Measurement and Simulation of Thermal Stability of Poly(Lactic Acid) by Thermogravimetric Analysis

ABSTRACT: The thermal degradation of poly(lactic acid) (PLA) biopolymer was studied as used by the thermogravimetry analyzer in a nitrogen atmosphere in the temperature range of 100–500°C. The reaction was found under these experimental conditions to be of first order with an activation energy of 94.0 and 105.3 kJ/mole and pre-exponential factor $6.43 \times 10^7$ and $1.91 \times 10^8$ 1/s, respectively. Slight differences have been found in activation energy depending on the analytical methods used and reported in other previous articles. It was found that the activation energy of thermal degradation increased with increasing the molecular weight of PLA. Moreover, the behaviors involved in the thermal degradation of PLA in nitrogen atmosphere were studied by using the numerical simulation of the kinetic model to dynamical thermogravimetric data. The maximum decomposition temperature, shape index for dynamic condition and life, and degree of decomposition for the isothermal condition of thermal behavior of PLA are predicted via mathematical simulation in this study.

KEYWORDS: thermal degradation, poly(lactic acid), thermogravimetry, activation energy

Introduction

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polymer with excellent mechanical properties which is now beginning to widely apply for recyclable packing materials and for medical applications in Taiwan [1]. It is well known that PLA belongs to biopolymers because their repeated aliphatic ester structure is relatively easy to breakdown, are easy to hydrolyze, and have poor thermal stability [2,3]. Although it is known that PLA belongs to a group of biopolymers with poor thermal stability, the main techniques used to process this material into mechanical devices and its fibers are compression, extrusion, injection-molding, and melt-spinning [4–6]. In all cases the manufactured products have been demonstrated to be partially degraded with respect to the PLA materials, so that predicted degradation behaviors are revealed. Many studies on the thermal degradation and thermal stability of PLA have been reported. The parameters which have been reported to influence PLA thermal stability include moisture, hydrolyzed monomer and oligomer, and residual metal catalyst, etc. Thermal degradation of PLA is a single stage process. This stage mainly involves the nonradical decomposition, radical alkyl-oxygen homolysis, and radical acryl-oxygen homolysis. This polymer material is the precursor to the formation of an intra-molecular transestertification, which undergoes ester pyrolysis, and unzipping depolymerization random chain scission [7–12]. McNeil and Leiper investigated the degradation of PLA under conditions of both controlled and isothermal heating [13,14]. They reported that the pyrolysis was a first-order reaction kinetic equation, the apparent activation energy as 119 kJ/mole in the temperature 240–270°C. Babanalbandi et al. reported the activation energy values for PLA pyrolysis behavior using an isothermal method. They showed that the activation energy value changed 72–97 kJ/mole in a complex way, accompanied by a weight loss [15]. Aoyagi et al. also reported a similar result of a complex change in the activation energy value 80–160 kJ/mole [16]. Fan et al. studied the pyrolysis mechanism of PLA with different chain end structure. They reported the pyrolysis was a zero-order reaction kinetic equation, the apparent activation energy as 80–100 and 100–120 kJ/mole through unzipping depolymerization and lactide elimination, respectively [17]. Wachsen et al. studied the kinetics of change in molecular weight by using a two-parameter model during thermal treatment of PLA in nitrogen atmosphere in the temperature range of 180–230°C. It was found the radical degradation reactions need only be taken into consideration at temperatures above 250°C and the activation energy was 120 kJ/mole for the purified PLA [18]. Kopinke et al. studied PLA by means of thermogravimetrical techniques. They obtained the activation energy value was 110 kJ/mole [19]. Sivalingam and Madras investigated the thermal degradation of PLA under conditions of both dynamic and isothermal heating. They reported that the pyrolysis of the apparent activation energy were 42.7 and 105.4 kJ/mole for the random chain scission and the specific chain scission for the dynamic heating by using the Friedman analytical method and 92.9 kJ/mole for isothermal holding method, respectively [20]. However, no literature has reported the relative significance of aging time to the degrade reaction of the PLA. Understanding the influence of PLA stability is relevant for providing the degradation property of manufactured products. These characteristic properties of PLA are important in determining how molten PLA should be processed without causing serious thermal decomposition. The thermogravimetric analysis (TGA) has been widely used to investigate the decomposition characteristics of many materials and to determine the kinetic parameters such as activation energy, pre-exponential factor, and reaction order [21–25]. Numerous investigations of the thermal degradation of various polymers have shown the value of the thermogravimetric analysis.
analysis with dynamic and isothermal techniques. With proper experimental procedures, information about the degradation kinetics of decomposition can be obtained. TGA provides a method for thermal stability testing [26–33]. Many investigations of the thermal degradation of various polymers have shown the value of the technique of the thermogravimetric analysis. Despite there being so many reports on PLA pyrolysis, to date we are not aware of any report on the thermal degradation of degree of decomposition of lifetime for PLA having been published. In this paper, the TGA technique is applied to simulate overall thermal degradation of poly(lactic acid) biopolymer for degree of decomposition of lifetime. The apparent activation energy was evaluated by dynamic and isothermal thermogravimetric method. The thermal degradation behavior of PLA was examined for three different analytical models. Moreover, the behaviors involved in the thermal degradation of PLA were studied by using numerical simulation of kinetic model to dynamical thermogravimetric data. The maximum decomposition temperature, shape index for dynamic condition and life, and degree of decomposition for isothermal condition of thermal behavior of PLA are predicted via mathematical simulation in this study.

