Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 673–677

THERMAL BEHAVIOR OF THE MALEIC ANHYDRIDE MODIFIED POLY(3-HYDROXYBUTYRATE)

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Poly(3-hydroxybutyrate), PHB has been structurally modified through reaction with maleic anhydride, MA. Transesterification reaction was carried out fixing the PHB and MA and besides time and temperature the concentration of the triethylamine (used as catalyst) was changed. Glass transition, melting and crystallization temperature obtained from DSC curves and thermal degradation temperatures obtained from TG traces were used to evaluate the influence of the reaction conditions on the modification of PHB according to factorial design. On the base of the results the optimum conditions are to perform the PHB modification reaction with MA reaction at 110°C for 1 h with 5% *v*/*v* triethylamine.

Keywords: *maleic anhydride, poly(3-hydroxybutyrate), transesterification reaction*

Introduction

Poly(3-hydroxybutyrate) (PHB) is a thermoplastic biopolymer produced and accumulated intracellularly in a wide variety of bacteria during unbalanced growth from renewable carbon sources at a controlled biotechnological process [1–3]. In Brazil, the bacteria *Ralstonia eutropha* is used to produce this substance. The poly(3-hydroxybutyrate) content of the PHB homopolymer is almost 70% by dry mass [4]. Biocompatibility and biodegradability are the major characteristics of PHB [1]. Despite of the high melting temperature of the crystalline part (approximately 175°C), its thermal instability and brittleness are the main disadvantages of the application of PHB as biomaterial. General packages, injected products, disposable materials in cosmetic industries [5] and also biocompatible and easily absorbable products in the organism give to PHB a high potential use as biomaterial in biomedical applications as scaffolds for bone reconstruction [6–8], suture surgical fibers [9] and capsules for drug delivery [10]. In order to improve its above described disadvantages some alkane monomer was built into the polymer chain during its biosynthesis, e.g. 3-hydroxyvalerate, obtaining thus a random copolymer [11, 12].

The main purpose of the present work was to study the modification of PHB films by structural reaction with maleic anhydride (MA) at a fixed proportion (90/10 mass/mass% PHB/MA) through factorial planning and also its relation with the modification reaction conditions using triethylamine as a catalyst with two different concentrations, time and temperature range for transesterification. Experiments have been done using differential scanning calorimetry (DSC) and thermogravimetry (TG).

Experimental

Film preparation

180 mg of PHB homopolymer provided by PHB Industrial and 20 mg of MA (Merck) were added in two independent vials (8 mL) each containing 2 mL chloroform (J. T. Baker). The vials were sealed and heated at 100°C for 10 min and then the PHB solution was stirred (at 90 rpm) for 20 h at room temperature (25°C). After stirring the MA solution was put to the polymer solution in order to obtain a 90/10 mass/mass% PHB/MA ratio. The resultant solutions were evaporated at ambient temperature to obtain the films that were completely dried under vacuum at 40°C for 12 h. Tables 1 and 2 present high (+) and low (–) levels of triethylamine concentrations, time and temperature of transesterification reaction according to 2^3 factorial planning experiments [13]. Additional PHB/MA (90/10) and pure MA and PHB films were prepared in a similar way according to the above description in high level of time and temperature reaction without the presence of triethylamine.

Table 1 Parameters and levels used in the reaction

Reaction parameters	Level	
	high (+)	low (–)
Temperature/°C	110	60
Time/h	4	1
Triethylamine/*v*/*v*%	10	5

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1388–6150/$20.00

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Table 2 Combination of different level conditions of each transesterification experiments

Films	Temperature	Time	Triethylamine
1	–	–	–
2	+	–	–
3	–	+	–
4	+	+	–
5	–	–	+
6	+	–	+
7	–	+	+
8	+	+	+

Thermal behavior

MA, PHB homopolymer and PHB/MA film samples (6 mg), according to Table 2, were firstly heated in a DSC 2910-TA Instruments from 40 to 195°C and then kept at isothermal conditions for 5 min. The samples were immediately quenched with liquid nitrogen and then a second heating was carried out from –50 to 200°C in order to obtain thermal parameters as glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m) and melting enthalpy (ΔH_f). The heating rate in the first and second analyses was 20°C min^{-1} in a sealed aluminum reference and sample crucibles under nitrogen atmosphere (50 mL min^{-1}).

