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KINETIC MODEL OF POLY(3-HYDROXYBUTYRATE) THERMAL DEGRADATION FROM EXPERIMENTAL NON-ISOTHERMAL DATA

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The non-isothermal data given by TG curves for poly(3-hydroxybutyrate) (PHB) were studied in order to obtain a consistent kinetic model that better represents the PHB thermal decomposition. Thus, data obtained from the dynamic TG curves were suitably managed in order to obtain the Arrhenius kinetic parameter E according to the isoconversional F–W–O method. Once the E parameters is found, a suitable log$A$ and kinetic model ($f(\alpha)$) could be calculated. Hence, the kinetic triplet (E±SD, log$A$±SD and $f(\alpha)$) obtained for the thermal decomposition of PHB under non-isothermal conditions was E=152±4 kJ mol^{-1}, log$A$=14.1±0.2 s^{-1} for the kinetic model, and the autocatalytic model function was: $f(\alpha)=\alpha^m(1-\alpha)^n=\alpha^{0.42}(1-\alpha)^{0.56}$.

Keywords: *biodegradable polymers, non-isothermal kinetic, PHB thermal degradation*

Introduction

Plastics originated from petroleum present some very desirable mechanical properties for large spectra of applications and at a relatively low price. Stability in regard to all kinds of degradation is one of the most important properties for polymeric-materials applications and thus, oil-based plastics have been extensively used due to high thermal and chemical stability. However, this extremely important in-service property is a serious environmental problem due to a low degradability rate. Thus, biodegradable and biocompatible plastics represent an alternative to conventional plastics. Among these bioplastics, the poly(hydroxyalcanoates) (PHAs), especially poly(3-hydroxybutyrate) (PHB), is aliphatic polyester that has been extensively studied. PHB is produced in a fed batch fermentation process by a widely available bacteria strain from renewable cheap carbon sources such as white sugar cane [1, 2]. However, these advantages are not enough to substitute commodity plastics, since PHB's mechanical properties are limited and the production cost is not yet competitive on the plastics engineering market. Having an elevated crystalline phase (60 to 80%), the PHB plastic is brittle and its thermal degradation starts near the crystalline melting point (about 180°C). So, when it is molded at least 190°C, the processed polymer will fail in its potential applications [3, 4].

Kinetics of PHB thermal degradation has been studied from non-isothermal and isothermal data. Thermogravimetric analysis (TG) and its first derivative (DTG) have been successfully applied to establish the thermal degradation of a polymer, particularly PHB [5–8]. TG, coupled to other techniques, for example GC-MS, has been used to analyze the volatile product released from PHB decomposition [9]. In order to understand the random chain scission mechanistic (*cis*-elimination) of PHB, the Arrhenius kinetic parameters like activation energy (E) and pre-exponentional factor (A) have been calculated applying the Kissinger or Flynn–Wall–Ozawa (F–W–O) methods [10]. Nevertheless, the kinetic model, $f(\alpha)$, where α is the fractional reaction of PHB decomposition, still remains without a representative function in regard to its specific kinetic exponentials. PHB degradation was studied using TG in order to calculate the kinetic triplet (E, log$A$ and $f(\alpha)$) from experimental non-isothermal conditions.

Kinetic considerations

By using TG non-isothermal procedures, the thermal decomposition of a material can be mathematically described by the kinetic triplet (E, log$A$ and $f(\alpha)$). A solid-state Arrhenius-type reaction can be expressed by the general equation [11–14]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (1)$$

where the fractional degradation (α) is temperature (T) dependent during an increasing constant heating rate (β). Accordingly, the isoconversional F–W–O method, that is the angular coefficient of a

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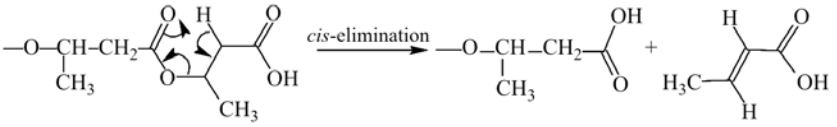

Fig. 1 Suggested mechanism for the thermal decomposition of PHB [3, 9, 24]

plot of logβ *vs.* 1/*T* at different and constant α, gives the *E*(α), and from known *E*(α) the approximated *A* values can be obtained [11–16].

In order to calculate the best fit kinetic model that represents PHB degradation, the *y*(α) and *z*(α) functions have been defined [17–19].

