Kinetic study of crystallization of PHB in presence of hydroxy acids

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Abstract Poly(3-hydroxybutyrate), PHB, has been structurally modified through reaction with hydroxy acids (HA) such as tartaric acid (TA) and malic acid (MA). The crystallization kinetic of the samples was evaluated by isoconversional method through nonlinear fitting to obtain the estimation for activation energy (E_a) and pre-exponential (A) values. The thermal behavior of the crystallization temperature, 44.8 and 58.9 °C at 5 °C/min, and results obtained to the average activation energy, 73 ± 9 kJ mol^{-1} and 63 ± 1 kJ mol^{-1}, to PHB/MA and PHB, respectively, are suggesting that malic acid may be deriving plasticizer units from its own PHB chain. PHB/TA show increase in the medium value of E_a, 119 ± 2 kJ mol^{-1} and $T_c = 48.2$ °C (at 5 °C/min), indicating that tartaric acid is probably interacts in different way to the of PHB chain (E_a=73 $\pm$ 9 kJ mol^{-1}, $T_c = 44.8$ °C at 5 °C/min).

Keywords PHB · PHB-hydroxyacids · Nonlinear fitting · Crystallization · Nonisothermal kinetic

Introduction

PHB is a biocompatible and biodegradable thermoplastic polymer, with a melting temperature of approximately 175 °C, besides thermally unstable and brittle. Their poor characteristics for industrial processes is the main disadvantages in application of PHB as biomaterial [1–7]. In

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order to increase the possibilities for application it becomes necessary to study new PHB blends [8]. By this way, hydroxy acids such as tartaric (TA) and malic (MA) acids that there are substances with same chemistry nature of the PHB, could present potential to react in the chain of the homopolymer [9]. In the same way, the new material could present the advantage for not change the biodegradability of PHB which is one of its main characteristic.

The aim of this work was to evaluate the kinetic parameters, activation energy and pre-exponential, for PHB homopolymer, PHB/TA and PHB/MA blends mainly regarding to crystallization from the melted and quenched films. Furthermore, in this paper a new isoconversional method was used to obtain the reliable and consistent kinetic information. Activation energy were estimated in temperatures corresponding to fixed conversion degree (α) values, it avoiding the use of explicit kinetics models [10, 11]. Thus, the activation energy (E_a kJ mol^{-1}) data were obtained applying the isoconversional method proposed by Capela and Ribeiro from nonlinear fitting procedure.

Kinetic theory

To perform the kinetic analysis under non-isothermal conditions is usually to consider the integral kinetic equation, defined by

$$\beta = \frac{AE}{Rg(\alpha)} \int_{E/RT}^{\infty} \frac{\exp(-z)}{z^2} \mathrm{d}z, \tag{1}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ is a constant heating rate (T is the temperature and t is the time), $g(\alpha)$ is the integral form of the reaction model as function of the extent of reaction α, A is the pre-exponential factor, E is the activation energy and R is the gas constant.

Kinetic parameters are estimated by fitting Eq. 1 to experimental data. As a consequence, it is required to find a suitable solution to the integral on the right side of Eq. 1, known as temperature integral. A difficulty results from the fact that this integral does not have an exact analytical solution. In this work, the kinetic parameters are obtained through isoconversional method using an approximation to the temperature integral based on the convergent of a Jacobi fraction [12]. The replacement of the integral in Eq. 1 by this approximation results in the following expression for heating rate β as function of the $z_\alpha = 10^3/RT_\alpha$ (the subscript indicates the dependence on the extent of reaction α):

$$\beta = \frac{\exp(B_\alpha - E_\alpha z_\alpha)}{x_\alpha} \frac{E_\alpha^3 z_\alpha^3 + 14E_\alpha^2 z_\alpha^2 + 46E_\alpha z_\alpha + 24}{E_\alpha^4 z_\alpha^4 + 16E_\alpha^3 z_\alpha^3 + 72E_\alpha^2 z_\alpha^2 + 96E_\alpha z_\alpha + 24},$$

(2)

where the activation energy is in kJ/mol and the parameter B_α is defined as:

$$B_\alpha = \ln\left(\frac{10^3 A_\alpha}{Rg(\alpha)}\right)$$

(3)

E_α and B_α can be estimated by the non-linear fitting from Eq. 2 to the β values as function of z_α while the parameter A can be obtained from Eq. 3.

Now, if $G(\alpha)$ will be a function defined by:

$$G(\alpha) = 10^3 R^{-1} \exp(-B_\alpha)$$

(4)

then, from Eq. 3 follows that

$$A_\alpha = \frac{g(\alpha)}{G(\alpha)}$$

(5)

Estimation of $g(\alpha)$, not necessarily a typical physical-geometric model can be obtained from non-linear fitting of $G(\alpha)$ against α and thus, substituting it in the Eq. 5 the A_α values can be calculated.