The thermal degradation of MA, PHB homopolymer and PHB/MA films (10 mg) was followed using a TA 2960 SDT, TA Instruments in the 40–450°C temperature range in open alumina reference and sample pans under dynamic nitrogen atmosphere (flow rate: 50 mL min^{-1}) and at heating rate of 20°C min^{-1}.

Results and discussion

Thermal degradation study by TG

Figure 1 presents TG curves of PHB homopolymer and MA. Only one degradation step from 270 to 330°C and from 140 to 190°C, respectively was observed. Nevertheless, in the TG curve of PHB/MA (90/10) film three mass loss steps were seen. The first step, from 125 to 180°C resulting 6.4% of mass loss of the initial sample mass, is due to the vaporization/decomposition of MA and the resultant product from the reaction between MA and triethylamine. The third step, between 260 and 325°C, which corresponds to 79.5% of mass loss is attributed to PHB degradation. The intermediary step where between 180–240°C, 11.3% mass change was detected may due to a new polymeric chain structure that could be formed by the incorporation through transesterification of maleate units. The *cis*-elimination mechanism has already been proposed for the thermal degradation of PHB [14–16].

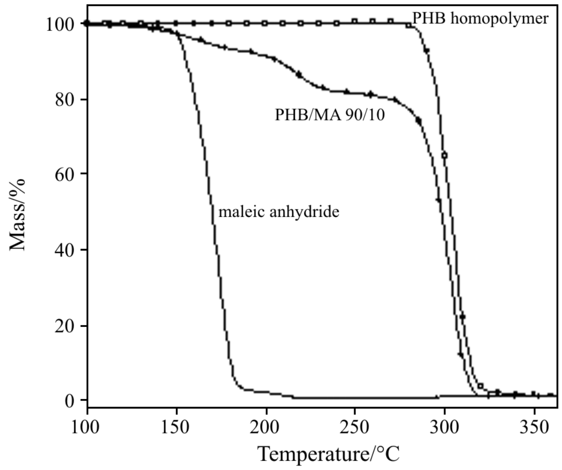

Fig. 1 TG curves for thermal degradation of MA, PHB homopolymer and PHB/MA (90/10)

The possible degradation mechanism for the PHB maleate is suggested in Fig. 2 in agreement with the expected structure of MA units incorporated to the PHB chain. According to the TG curves (Fig. 3) and the numerical data (Table 3) it can be stated that the three-mass-loss-step decomposition is a commonly representative for the thermal behavior of the PHB-maleic anhydride films prepared under different reaction conditions (catalyst content, temperature and time).

Better condition to incorporate the maleic anhydride into the PHB structure can be found by analysis of the first degradation (Δm_1) step (see above for MA). Thus, the lowest values of Δm_1 correspond to a

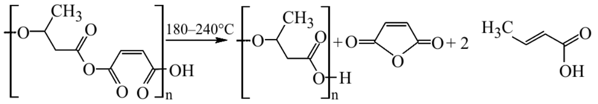

Fig. 2 Thermal decomposition of PHB maleate in the second thermal decomposition step (Δm_2)

Table 3 Mass loss values of the thermal degradation of PHB/MA films

Sample	Thermal degradation steps/%		
	Δm_1	Δm_2	Δm_3
1	10.8	12.1	75.0
2	11.5	7.8	77.5
3	10.0	8.5	80.0
4	8.6	13.9	75.6
5	10.3	6.3	79.8
6	9.4	10.1	80.4
7	10.9	9.7	76.5
8	6.5	10.2	79.8

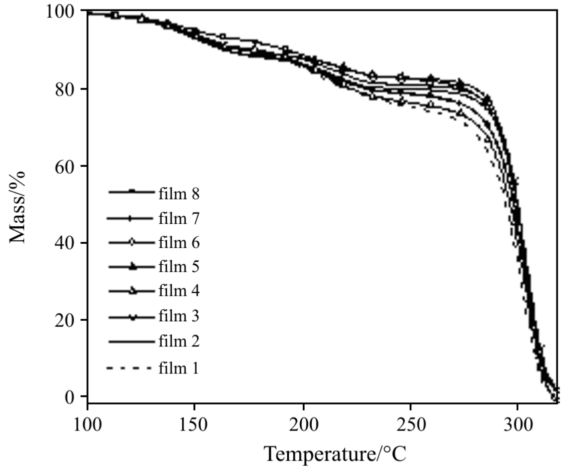

Fig. 3 TG curves for thermal degradation of PHB/MA sample films 1 to 8 (Table 2)

highest extent of transesterification between MA and PHB. Then, Δm_1 is one of the parameters which were considered in the statistical test.