Koga has utilized the generalized time introduced by Ozawa in order to calculate the *y*(α) and *z*(α) functions from non-isothermal and isothermal thermogravimetric data for a solid-state reaction, since the *E* and log*A* are known [20–23].

$$y(\alpha)=\frac{\mathrm{d}\alpha}{\mathrm{d}\theta}=Af(\alpha) \tag{2}$$

$$y(\alpha)\theta=f(\alpha)g(\alpha)=z(\alpha) \tag{3}$$

The maximum of the normalized *z*(α) and *y*(α) functions *vs.* the α plot is indicative of the kinetic model function and kinetic exponents that theoretically better represent the studied process [18, 24, 25].

Thus, it is possible to define the kinetic triplet (*E*, *A* and *f*(α)) that better represent a non-radical cis-elimination mechanism (Fig. 1) that has been proposed for PHB thermal degradation [3, 9, 26].

Experimental

PHB Characterization by GPC

PHB homopolymer of natural origin was purchased from Sigma-Aldrich (Steinheim, Germany). The M_w was 485 kDa and M_w/M_n was 1.6. These values were determined by gel permeation chromatography (GPC) at 35°C using a Waters pump model 1515 and a refractive index detector model 2424. Chloroform was used as the solvent (1 mL min^{-1}) with a calibration curve obtained from monodisperse polystyrene standards (Shodex) separated in a set of Styragel® columns.

Kinetic experimental conditions

Powdered samples (14.0±0.1 mg) of PHB were submitted to the thermal-degradation kinetic study. Samples and reference (α-alumina powder) were heated in an open α-alumina pan in a SDT2960 from TA Instruments from 40 to 450°C, under nitrogen atmosphere (50 mL min^{-1}) at three different heating rates (5, 10 and 15°C min^{-1}).

Results and discussion

Kinetic parameters determination

Similar to the PHB degradation reported in literature [9, 26], only one step to the polymer thermal decomposition was noted (Fig. 2, Table 1). The kinetic parameters, *E* and log*A*, for the PHB thermal degradation were calculated applying software (TGAKin V4.0A) developed by Blaine [27] from experimental TG-DTG curves (Fig. 2) using the F–W–O isoconversional method. The *E*=152±4 kJ mol^{-1} and log*A* 14.1±0.2 min^{-1} average values obtained from the interval 0.25<α<0.85 of the PHB degradation are in agreement with the reported values [10, 26]. A typical F–W–O plot shown Fig. 3 portrays the *E* values *vs.* fractional PHB thermal degradation for a specific degree of reaction conversion.

The next step in the kinetic study, having the available *E* and log*A* parameters, is to evaluate the best kinetic model function *f*(α) to theoretically reproduce the PHB thermal degradation. Some kinetic model functions are shown in Table 2 [24, 25, 28, 29].

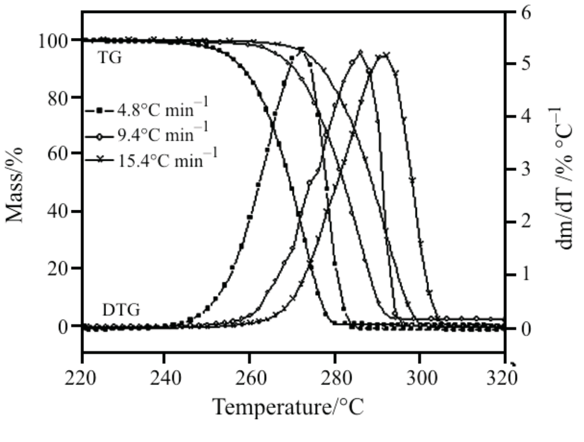

Fig. 2 TG-DTG curves for thermal decomposition of PHB at different heating rates

Table 1 Initial and final PHB degradation temperatures at different heating rates

Heating rate/ °C min^{-1}	Initial temperature/°C	Final temperature/°C
4.8	225	285
9.4	240	290
15.4	245	310

Table 2 Description, symbol and main characteristics of the evaluated mathematical kinetic model functions $f(\alpha)$

Mechanism (symbol)	$f(\alpha)$	Main characteristics
Johnson–Mehl–Avrami (JMA)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	nucleation and growth (n=1.5, 2, 3, 4)
Reaction order (RO)	$(1-\alpha)^n$	n order
Šesták and Berggren (SB)	$\alpha^m(1-\alpha)^n$	autocatalytic

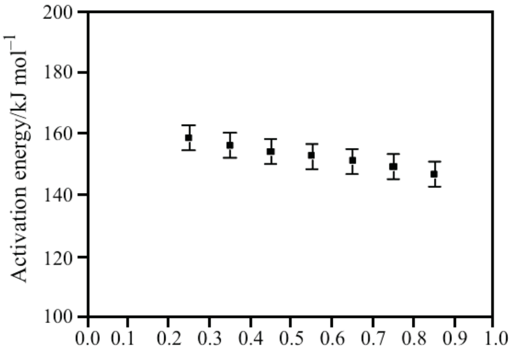

Fig. 3 The values of E_a at various α calculated using the Flynn–Wall–Ozawa method for the thermal decomposition of PHB