Experimental

Film preparation

Granules (180 mg) of PHB homopolymer from PHB Industrial S/A and 20 mg of hydroxy acids (HA) were added in two independent vials (8 mL) containing 2 mL of chloroform and 2 mL of acetone respectively. The vials were sealed and heated at 100 °C for 10 min and then stirred (90 rpm) for 20 h at room temperature (25 °C). After stirring the HA solution was completely transferred to polymer solution in order to obtain a 90/10% (mass/mass) ratio of PHB/MA and PHB/TA. The resultant solutions were evaporate at ambient temperature to obtain the films and then they were completely dried under vacuum at 40 °C for 12 h.

Thermal behavior

PHB homopolymer, PHB/TA 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 195 °C for 5 min. The samples were immediately quenched by using liquid nitrogen and then a second heating were carried out from −50 to 200 °C in order to determine the crystallization temperature (T_c). The analyses were performed in a sealed aluminum reference and sample crucibles under nitrogen atmosphere (50 mL min^{-1}). The kinetic parameters were obtained using different heating rates (5, 10 and 15 °C min^{-1}).

Results and discussion

The studies regarding to interaction between PHB and hydroxy acids such as malic acid (MA) and tartaric acid (TA) was carried in a fixed proportion (90/10 mass/mass of PHB/MA). The thermal behavior of PHB had already changed after reacting with hydroxy acids with special regard to the crystallization temperature. Table 1 summarizes the crystallization temperature of PHB and PHB/hydroxy acid films at different heating rates (β).

It can be observed that the crystallization temperature of PHB is unaltered or increased depending on hydroxy acids, and it may be indicative of a new blend. In Fig. 1 the DSC curves of PHB homopolymer are shown. The thermal behavior of PHB/TA and PHB/MA are similar to PHB homopolymer.

In Fig. 2 an example is shown how to estimate the activation energy by the non-linear fitting from Eq. 2 to the β values as function of Z_α, $1,000/RT_\alpha$, to extent of reaction $\alpha = 85\%$. The values to the other extent of reaction can be found in Table 2.

Table 1 Crystallization temperature for PHB homopolymer and film blends

Films	Crystallization temperature/°C	β/°C min^{-1}
PHB homopolymer	44.8	5
	51.3	10
	55.6	15
PHB/MA	58.9	5
	68.2	10
	73.6	15
PHB/TA	48.2	5
	53.8	10
	55.5	15

Fig. 1 Experimental DSC curves of PHB homopolymer

Fig. 2 Adjustment of β versus conversion degree ($\alpha = 85\%$) for PHB/malic

Figure 3 shows the E_a data as a function of the conversion degree (α) for the crystallization of the compounds, obtained from Eq. 2. The average activation energy values for the PHB homopolymer, PHB/MA and PHB/TA films were 73 ± 9 KJ mol^{-1}, 63 ± 1 kJ mol^{-1} and 119 ± 2 kJ mol^{-1} in the $0.05 < \alpha < 0.95$ interval. In Table 2 the correlation coefficient and E_a, data are summarized, where the averages are 0.9966, 0.9990 and 0.9686 respectively, and the calculated values for the Arrhenius pre-exponential factor, A. Compared to PHB homopolymer, the PHB/MA film shows decrease in
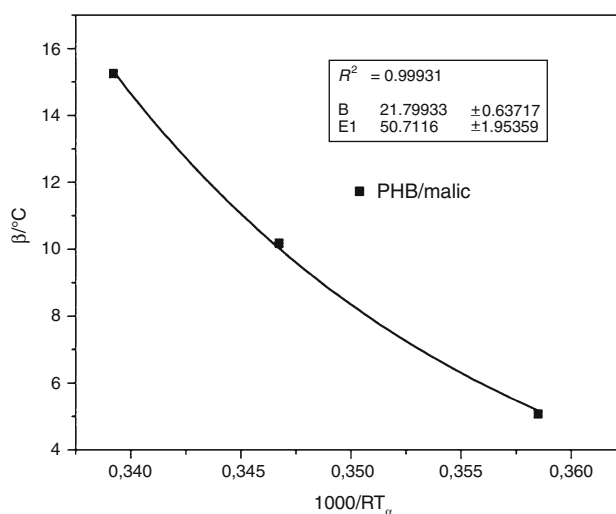
activation energy of crystallization of approximately 10 KJ mol^{-1}, but an increase in the correspondent temperature, (about ~ 15 °C) can be observed and it may indicate an influence of malic acid interacting in the PHB chain and deriving plasticizer units from its own PHB. The PHB/TA sample shows a strong increase in E_a values compared to the PHB meanwhile the crystallization temperatures are similar.