DSC experiments

Figure 4 shows the first and second heating DSC curves of the samples. In Table 4 the numerical values of T_g, T_c, T_m, ΔH_f, ΔH_c and C_f (% of crystallized PHB) are listed. The C_f was calculated according to the melting enthalpy of a 100% crystalline PHB (ΔH=146.0 J g^{-1}) [17, 18].

DSC curves of the first heating (Fig. 4) show only one endothermic peak, which corresponds to the melting of PHB homopolymer and PHB/MA film at 176 and 172°C, respectively. In the second scan, for samples heated to 190°C and then quenched, the corresponding glass and crystallization transitions, T_g and T_c can be observed (Table 4). In the first heating, the broader melting peak observed for PHB homopolymer may due to a partial melting of the crystalline part followed by a recrystallization and melting of the major crystalline part of the sample [19, 20]. The mass loss in the TG curves of the PHB/MA system (Fig. 1) reflects in the form of a broad DSC peak in Fig. 4, which is due to MA decomposition. Compared to the PHB homopolymer, the PHB/MA film has a lower T_g value and much more pronounced crystallization peak and a similar melting point. These features points to a partial new structure formation with a possible incorporation of the MA units into the PHB chain given a more branched configuration.

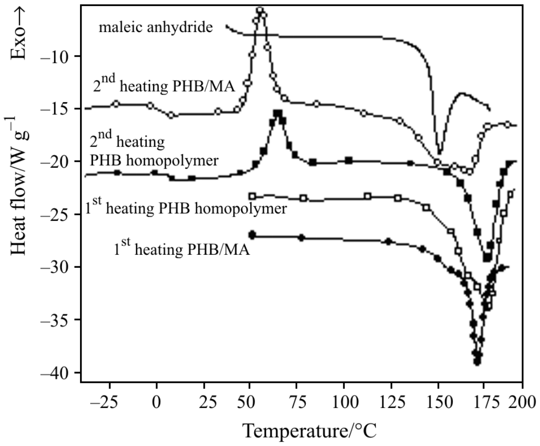

Fig. 4 DSC curves of MA, PHB homopolymer and PHB/MA (90/10)

Figure 5 presents DSC curves on the first heating of the films shown in Table 2. The broad endothermic peak between 150–180°C is due to melting. Additionally, DSC curves show some not so pronounced peaks in the 125–150°C temperature range, which can be attributed to the thermal decomposition of MA units. The DSC curves in Fig. 6 were recorded from the quenched samples (in Fig. 5). T_g, T_c and T_m peaks can be observed. However, the sample properties were affected by the different reaction conditions.

The T_g, T_c, T_m, ΔH_f, ΔH_c and C_f values taken from the DSC curves in Figs 5 and 6 or calculated are sum-

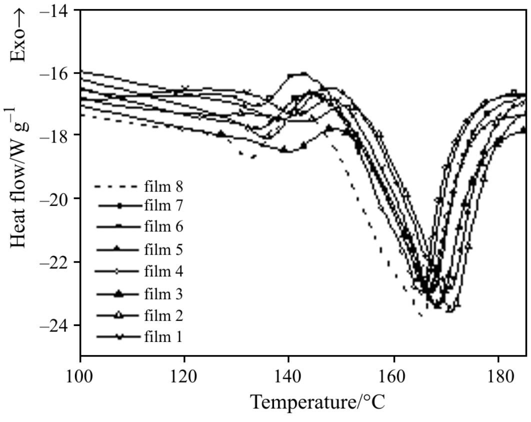

Fig. 5 DSC curves of the first scan of PHB/MA (90/10) films (Table 2)

Table 4 Numerical values of the 1st and 2nd heating taken and/or calculated from the DSC curves

Sample	1st heating			2nd heating				
	ΔH_f/J g^{-1}	C_{f1}/%	T_{m1}/°C	T_g/°C	T_c/°C	ΔH_c/J g^{-1}	C_{f2}/%	T_{m2}/°C
PHB/MA	47.1	32.2	171.7	0.7	55.8	42.8	40.3	167.0
PHB	64.6	44.3	176.9	8.1	65.2	36.7	54.1	176.7