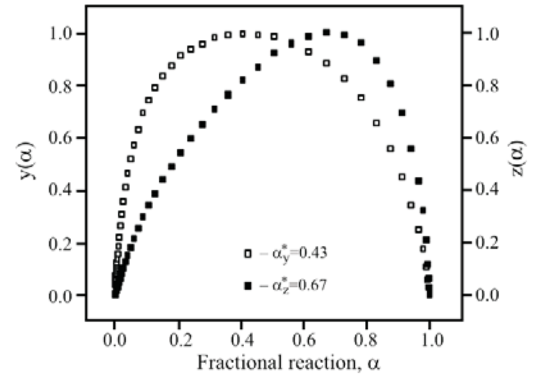

Fig. 4 Normalized $y(\alpha)$ and $z(\alpha)$ functions *vs*. fractional reaction for the thermal decomposition of PHB

Evaluation of the kinetic model functions

Thus, the α maximum for the $z(\alpha)$ and $y(\alpha)$ (Eqs (2) and (3)), respectively α^*_z=0.67 and α^*_y=0.43, were calculated from experimental non-isothermal data to obtain the PHB degradation (Fig. 4). According to the Málek's method, if $0<\alpha_y<\alpha_z$ and the α_z maximum value is near 0.60–0.66, it is possible to suggest the JMA and/or SB model to represent the PHB thermal degradation mechanism [17].

In order to evaluate the applicability of the suggested kinetic model function, a simulated DTG curve for the PHB thermal degradation was calculated considering a JMA with $n>1$ and the SB's kinetic models (Table 2). The exponent n in the JMA model was determined according to the maximum of the $y(\alpha)$ function, (α^*_y), as represented by the following equation [17, 18, 30]:

$$n=\frac{1}{1+[\ln(1-\alpha_y)]}=2.28 \tag{4}$$

In this way, the simulated normalized DTG curve (Eq. (1)) can be represented as below:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)2.28(1-\alpha)[-\ln(1-\alpha)]^{1-\frac{1}{2.28}} \tag{5}$$

Otherwise, the kinetic exponents, m and n, of the SB model (Table 2) can be calculated in two steps. First, the p value is determined by the succeeding equation [24, 30] considering the obtained α^*_y:

$$p=\frac{\alpha^*_y}{1-\alpha^*_y}=0.75 \tag{6}$$

A plot of $\ln y(\alpha)$ *vs*. $\ln(\alpha^p(1-\alpha))$ for the $0.3>\alpha>0.8$ interval follows a linear relationship where the slope is the n value. Finally, the m value can be calculated from the correlation $m=pn=0.42$. And thus, the $f(\alpha)$ for the normalized simulated DTG curve considering the autocatalytic kinetic model function is represented by the equation:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)\alpha^{0.42}(1-\alpha)^{0.56} \tag{7}$$

An overlay graph is plotted with normalized, simulated and experimental DTG curves of the PHB thermal degradation according to the JMA (Eq. (5)) and SB (Eq. (7)) kinetic model. Residual analysis was used to select the best kinetic model function, respectively, presented in Figs 5 and 6.

However, the results presented in Figs 5 and 6 may be not enough to select the most suitable kinetic model function for PHB thermal decomposition, although the residual analysis indicates a best fit for the SB kinetic model function. With two reasonable kinetic models proposed, since they have different interpretation mechanisms, it is necessary to apply another mathematical tool to evaluate the applicability of the tested functions [31].

Using a reference point (α=0.5) in the DTG curve, it is possible to plot the relationship between the obtained data from the simulated (SB and JMA) and the experimental DTG based on the following equation [31].

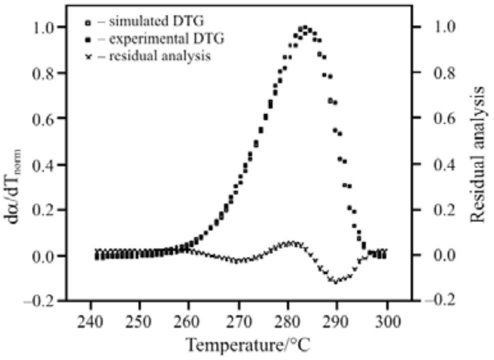

Fig. 5 Normalized experimental and simulated DTG curves and residual analysis using the JMA model (*n*=2.28)

