

Kinetics of Thermodegradation of Palm Kernel Oil Derived Medium-Chain-Length Polyhydroxyalkanoates

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ABSTRACT: Oligomeric hydroxyalkanoic acids have potential industrial, medical, and pharmaceutical applications and they can be produced from the degradation of high molecular weight polyhydroxyalkanoates by a number of different ways. Thermal decomposition takes place in the absence of organic solvent and other chemicals and this justified the method of producing low molecular weight PHA as green chemistry. The kinetics for thermal degradation of medium-chain-length polyhydroxyalkanoates (mcl-PHA) prepared from saponified palm kernel oil (SPKO) was studied by thermogravimetric analysis (TGA) technique. Employing the nonisothermal Kissinger's method, the degradation activation energy, E_{a} and pre-exponential factor, A , were 129 kJ mol^{-1} and $1.15 \times 10^{10} \text{ s}^{-1}$, respectively. Specific degradation rate constant, k was found to increase at higher heating rate. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Numerous research papers have been published in recent years on the changes in chemical and physical properties of polymers when they are exposed to heat over a wide range of temperatures.¹ These studies are relevant for understanding the changes during molding of the thermoplastic, in the subsequent processing, and in its end-use application when exposed to elevated temperatures. Most high molecular weight organic polymers tend to decompose when heated to high temperature. Thermal stability has become an important parameter which must be taken into consideration when selecting polymers for engineering and medical applications or in the packaging of food at high temperatures. Thermal degradation is entropically favorable due to the increase in entropy or randomness for the degradation of a polymer into lower molecular weight compounds.

Medium-chain-length polyhydroxyalkanoates (mcl-PHAs) are biopolymers synthesized by bacteria; more specifically they are bacterial polyesters, consisting of 6 to 14 carbon-chain-length monomers.^{2,3} These biopolymers possess low glass transition temperatures, low crystallinity, and thermoplastic properties.^{4,5} The thermal stability of mcl-PHA is one of the determining factors in the processing and application of the biopolymer.⁶ Its tendency to break down at high processing temperatures can limit the application of a specific mcl-PHA as a thermoplastic.^{7,8}

Oligomeric hydroxyalkanoic acids have potential industrial,⁹ medical,¹⁰ and pharmaceutical¹¹ applications. The ease of thermodegradation of mcl-PHAs at controlled conditions offer an environmental friendly method, without the use of solvent and other chemicals, to the production of oligomeric hydroxyalkanoic acids.¹² Therefore, the kinetics of thermodegradation of mcl-PHA need to be studied in order to develop a proper process for both the specific applications of the biopolymer as a thermoplastic, as well as a means to produce oligomeric hydroxyalkanoic acids.

TGA can be a fast and practical method to evaluate the rates of the thermal degradation. Various methods to evaluate the kinetic parameters from the TGA data have been compared in a recent review article.¹³ The evaluation by using a single TG curve recorded at a certain heating rate does not lead to reliable results. Preferably, a set of TG curves recorded at different heating rates can provide better information concerning the overall mechanism and the kinetics of the investigated degradation process. In this article, we have adopted the nonisothermal Kissinger's method¹⁴ to determine the overall kinetic parameters of thermal degradation.

EXPERIMENTAL

Materials

Medium-chain-length PHAs were produced by *Pseudomonas putida* PGA1 using fed-batch fermentation. Bacterial cultivation

