40 to 450 °C in open alumina reference and sample pans under dynamic nitrogen atmosphere (50 mL min^{-1}) with 20 °C min^{-1}.

Results and discussion

Simultaneous TG–DTA analysis

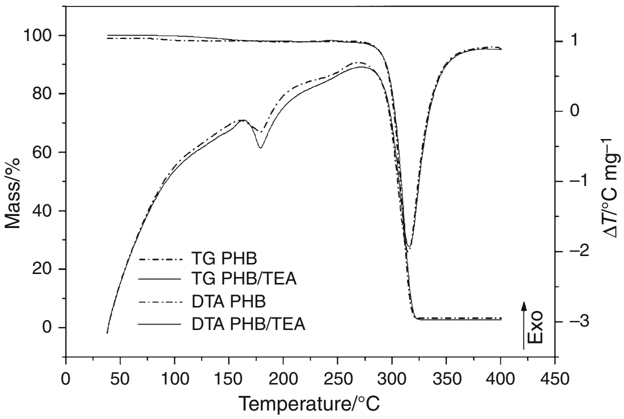


Fig. 1 TG curves for thermal degradation of films PHB and PHB/TEA

TG–DTA curves for the thermal behavior of the PHB homopolymer and PHB/TEA are illustrated in Fig. 1. The main degradation step in both samples was observed between 270 and 325 °C. The mass loss is about 98%, which is attributed to PHB thermal degradation with endothermic DTA peaks at 315 °C. The PHB melting point is noted at 164.7 °C in the DTA curves. In view of the evaluated TG–DTA curves, it is possible to infer that TEA does not influence in the PHB thermal behavior.

TG–DTA curves presented in Fig. 2 illustrate the thermal behavior of MA and MA/TEA samples.

MA DTA curve presents an accentuated and broad endothermic peak from 140 to 200 °C attributed to the melting and volatilization of the maleic acid due to the MA hydrolysis by the moisture during the sample preparation.

On the other hand, MA/TEA presents endothermic DTA peak in 201.06 °C, which is attributed to the TG thermal decomposition of the viscous sample. The complex MA/TEA [17] lost 80% of its mass from 75 to 300 °C and 19% of carbonaceous residue left.

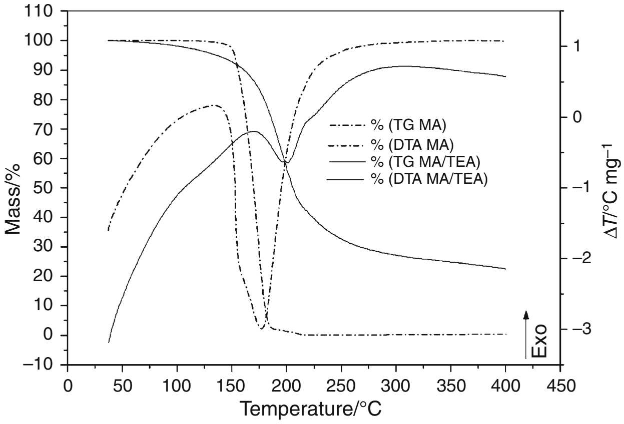


Fig. 2 TG–DTA curves for thermal degradation of MA and MA/TEA

Figures 3 and 4 illustrate the TG and DTA curves, respectively, for the thermal behavior of the PHB/MA films in different proportions (Table 1). Temperature interval presented in Table 2 quantifies the thermal degradation steps from Fig. 3.

The first thermal degradation step from 50 to 185 °C is attributed to the volatilization of the solvent and TEA, MA residual. On the other hand, the thermal decomposition between 255 and 325 °C is attributed to PHB degradation [18, 19]. The intermediate thermal degradation step, between 185 and 255 °C, indicates the PHB chain modified by MA due to the potential transesterification reaction. MA molecules have been introduced in the PHB chain that leads the polymer structure to a lower thermal stability. The higher MA proportion in the films increasing the PHB–MA interaction, especially for the film 1 (80/20), that present elevated mass loss in the second thermal degradation step. Consequently, it was lost a smaller amount mass in the first and third thermal degradation step for the film 1 related to the other films than the expected.