Table 5 Representative parameters of 1st and 2nd heating of the PHB/MA films

Sample	1st heating			2nd heating				
	ΔH_f/J g^{-1}	C_{f1}/%	T_{m1}/°C	T_g/°C	T_c/°C	ΔH_c/J g^{-1}	C_{f2}/%	T_{m2}/°C
1	70.4	48.2	166.2	0.2	61.4	47.3	37.9	148.8
2	44.5	30.5	171.2	15.0	64.9	28.1	22.6	144.2
3	77.5	53.0	168.3	–12.7	57.5	50.1	45.3	149.5
4	83.2	57.0	165.4	–15.7	57.9	54.2	40.5	143.1
5	74.0	50.7	171.0	–9.6	57.3	50.0	45.4	150.8
6	92.7	63.5	166.0	1.2	60.9	42.3	40.0	153.6
7	91.2	52.5	167.0	–13.9	61.1	54.5	44.4	146.6
8	60.7	41.6	165.5	–10.3	63.2	37.2	27.8	147.9

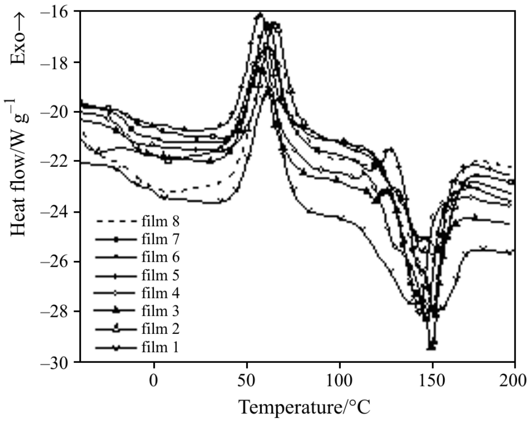

Fig. 6 DSC curves of the second scan of PHB/MA (90/10) films, quenched after the first heating (Fig. 5)

marized in Table 5. The lower T_g values are probably the results of scission process that may occur during heating and stirring of the samples upon the film preparation. Furthermore, the transesterification reaction may promote some rupture in the PHB chains.

Experimental design

The structure of PHB may be modified with maleic anhydride through transesterification reactions upon heat treatment in the presence of tertiary amine (triethylamine) as catalyst. Thermoanalytical investigation have been done in order to quantify the influence of triethylamine concentration, temperature and time (Tables 1 and 2) on the modification reaction of a fixed PHB/MA (90/10) film. T_{m1} parameters were obtained from the first scan and T_g, T_c and crystalline fraction, C_{f2} from the second scan. On the other hand, thermal degradation, Δm_1, was obtained from the first mass loss step of the TG curves. Consequently, in the experimental design T_{m1}, T_g, T_c, C_{f2} and Δm_1 were considered as the main parameters promoting more significant modification in the PHB homopolymer by MA molecules.

The higher T_g and T_c and the lower Δm_1, T_{m1} and C_{f2} values were the criteria considered in the factorial design as a function of the desired properties in the modified PHB/MA.

In order to quantify the influence of each parameter in the reaction it was necessary to apply the t Student test with 95% of significance and considering the degrees of freedom (n–1=7), where n represents the number of different experimental conditions. Hence, the theoretical value to t_{tab} is 1.895 [13, 21]. Then, according to the results listed in Table 6 only the calculated t values, where t_{cal}>1.895 presents an important influence are considered. In this point of view, temperature and time of reaction are the significant parameters during the transesterification reaction but the concentration of triethylamine has only a moderate effect.

Table 6 Calculated t values *vs*. the respective parameters

t_{cal}	Parameters				
	T_g/°C	T_c/°C	T_{m1}/°C	C_{f2}/%	Δm_1/%
$t_{temperature}$	2.04	2.21	1.61	3.05	3.33
t_{time}	8.24	8.24	2.41	0.92	3.33
$t_{catalyst}$	1.21	0.18	3.11	0.96	2.11

Statistically the evaluated parameters denote that it is possible to obtain some improved thermal responses by the DSC and TG curves when PHB modification reaction is conducted in the high temperature level (110°C) for 1 h and with a low level of catalyst concentration (5%).

Conclusions

Thermoanalytical results obtained from the DSC and TG curves of the prepared films within an experimental design allow to define the most adequate reaction conditions in order to promote the structural modification of PHB with maleic anhydride in a fixed proportion

(90/10). Probably, transesterification reaction conditions play an important role in the incorporation of MA units into the PHB chains. Reaction conditions can be optimized by adjusting the temperature at 110°C, time for 1 h and the triethylamine concentration in 5%.

Acknowledgements

The authors acknowledge the CNPq by the financial support.

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DOI: 10.1007/s10973-006-7852-3