Experimental

Poly(lactic acid) (PLA) was commercially purchased from Nacalai Tesque, Co., Ltd., Kyoto, Japan. The samples of weight-average molecular weight $M_w$ were 5,000 (PLA-5) and 10,000 (PLA-10) g/mole, respectively. The samples were used as received without further purification. The powder sample was preheated before thermogravimetric analysis. It’s useful to eliminate undesired volatile impurities [34]. For the determination of the rate of degradation at various heating rates a Shimadzu gravimetric analysis system TGA-50 was employed. The pyrolysis data were collected at regular intervals (one time per second) by a TA-60WS data platform and recorded into an analytical computer system. The computation of kinetic parameters for the thermal degradation program was carried out from TGA data using a software program and running on a Tatung Co. Taiwan compatible PC. The samples of PLA biopolymer were studied under nitrogen gas purges of 10 mL/min at various heating rates of 5, 10, 20, and 40°C/min by heating on PLA biopolymer samples in the weight range 5 mg were applied temperature from 100 to 500°C. For the determination of the rate of degradation at constant temperature for isothermal, PLA biopolymer samples in the weight range 5–7 mg were heated to the described temperature at a maximum rate of 99°C/min using the gravimetric analysis system under nitrogen gas purge of 10 mL/min. Variable temperature studies were made with the same instrument by heating PLA biopolymer samples at temperature of 250, 275, 300, and 325°C/min under nitrogen gas purge of 10 mL/min were applied.

Results and Discussion

The Experimental Data of Thermal Degradation of Poly(Lactic Acid)

In TGA measurements, the degree of decomposition can be calculated as follows [35]:

$$X = \frac{W_r - W_o}{W_o}$$  \hspace{1cm} (1)

where $X$ is weight loss fraction; $W_r$ is the residual weight of the sample, mg; $W_o$ is the initial weight of the sample, mg. The thermogravimetric and differential thermogravimetric (TG-DTG) curves of thermal degradation of poly(lactic acid) obtained at various heating rates under nitrogen atmosphere, are shown in Figs. 1 and 2. In each environment, a single stage degradation process is indicated with an ultimate solid state at 500°C of PLA. The TG-DTG curves of PLA showed one decomposition peak. At a lower heating rate, the retention time required for the PLA to a given temperature is longer. This would generally result in a higher conversion. Thus, the residual mass curve with a lower heating rate is below or to the left of that with a higher heating rate. The differential residual mass after degradation is expressed on a differential residual mass percent, $dX/dt$. The maximum rates occur at differential reaction temperature for various heating rates. A higher heating rate shifts the rate curve to the higher temperature range, and also results in a higher peak rate. It can be seen that there is one distinct peak rate in the degradation process. The thermal degradation behaviors of PLA were very complex because various reactions occurred concurrently. The broad peak is due to several decomposition reactions. The main products are carbon dioxides, acetaldehyde, a

![FIG. 1—The thermogravimetric curves of poly(lactic acid) (PLA-5) with different heating rates under nitrogen gas.](image-url)

![FIG. 2—The differential thermogravimetric curves of poly(lactic acid) (PLA-5) with different heating rates under nitrogen gas.](image-url)
Dynamic and Isothermal Thermal Stability Testing