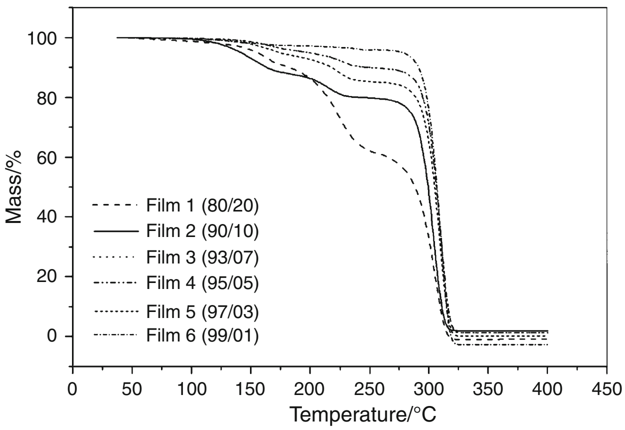


Fig. 3 TG curves for thermal degradation of PHB/MA films

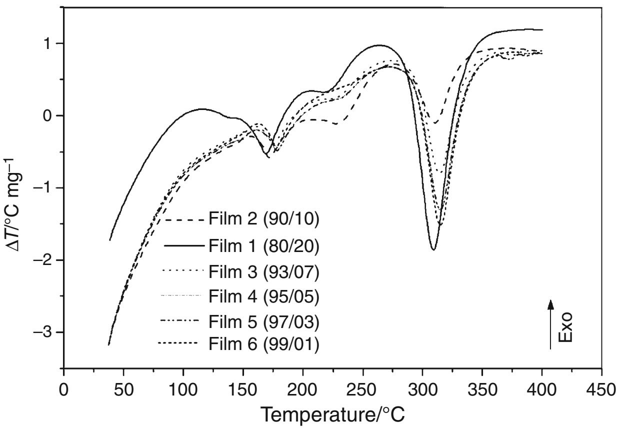


Fig. 4 DTA curves for thermal degradation of PHB/MA films

Figure 4 presents DTA curves with three endothermic peaks that are attributed to PHB melting point, PHB modified by MA, and PHB thermal degradation, respectively. The melting point and the temperature at maximum rate of degradation are presented in Table 3. There is a tendency to low the values of the melting temperature when increasing MA proportion, and the decomposition peaks were observed in short temperature interval from 310 to 314 °C. The intermediate endothermic peaks are related to the thermal decomposition of the PHB/MA with the MA content varying from 7 to 20%. Slight baseline deviations apparent in other DTA curves are due to the presence of small amount of residual MA.

DSC thermal behavior

In order to study the thermal behavior of the PHB homopolymer and PHB/MA films, the samples were first-heated in the DSC cell. DSC curves are presented in Fig. 5 and express the thermal behavior of the PHB homopolymer and PHB/TEA. It is not observed that crystallization peak in the first heating and the main endothermic peaks at 159.5 °C represent the PHB homopolymer and the peak at 152.2 represents the PHB/MA melting point.

The DSC curves illustrated in Fig. 6 obtained immediately after isothermal heating at 195 °C reflect typical

Table 2 Mass loss values for the thermal degradation of PHB/MA films

Film (PHB/ MA)/%	Thermal degradation steps/%		
	1st (50–185 °C)	2nd (185–255 °C)	3rd (255–325 °C)
1 (80/20)	7.5	29.1	61.8
2 (90/10)	11.5	7.8	77.5
3 (93/07)	5.5	8.1	84.8
4 (95/05)	3.9	5.6	88.0
5 (97/03)	4.2	5.5	88.0
6 (99/01)	2.4	1.5	95.1

Table 3 Temperature values for melting point, 2nd and 3rd thermal degradation step of the PHB/MA films