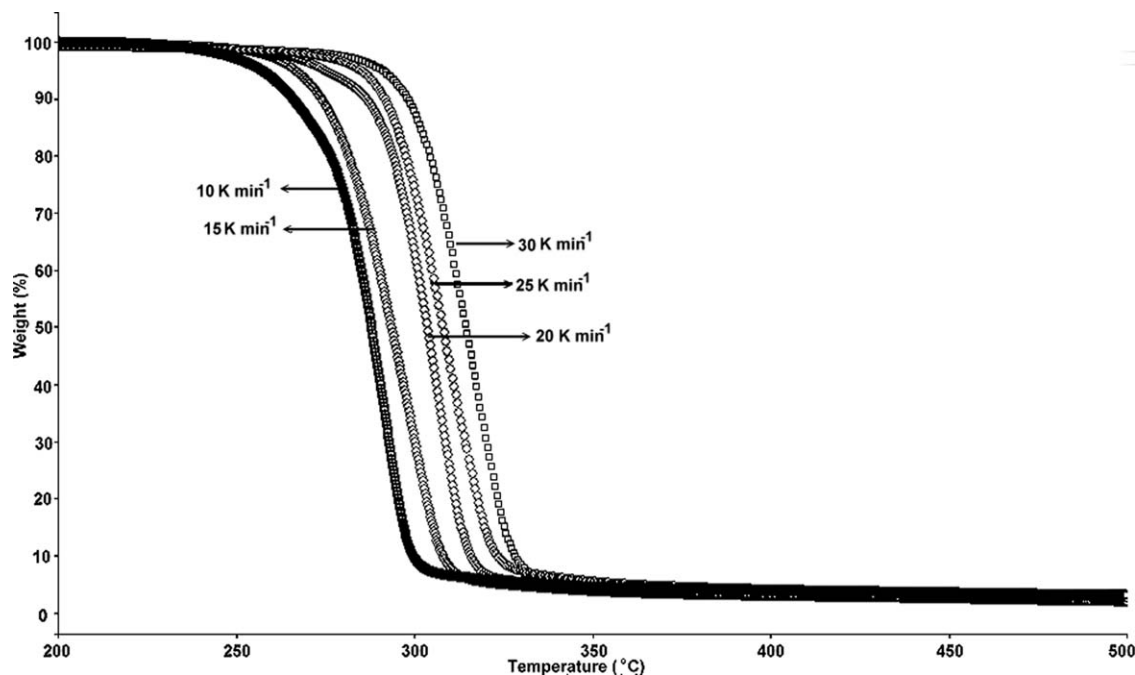


Figure 1. TGA curves of mcl-PHA at different heating rates.

was carried out at 30°C, 600 rpm and pH 7.0 in a 5-L stirred tank reactor (Biostat®B, BBraun International, Germany) using saponified SPKO as the sole carbon and energy source. The details of synthesis and characterizations of the mcl-PHAs have been reported elsewhere.¹⁵ Purified mcl-PHAs were obtained by dissolving the polymer in chlorinated solvent, followed by precipitation in cold methanol, separated by filtration, and drying *in vacuo*.

Instrument and Measurements

Kinetics of mcl-PHA thermal degradation was studied by using data from TGA measurements. Samples were analyzed by nonisothermal procedure using Perkin Elmer TGA6 (USA) at multiple heating rates of 10, 15, 20, 25, and 30 K min⁻¹. The nitrogen flow rate was fixed at 20 mL min⁻¹. Each thermogravimetry experiment was repeated twice. Kissinger equation,¹⁴ eq. (1), was employed in the kinetic analysis of the thermal decomposition to obtain the decomposition activation energy, E_d , and kinetic pre-exponential factor, A .

$$-\ln q/T_p^2 = E_d/RT_p - \ln (AR/E_d) \quad (1)$$

where q is heating rate (K min⁻¹), T_p is temperature of maximum rate of degradation (K), R is gas constant (J K⁻¹ mol⁻¹), E_d is degradation activation energy (kJ mol⁻¹), and A is pre-exponential factor (s⁻¹).

The plot of $-\ln (q/T_p^2)$ versus $1/T_p$ produces a straight line. The activation energy and pre-exponential factor were calculated from gradient of the straight line that gives E_d/R , and the intersection at y -axis equals to $-\ln (AR/E_d)$ where A is then obtained.^{16,17}

The thermal degradation rate constant, k can be calculated from the Arrhenius equation, eq. (2), for each temperature of interest.¹⁸

$$k = Ae^{-E_a/RT} \quad (2)$$

The entropy of activation (ΔS) was calculated using eq. (3).¹⁹

$$A = (kT_p/h)e^{\Delta S/R} \quad (3)$$

where A is Arrhenius parameter (s⁻¹), k is Boltzman constant (J K⁻¹), T_p is temperature of maximum rate of degradation (K), h is Planck constant (Js), ΔS is entropy of activation (J K⁻¹ mol⁻¹), and R is gas constant (J K⁻¹ mol⁻¹).

RESULTS AND DISCUSSION

The thermal degradation of mcl-PHA was investigated by TGA in the temperature range from 50°C to 900°C. Figures 1 and 2 showed the TGA and derivative of thermogravimetric (DTG) thermograms at five different heating rates. All TGA thermograms showed a smooth one-step weight loss curve between 200°C to 500°C. Increasing heating rate shifted the TGA and DTG curves to higher temperature zone. Temperature at the peak of the DTG curve peak corresponded to the temperature where the rate of degradation was at its maximum.