The thermal stability of the PLA biopolymer was evaluated from TGA studies. Figs. 1 and 2 showed the TGA curves of the PLA biopolymer at four various heating rates, 5, 10, 20, and 40 °C/min under nitrogen gas. The thermal decomposition kinetic parameters, viz. activation energy $E_a$, pre-exponential factor $A$, and order parameter $n$, for the thermal decomposition of PLA biopolymer were evaluated from the TGA data. The kinetic parameters were calculated using the following Flynn and Wall [36] equation. The activation energy of a polymer degradation process is obtained from the following equation:

$$E_a = -18.2 \times d \left( \log RH \right) / d(1/T)$$  \hspace{1cm} (2)

where $E_a$ is activation energy, kJ/mole; $RH$ is heating rates, °C/min; $T$ is absolute temperature, K. If Flynn’s equation is valid for the thermal degradation of PLA, then a plot of $\log(RH)$ versus $1/T$ at various $X$ should be given straight lines. The $\log(RH)$ dependence of the reciprocal of temperature for different residue weight for PLA-5 is given in Fig. 3. A linear relationship dependence of $\log(RH)$ and the reciprocal of temperature for all $X$ values are observed. From this dependence the activation energies were evaluated by linear regression analysis of the data points. Similar results were observed with other molecular weight PLA-10. The average activation energies are calculated and shown in Table 1 for the molecular weight PLA with 5,000 and 10,000 g/mole, respectively. As shown in Table 1, the activation energy of PLA was increased with increasing the molecular weight. From the above relation, it is demonstrated that the higher the molecular weight is, the higher its stability is. That is, the thermal stability of higher molecular weight PLA, the larger is the activation energy for decomposition.

The isothermal stability of the PLA biopolymer was evaluated from TGA studies. Figure 4 showed the TGA curves of the PLA biopolymer at various isothermal temperature, 250, 275, 300, and 325 °C under nitrogen gas. As shown in Fig. 4, the residue of weight was decreased with an increasing of the heating time in the range of the 0–20 min.

The kinetic parameters of the high temperature degradation can be obtained from a single TGA thermogram. In particular, the differential method of Freeman and Carroll [37] has been widely used to determine the order and activation energy of the degradation. The rate of degradation may be written as follows

$$dX/dt = k_d(1 - X)^n$$  \hspace{1cm} (3)

where $dX/dt$ is the decomposition rate, s$^{-1}$; $X = (W_o - W_r)/W_o$ is weight loss fraction; $n$ is the empirical order of decomposition; $k_d$ is the decomposition rate constant, s$^{-1}$. A first-order kinetic evaluation measurement of PLA [13,14]. Equation 3 can be rewritten in the form:

$$-\ln(1 - X) = k_d t$$  \hspace{1cm} (4)

If Freeman’s equation is valid for the thermal degradation of PLA, then a plot of $-\ln(1-X)$ versus aging time at various isothermal temperatures should give straight lines, the decomposition order $n$ can be obtained from the slope. When $-\ln(1-X)$ is plotted against time for nitrogen gas atmospheres is shown in Fig. 5 for PLA-5. A linear relationship between the $\ln(dX/dt)$ versus $\ln(1-X)$ at the isothermal under four various temperatures. From this dependence, decomposition order was evaluated by linear regression analysis. These fits were obtained by the least square method. The decomposition order $n$ was 1.0 for PLA under nitrogen gas conditions. From Fig. 5, the slope $k_d$ at various temperatures can be obtained. Moreover, the

### TABLE 1—The thermal decomposition kinetic data of the poly(lactic acid).

<table>
<thead>
<tr>
<th>PLA</th>
<th>$\dot{M}_w$ (g/mole)</th>
<th>$E_a$ (kJ/mole)</th>
<th>$A$ (1/s)</th>
<th>$E_a$ (kJ/mole)</th>
<th>$A$ (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overall Avg.</td>
<td>$n$ Order</td>
<td>Early Stage</td>
<td></td>
<td>$n$-order</td>
</tr>
<tr>
<td>PLA-5</td>
<td>5,000</td>
<td>90.3</td>
<td>1.0</td>
<td>67.9</td>
<td>5.6$\times 10^3$</td>
</tr>
<tr>
<td>PLA-10</td>
<td>10,000</td>
<td>111.1</td>
<td>1.0</td>
<td>68.9</td>
<td>7.7$\times 10^3$</td>
</tr>
</tbody>
</table>
temperature dependence of the $k_d$ for PLA biopolymer is given in Fig. 6. An Arrhenius-type, $k_d = A \exp(-Ea/RT)$, dependence of $\ln(k_d)$ on temperature is observed. Similar results were observed with other molecular weight PLA-10. From this dependence the activation energies were evaluated by linear regression analysis of the data points shown in Table 1 under nitrogen. The activation energies of the early stage are similar to the activation energies calculated by using Flynn’s model for PLA with the 5,000 and 10,000 g/mole molecular weight, respectively. There were slight differences in activation energies which can be attributed to the analytical method used. Moreover, the activation energy from isothermal heating of PLA biopolymer was increased with an increase of molecular weight.