Film (PHB/ MA)/%	Temperature values/°C		
	Melting point	2nd degradation step	3rd degradation step
1 (80/20)	158.8	231.5	310.3
2 (90/10)	147.9	223.2	309.0
3 (93/07)	164.3	230.4	314.2
4 (95/05)	164.3	–	314.8
5 (97/03)	164.1	–	314.8
6 (99/01)	165.1	–	314.8

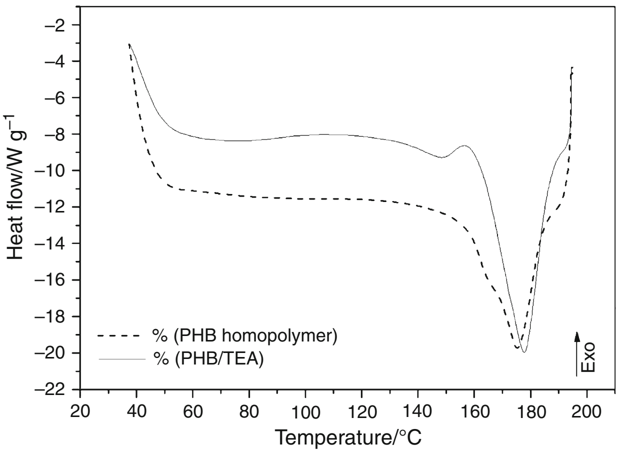


Fig. 5 First-heating DSC curves for PHB homopolymer and PHB/TEA

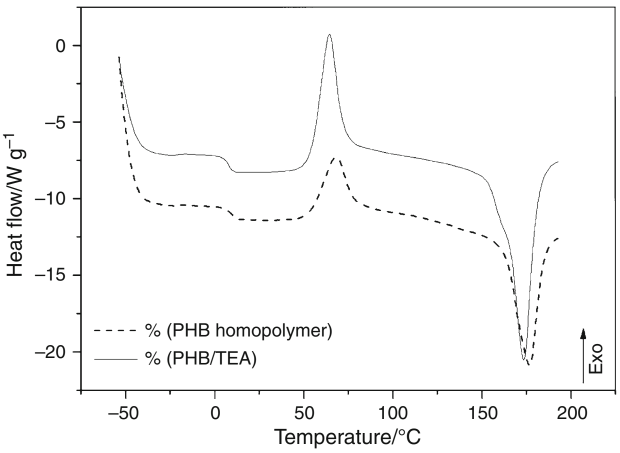


Fig. 6 DSC curves for the second heating of the PHB homopolymer and PHB/TEA

behavior for a thermoplastic. The glass transition temperatures, the exothermic crystallization peaks, and the melting point were obtained.

The values of T_g, T_c, T_m, ΔH_f, ΔH_c, and Cf (% of crystallized PHB) were determined or calculated from the DSC curves (Fig. 6) listed in Table 4. The Cf was calculated according to the enthalpy of fusion for 100% crystalline PHB ($\Delta H = 146.0$ J g^{-1}) [15, 20], exclusively for the peak attributed to the PHB melting, independently from the film compositions.