The relationship between heating rate and temperature of maximum degradation is shown in Table I. The linear plot of $-\ln (q/T_p^2)$ against $1/T_p$ is shown in Figure 3.

The plot has a correlation coefficient of $R^2 = 0.993$, indicating a good fit to the Kissinger equation. The gradient is equal to E_d/R , thus E_d could be determined. The intercept at y -axis is equal to $-\ln (AR/E_d)$, which then enable the pre-exponential factor, A , to be calculated. Thus, E_d and A were calculated to be 129 kJ mol⁻¹ and 1.15×10^{10} s⁻¹, respectively.

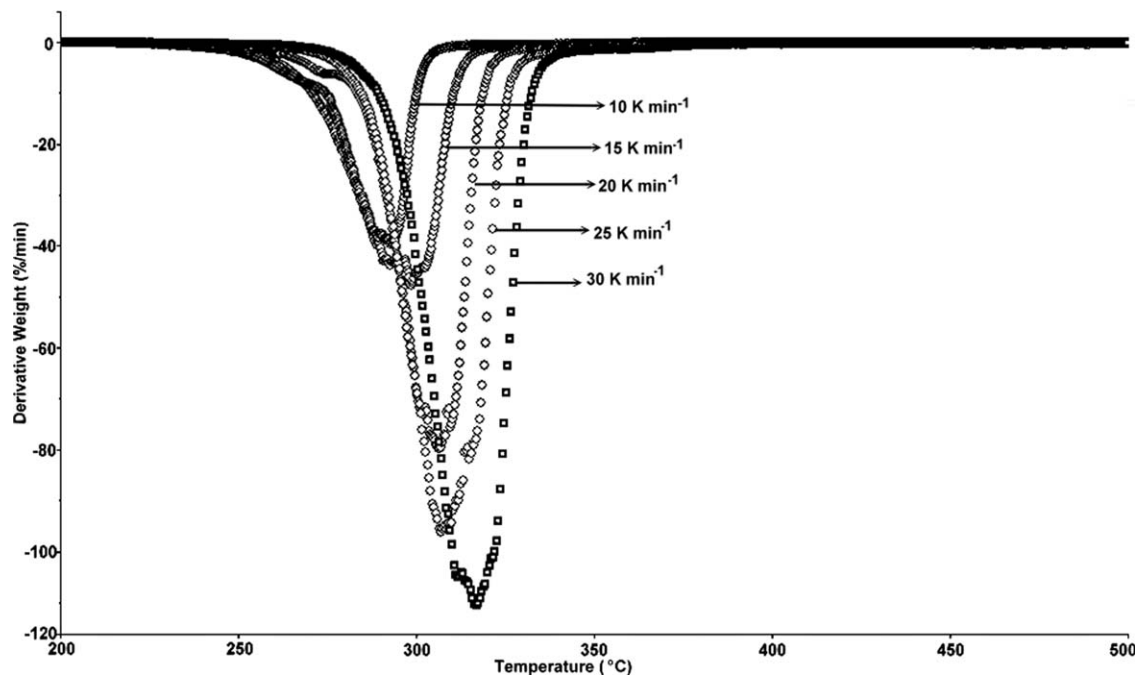


Figure 2. DTG curves of mcl-PHA at different heating rates.

The change of activation entropy (ΔS) estimated from eq. (3) has a value of $-57.6 \text{ J K}^{-1} \text{ mol}^{-1}$. The relatively small ΔS indicates that the mcl-PHA could be thermally unstable at high temperature.

In our earlier investigation on the thermal degradation of mcl-PHA made from oleic acid,¹² the E_d was much lower at 85.3 kJ mol^{-1} . This would mean that mcl-PHA derived from PKO is more stable to heat than that derived from oleic acid. The difference in the thermal stability is due to the fact that the mcl-PHA produced from SPKO consisted of a mixture of monomer units, derived from the carbon substrate of mixture of mainly saturated fatty acids with various different chain lengths, whereas the oleic acid derived PHA was produced from a single type of fatty acid that contain one unsaturation.

The values of specific degradation rate constant (k), for temperature ranging from 565 to 587 K were given in Table II. The specific degradation rate constant, k increased when the heating rate was increased.