The Kinetic Model for Describing the Thermal Degradation of PLA

The Friedman method [38] has been applied to the decomposition stages of PLA. This is a widely used method and is based on the following general kinetic equation:

$$dX/dt = k(1 - X)^n$$

where $dX/dt$ is the decomposition rate and $k$ is the decomposition rate constant, which can be expressed by Arrhenius equation:

$$k = A \exp(-Ea/RT)$$

where $A$ is the pre-exponential factor (1/s), $Ea$ is the activation energy (J/mole), $R$ is the gas constant (8.314 J/g-mol·K), and $T$ is Kelvin temperature (K). Substitution of Eq 6 into Eq 5 yields:

$$dX/dt = A \exp(-Ea/RT)(1 - X)^n$$

In order to analyze this fact and elucidate the reason for the failure of the above methods, a kinetic model was used for describing the thermal degradation of PLA. Sivalingam et al. [39] who studied the vinyl polymer copolymers pyrolysis by thermogravimetric analyzer have suggested the multiple regression models for describing the thermal decomposition of polymer. A different methodology proposed by Sivalingam et al. was used to obtain the corresponding parameters, the results obtained with the experimental data and with the correlation obtained in this study. A methodology for the determination of all three parameters, ($n$, $A$, and $Ea$), using regression is presented. Equation 7 can be rewritten in the following form if $y = \ln(dX/dt)$, $X_1 = 1/T$, $X_2 = 1 - X$, $a = \ln A$, $b = -Ea/RT$, and $c = n$, where $a$, $b$, and $c$ are constants:

$$y = a + bX_1 + cX_2$$

There are two independent variables in the above equation, $X_1 (= 1/T)$ and $X_2 (= \ln(1 - X))$, and one dependent variable, $y (= \ln(dX/dt))$. The purposed regression method inputs all the variables and determines the activation energies, order, and frequency factor in a single stage. The multiple regressions method was accomplished by the software, Microsoft Office Excel 2005, and used the method based on the lowest residual sum of squares. The optimization methods [40–43] were used in order to calculate the kinetic parameters. The function to be minimized ($\tau$) was:

$$\tau(A, Ea, n) = \sum_{i=1}^{m} (X_{exp} - X_{calc})^2$$

where $m$ is the number of data point, the subscripts exp and calc mean experimental and calculated values using the model proposed.

The estimation of the order, pre-exponential factors, and the activation energies are given in Table 1. The values reported in Table 1 for all the techniques represent the average based on all heating rates and the represented experiments for PLA with the 5,000 and 10,000 g/mole molecular weight, respectively.

Decomposition Behavior of PLA via Model Simulation

The PLA decomposition can be associated with one overall reaction, which may be represented by processes with PLA mass retained for the PLA during dynamic heating:

$$\text{PLA}_{(s)} \rightarrow \text{Gas}_{(g)}(\uparrow)$$

where Gas and PLA corresponds to the gas (carbon dioxide, acetaldehyde, ketene, carbon monoxide, etc.) and the initial generated in the decomposition, and $k$ is the decomposition rate constant. To determine the way in the weight fractions of the component in such a mechanism, which depends on time (temperature). The material balances for the foregoing of reactions the rate equations can be also written as:
where $n$ is the empirical order of the decomposition. This system of equation can be written as an Arrhenius type function of the temperature:

$$\frac{dX}{dt} = -A \exp(-Ea/RT)X^n \tag{11}$$

where $A$ and $Ea$ are the pre-exponential factor and the activation energy of the reaction. The systems of reaction were using a fourth-order Runge Kutta algorithm method [44] to solve the differential rate equation in this study. The method can be outlined very briefly as follows:

$$\frac{dX}{dt} = \frac{A \cdot RH \cdot \exp\left(-\frac{Ea}{RT}\right) \cdot (1-X)^n}{1} \tag{12}$$