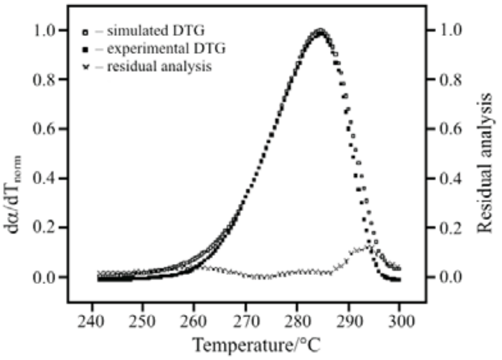

Fig. 6 Normalized experimental and simulated DTG curves and residual analysis using the SB model (*n*=0.56 and *m*=0.42)

$$\frac{\mathrm{d}\alpha/\mathrm{d}\theta}{(\mathrm{d}\alpha/\mathrm{d}\theta)_{\alpha=0.5}}=\frac{\mathrm{d}\alpha/\mathrm{d}t}{(\mathrm{d}\alpha/\mathrm{d}t)_{\alpha=0.5}}\frac{\exp(E/RT)}{\exp(E/RT_{0.5})} \qquad (8)$$

where $\mathrm{d}\alpha/\mathrm{d}\theta$ corresponds to the generalized reaction rate obtained by extrapolating the reaction rate in real-time, $\mathrm{d}\alpha/\mathrm{d}t$, to infinite temperature [31]. In a specific kinetic model function the $f(0.5)$ value is constant at a fixed value of $\alpha=0.5$. Figure 7 shows the normalized experimental, simulated JMA and SB (Eqs (5) and (7)) DTG curves at the respective $(\mathrm{d}\alpha/\mathrm{d}\theta)/(\mathrm{d}\alpha/\mathrm{d}\theta)_{\alpha=0.5}$ values.

The first half of the PHB degradation for both JMA and SB (Fig. 7) kinetic models present an acceptable fit to the experimental non-isothermal data. This may suggest that initial thermal decomposition could be represented by the JMA kinetic model, that is to say, the beginning of the thermal decomposition step may be governed by a nucleation process. When *trans*-crotonic acid starts to be released from the chain's interface, a deviation from JMA model occurs and an autocatalytic one predominates represented by the SB model [32]. The product of the PHB degradation can influence the electronic vibration stability of polyester carbonyl group and this may be responsible for the decrease in the activation energy when the decomposition process advances (Fig. 4).

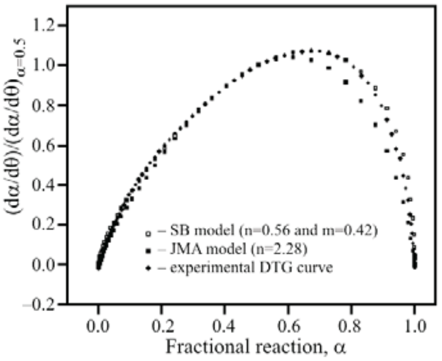

Fig. 7 Comparison of the experimental and simulated master plots of $(\mathrm{d}\alpha/\mathrm{d}\theta)/(\mathrm{d}\alpha/\mathrm{d}\theta)_{0.5}$ *vs.* α for the thermal decomposition of PHB

Knowing that the SB model is the better one to represent the thermal decomposition of PHB, the suitable log*A* can be calculated according to the defined kinetic exponents using the equation below [33]:

$$A=\frac{\beta E}{RT_{\mathrm{p}}^{2}Q_{\mathrm{p}}}\exp\left(\frac{E}{RT_{\mathrm{p}}}\right) \qquad (9)$$

where T_{p} is the temperature of the DTG peak and Q_{p} is determined by the following equation:

$$Q_{\mathrm{p}}=n\alpha_{\mathrm{y}}^{\mathrm{m}}(1-\alpha_{\mathrm{y}})^{\mathrm{n}-1}-m\alpha_{\mathrm{y}}^{\mathrm{n}}(1-\alpha_{\mathrm{y}})^{\mathrm{n}} \qquad (10)$$

The found value, $\log A=14.6\ \mathrm{s}^{-1}$, is in agreement with the previous determined value considering a first order reaction [11].

It was verified that the PHB degradation is not easily explained by a simple first order reaction or reaction chain mechanism, because there is a tendency to have a random scission chain with possible autocatalytic contribution [9].

Conclusions

Experimental data from PHB degradation under non-isothermal conditions allowed the kinetic triplet (*E*, log*A* and $f(\alpha)$) to be calculated. The kinetic procedures applied were consistent in order to obtain the kinetic parameters and a mathematical kinetic model function. Based on the best fit between normalized simulated data with respect to the JMA and SB kinetic model function and experimental data, it was evident that the PHB thermal degradation presents an initial step explained by an induction characteristic that is governed by nucleation, although a deviation from the JMA equation to the predominate chemical event during an autocatalytic reaction was observed. Hence, the SB kinetic model function is the most adequate to theoretically represent the entire PHB degradation.

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