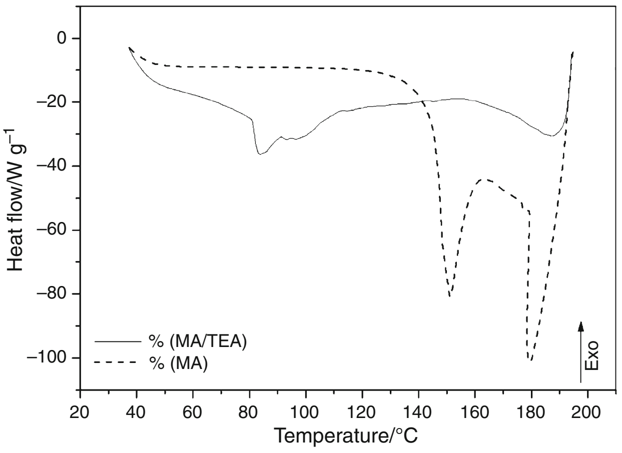


Fig. 7 DSC curves for MA and MA/TEA

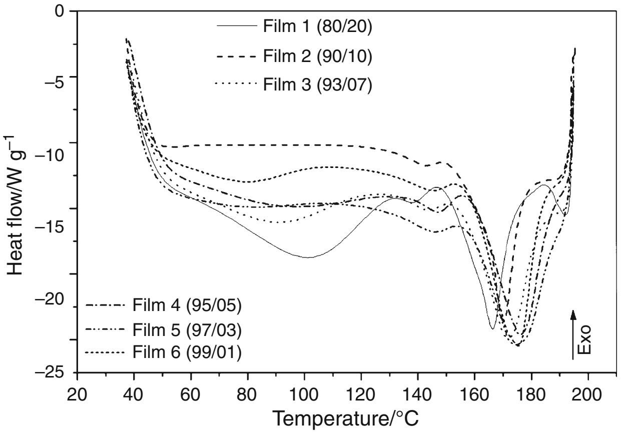


Fig. 8 First-heat DSC curves for PHB/MA films

The presence of TEA in film preparation has a moderate influence on the thermal properties evaluated. Generalized small values decrease is noted when the values for PHB homopolymer were compared with those for PHB/TEA (Table 4). In this situation, the decrease may be attributed to the thermal cleavage of the chain.

DSC curves for the samples of MA and MA/TEA are showed in Fig. 7. The broad endothermic peak from 80 to 110 °C indicates the volatilization (TEA boiling point at 89 °C [21]) of residual TEA. The endothermic peak at 187.7 °C is related to the decomposition of the product reaction between MA and TEA. As a result, with the

Table 4 Parameter values in first heating and in the second heating for the PHB homopolymer and PHB/TEA

Sample	First heating			Second heating				
	ΔH_f/Jg^{-1}	%Cf$_1$	T_{m1}/°C	T_g/°C	T_c/°C	ΔH_c/Jg^{-1}	%Cf2	T_{m2}/°C
PHB/TEA	83.6	58.5	152.2	8.2	64.4	46.7	61.6	150.7
PHB homopolymer	102.6	70.3	159.5	9.9	68.1	49.0	68.3	153.3

Table 5 Values determined or calculated from DSC curves for PHB/MA films on first and second heat

Sample	First heating			Second heating				
	ΔH_f/Jg^{-1}	%Cf$_1$	T_{m1}/°C	T_g/°C	T_c/°C	ΔH_c/Jg^{-1}	%Cf$_2$	T_{m2}/°C
1 (80/20)	69.9	59.9	145.1	1.0	63.3	44.3	32.4	128.3
2 (90/10)	44.5	33.9	151.6	1.5	64.9	28.1	25.1	137.2
2 (93/07)	69.0	50.9	151.2	−2.8	66.1	53.4	46.5	133.2
3 (95/05)	66.2	47.8	156.6	0.4	64.2	45.9	41.5	138.2
4 (97/03)	77.4	54.6	152.2	7.7	66.9	57.8	50.5	147.6
5 (99/01)	88.0	60.9	150.5	6.0	60.6	47.1	58.0	150.4

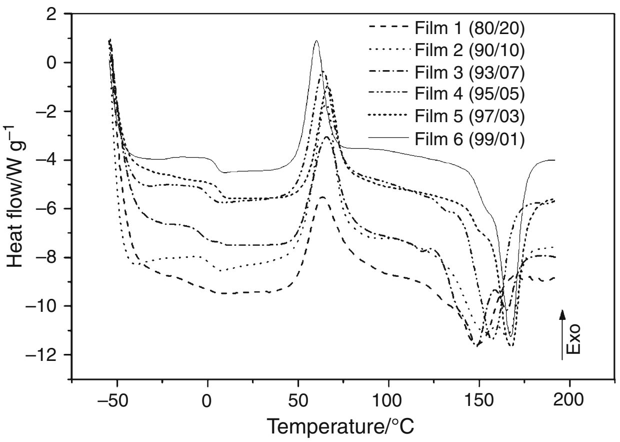


Fig. 9 DSC curves for the second heating of PHB/MA films

presence of TEA in the MA solution it was observed a very different thermal behavior that indicates an interaction between MA and TEA.