Table 2 Correlation coefficient (R^2) and activation energy (E_a) values

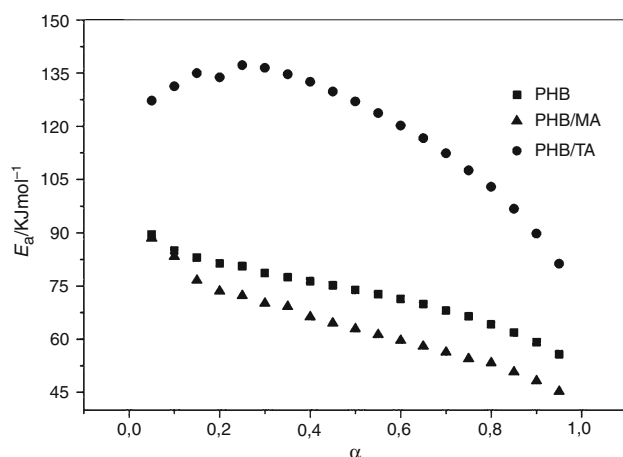| α	PHB/MA			PHB/TA			PHB		
	E_a/kJ mol^{-1}	R^2	A/min^{-1}	E_a/kJ mol^{-1}	R^2	A/min^{-1}	E_a/kJ mol^{-1}	R^2	A/min^{-1}
0.05	88	0.9962	2.99×10^8	127	0.9230	2.70×10^9	89	0.9989	4.12×10^9
0.10	83	0.9967	3.42×10^7	131	0.9325	1.53×10^7	85	0.9999	2.43×10^9
0.15	76	0.9974	9.13×10^6	135	0.9436	1.34×10^7	82	0.9999	1.38×10^9
0.20	73	0.9983	3.16×10^6	133	0.9547	6.63×10^6	81	0.9999	8.52×10^8
0.25	72	0.9987	1.32×10^6	137	0.9189	1.15×10^6	80	0.9997	5.72×10^8
030	70	0.9991	6.72×10^5	136	0.9349	1.04×10^6	78	0.9994	3.83×10^8
0.35	69	0.9991	3.58×10^5	134	0.9483	3.52×10^5	77	0.9992	2.56×10^8
0.40	66	0.9997	1.99×10^5	132	0.9589	2.03×10^5	76	0.9988	1.83×10^8
0.45	64	0.9998	1.16×10^5	129	0.9683	2.00×10^4	75	0.9985	1.28×10^8
0.50	62	0.9999	6.88×10^4	126	0.9754	1.45×10^4	73	0.9980	8.52×10^7
0.55	61	0.9999	4.00×10^4	123	0.9819	8.85×10^3	72	0.9975	5.74×10^7
0.60	59	0.9999	2.39×10^4	120	0.9871	6.08×10^3	71	0.9969	3.72×10^7
0.65	57	0.9999	1.41×10^4	116	0.9913	1.93×10^3	69	0.9963	2.27×10^7
0.70	56	0.9998	8.11×10^3	112	0.9948	1.38×10^3	68	0.9953	1.29×10^7
0.75	54	0.9997	4.49×10^3	107	0.9975	5.15×10^2	66	0.9945	7.14×10^6
0.80	53	0.9995	3.03×10^3	102	0.9989	2.62×10^2	64	0.9933	3.30×10^6
0.85	50	0.9993	1.21×10^3	96	1.0000	7.70×10^1	61	0.9918	1.43×10^6
0.90	48	0.9999	5.00×10^2	89	0.9989	1.48×10^1	59	0.9901	5.20×10^5
0.95	45	0.9988	1.66×10^2	81	0.9942	1.59×10^1	55	0.9878	1.47×10^5

Fig. 3 E_a data versus the conversion degree (α)

The variation in the $E_a(\alpha)$ versus α values (Table 2) indicate that crystallization does not occur in a homogeneous way for all α values [13–15]. For PHB/TA, E_a may be influenced by the interaction between tartaric acid and the PHB chains. Additionally, for both PHB/MA and PHB/TA films it can be suggested that E_α, is influenced by the conversion degree, and decreased due to the structural relaxation because of delocalization of the molecules. However, the crystallization of PHB containing hydroxy acids it is not easily explained by a simple first order reaction or reaction chain mechanism, because there is a tendency to a random scission chain with possible autocatalytic contribution of the short chain.

Conclusions

The peak temperature and activation energy regarding the crystallization of the PHB/malic and PHB/tartaric films showed that hydroxy acids have influence on the PHB crystallization but in different aspect. The presence of the malic acid may be acting as propitiator for formation of plasticizer deriving from its own PHB chain, which was not observed for the tartaric acid.

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