$$X' = f(X, T)$$

$$k_1 = \Delta T \cdot f(T_n, X_n)$$

$$k_2 = \Delta T \cdot f(T_n + \frac{\Delta T}{2}, X_n + k_1/2)$$

$$k_3 = \Delta T \cdot f(T_n + \frac{\Delta T}{2}, X_n + k_2/2)$$

$$k_4 = \Delta T \cdot f(T_n + \Delta T, X_n + k_3)$$

$$X_{n+1} = X_n + (k_1 + 2k_2 + 2k_3 + k_4)/6 \tag{14}$$

where $RH$ is empirical in thermal analysis is carried out at a constant heating rate, $RH(\text{°C/s}) = dT/dt$. Using the values of the activation energy 94.3 kJ/mole, the frequency factor $6.43 \times 10^5$ 1/s and the empirical order of decomposition of PLA-5, calculated by multiple regression model from the above section, under nitrogen decomposition. A series of simulated curves of TG and DTG curves from four different heating rates, 5, 10, 20, and 40 °C/min, can be generated as shown in Figs. 7 and 8. It can be clearly seen that the simulation and actual experimentation curves match closely. The generated as shown in Figs. 7 and 8. It can be clearly seen that the simulation and actual experimentation curves match closely. The maximum decomposition temperature, $T_{\text{max}}$, can be obtained from the temperature at the maximum decomposition rate. The data are listed in Table 2. The maximum decomposition temperatures of the thermal degradation of PLA-5 were 313.5, 333.3, 354.3, and 376.8 °C for four different heating rates, 5, 10, 20, and 40 °C/min, respectively. Similar procedures can be simulated with other molecular weight PLA by using data from Table 2 to get thermal degradation of PLA-10.

To quantitatively describe the peak shape of the differential thermogravimetric curve, a “shape index” was proposed by Kissinger [45]. Defined as the absolute value of the ratio of the slopes tangent to the curve at the inflection points, the shape index can be expressed analytically as

$$S = \left[ \left( d^2X/dT^2 \right) \left( d^2X/dT^2 \right)^2 \right]$$

where subscripts 1 and 2 refer to the value of these quantities at the inflection points, i.e., where $dX/dT = 0$, for each thermal degradation. Figure 9 is generated using Eqs 13 and 14 and $T_1$ as well as $T_2$ ($T_1$, $T_2$ are the temperatures at the first and second inflection points of the curve of $dX/dT$ versus temperature for each thermal degradation stage, respectively) can be obtained from the maximum points of the curve of $d^2X/dT^2$. All the values of $T_1$ and $T_2$ are summarized in Table 2. The value of $T_2/T_1$ was 1.200 for the decomposition stage of thermal degradation of PLA, respectively. The average value of 1.632 of shape index was also calculated which shows symmetric shape of the decomposition of PLA in the thermal degradation stage.

The decomposition time in isothermal condition for thermal degradation of PLA was based on Eqs 13 and 14, $1-X$ versus degradation time is shown in Fig. 10 via simulation. As can be seen, the decomposition at 175 °C is much faster than that at 125 °C. We can also see that 95 % of the PLA remains after 50 min at 125 °C compared to 25 % left at 175 °C. The results show that the degree of thermal degradation of PLA increases with increasing of the aging temperature and total time. Moreover, in order to calculate the estimated time of PLA to failure, a term called “lifetime,” $t_f$, is defined when the degree of decomposition reactions, i.e., $1-X = 0.95$ [46]. The predicted lifetime of PLA can be calculated using Eqs 13 and 14 as well as the values of the activation energy and frequency factor. It can be seen very clearly from Fig. 10 that statically used PLA polymer at temperature 125 °C will last one week (168 h) without failure.

**Conclusions**

In this paper, the thermal degradation of poly(lactic acid) (PLA) biopolymer was studied as used by the thermogravimetry analyzer in nitrogen atmosphere in the temperature range of 100–500 °C. The samples of PLA with different molecular weight were decomposed by using dynamic and isothermal methods, respectively. The reaction was found under these experimental conditions to be of first order with activation energy of 94.0 and 105.3 kJ/mole and pre-exponential factor $6.43 \times 10^5$ and $1.91 \times 10^6$ 1/s, respectively. Slight differences have been found in activation energy depending on the analytical methods used and reported in other previous articles. It was found that the activation energy of thermal degra-
tion increased with increasing the molecular weight of PLA. Moreover, the behaviors of involved in the thermal degradation of PLA in the nitrogen atmosphere were studied by using numerical simulation of kinetic model to dynamical thermogravimetric data. The maximum decomposition temperature, shape index for dynamic condition and life, and degree of decomposition for isothermal condition and life, and degree of decomposition for isothermal conditions, thermal degradation mechanism of PLA are predicted via mathematical simulation in this study. The average value of 1.632 of shape index was also calculated which shows symmetric shape of the decomposition of PLA in the thermal decomposition stage. The PLA polymer at temperature 125°C will last one week without failure.

### References