The first-heating DSC curves (Fig. 8) are similar for all the PHB/MA sample films, as indicated in Table 5. In general, all the samples presented a decrease in the thermal parameters determined in the first heating in comparison to the PHB homopolymer. The exception was the film 1 with PHB/MA 80/20% that has the lowest T_{m1}, on the other hand it has a higher Cf$_1$ value, probably, during the PHB melting there were thermal conditions to the physical chemistry interactions between MA and PHB chain. For this reason, the interaction needs more energy than only the melting of the film PHB/MA (80/20).

The DSC curves for the second heating (Fig. 9) follow the same behavior observed in the first heating, as indicated in Table 5. The incorporation of MA units makes difficult chain rearrangement during the quenching and then, as a consequence with the increase in the MA amount the crystallization fraction obtained is lower. With an incomplete crystallization formation, it is necessary smaller energy values to acquire the glass transition and melting.

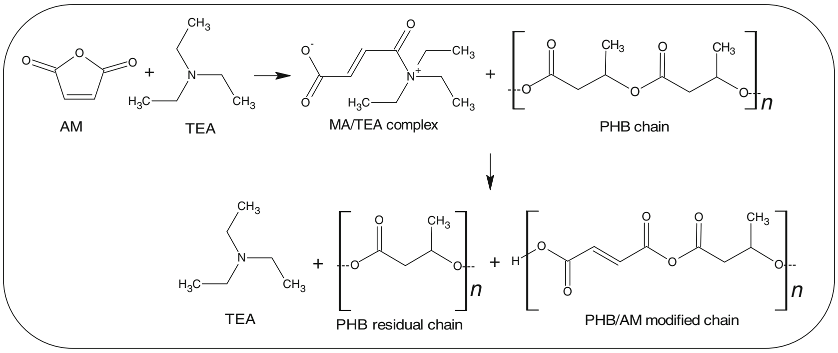
Evaluation of the PHB/MA reaction

This study of thermal behavior associated with a previously gas chromatographic analysis with flame ionization detector (GC–FID) [22] permits the inference that the PHB chain is modified by the incorporation of MA units.

Figure 10 illustrates the interaction between MA and TEA as evidenced before [17, 23], so the MA/TEA carboxylate anion is able to interact with PHB ester groups. Probably, this interaction provokes the scission of the PHB chain resulting in a modified PHB/MA structure, PHB residual chain, and regenerating the TEA.

Considering this interaction it was inferred that some proportion of MA and TEA remain available in the film and then, as presented early in the thermal behavior analysis they were released during the heating in the TG–DTA in the first step of thermal degradation. Concerning to the

Fig. 10 Proposal PHB/MA interaction



residual PHB chain, it was verified by TG–DTA and DSC curves that it maintains the same thermal properties of the PHB homopolymer.

Nevertheless, it was detected an another endothermic peak in the DSC curves before the typical melting for PHB homopolymer and, also it in the TG curves is noted thermal degradation about 230 °C which is attributed to the PHB chain modified by MA. The lower values for T_m, T_g, and Cf determinate by DSC confirm that the MA interacts with PHB chain.

Conclusions

TG–DTA and DSC thermal behavior studies of the PHB/MA films indicated that the MA and the TEA have an influence in the crystalline fraction and melting point of the PHB homopolymer. Also, in the PHB/MA films it was observed a decrease in the thermal stability in comparison with the PHB homopolymer. Probably, the MA and TEA interaction with PHB lead to scission chain. It indicated that the higher the MA proportion the more elevated the PHB scission chain is.

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