The temperature at the onset (T_{onset}) and complete degradation (T_{final}) were obtained from the TGA curve using the instrument software. Figure 4 showed a linear relationship between T_{onset} and T_{final} with the heating rate, q .

Table I. The Relationship Between Heating Rate and Temperature at Maximum Rate of Degradation

$q \text{ (K min}^{-1}\text{)}$	$T_p \text{ (K)}$	$1/T_p \times 10^3$	$-\ln(q/T_p^2)$
10	565	1.77	10.37
15	574	1.74	10.00
20	580	1.73	9.73
25	583	1.72	9.52
30	587	1.71	9.33

These are related as follow:

$$T_{\text{onset}} = 1.12q + 539 \quad (4)$$

$$T_{\text{final}} = 1.26q + 562 \quad (5)$$

The thermal degradation temperature can be expressed as equilibrium degradation temperature when the heating rate (q) approaches zero.²⁰ From eqs. (4) and (5), $T_{\text{onset}}(0) = 539 \text{ K}$ and $T_{\text{final}}(0) = 562 \text{ K}$. The peak width of DTG is given by $T_{\text{final}} - T_{\text{onset}} = 0.14q + 23$, which increases slowly with increasing heating rate.

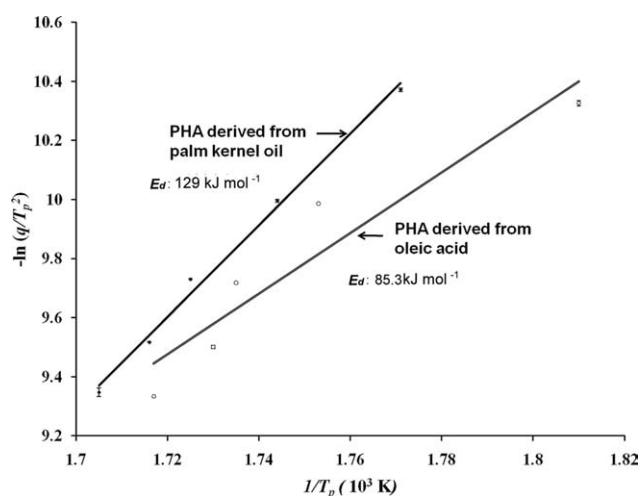


Figure 3. Kissinger plots. E_d value of the PHA produced from palm kernel oil was higher than PHA produced from oleic acid. Data on oleic acid-based PHA is taken from Ref.¹².

Table II. Degradation Rate Constants Calculated from Arrhenius Equation

q (K min ⁻¹)	T_p (K)	k , degradation rate constant, $\times 10^2$ s ⁻¹
10	565	1.37
15	574	2.08
20	580	2.78
25	583	3.20
30	587	3.84

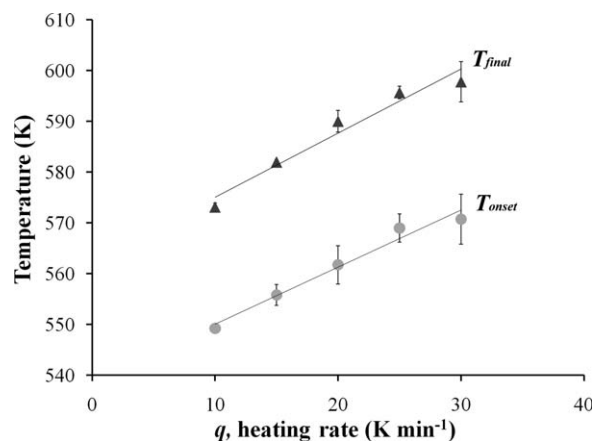


Figure 4. Linear relationship of T_{onset} and T_{final} with heating rate, q .

CONCLUSIONS

Kinetic parameters of mcl-PHA thermodegradation were determined by using Kissinger's method based on TGA measurements. E_d and A were found to be 129 kJ mol⁻¹ and 1.15×10^{10} s⁻¹, respectively, whereas the change of activation entropy (ΔS) has a value of -57.6 J K⁻¹ mol⁻¹. Both the temperatures of onset (T_{onset}) and complete (T_{final}) degradation have linear relationships with the heating rate. The peak width of DTG, given by $T_{\text{final}} - T_{\text{onset}}$, increases slightly with higher heating rate.

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