Kasetsart J. (Nat. Sci.) 47 : 781 - 789 (2013)

Non-Isothermal Crystallization and Thermal Degradation Kinetics of Biodegradable Poly(butylene adipate-co-terephthalate)/Starch Blends

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ABSTRACT

The non-isothermal crystallization behavior of biodegradable poly (butylene adipate-co-terephthalate)/starch (PBAT/S) blends was studied using differential scanning calorimetry under a nitrogen atmosphere from 25 to 225 °C at four constant cooling rates of 5, 10, 15 and 20 °C.min^{-1}. There was only one crystallization peak in the exothermic curve which shifted to a lower temperature as the cooling rate was increased. The crystallization temperature decreased from 98 to 84 °C, but the crystallization enthalpy increased from 11 to 12 J.g^{-1} as the heating rate was increased.

The thermal degradation(TG) of the PBAT/S blends was studied using thermogravimetric analysis under a nitrogen atmosphere from 100 to 800 °C at five constant heating rates of 1, 2, 5, 10, and 15 °C.min^{-1}. The TG curves showed two degradation stages occurring at 309–342 °C and 375–420 °C, which were the degradation of corn starch and PBAT, respectively.

The thermal degradation kinetics of the PBAT/S were analyzed using the isoconversion Flynn-Wall-Ozawa model-free method. The results showed that both the apparent activation energy and the logarithm pre-exponent factor increased with increasing conversion α. The average apparent activation energy and the average logarithm apparent pre-exponent factor for $\alpha = 0.1 – 0.9$ were 266 kJ.mol^{-1} and 37 min^{-1}, respectively. The reaction model $g(\alpha)$ determined from the master plot method for PBAT/S was a phase-boundary controlled reaction, where $g(\alpha) = [1– (1– \alpha)^{1/2}]$.

Keywords: PBAT/S, non-isothermal crystallization, thermal degradation kinetics, reaction model

INTRODUCTION

Polymeric materials are used in large quantities for packaging and industrial applications, which has caused a rapid increase in the amount of plastic waste. Recycling and the reuse of non-degradable polymeric materials are suitable options from an ecological and an economic perspective. An alternative way is to develop blends of polymer (Ge *et al.*, 2005; Girija *et al.*, 2005).

Up to now, biodegradable polymeric materials and composites have been developed from both petrochemical-based feedstock and from renewable resources to replace the conventional plastics in the interests of environmental protection; they exhibit satisfactory thermal and mechanical properties (Jun, 2000; Chrissafis *et al.*, 2006).

Poly(butylene adipate-co-terephthalate) (PBAT), is an aliphatic-aromatic biodegradablepolymer, which is synthesized from petrochemical-based

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Received date : 28/09/12 Accepted date : 06/06/13

feedstock. It shows properties similar to low-density polyethylene which is not biodegradable, but there are some properties that prevent the use of PBAT for extensive applications in the market, such as its high price and its thermal degradability temperature which is slightly higher than its melting point (Vroman and Tighzert, 2009; Sugish, 2008 and Mohanty and Nayak, 2010).

In this work, corn starch, an inexpensive naturally occurring degradable polymer, was blended with PBAT to induce thermal stability and reduce the cost of the product.

Characterizing the non-isothermal crystallization and thermal degradation kinetics of biodegradable poly (butylene adipate-co-terephthalate)/corn starch (PBAT/S) blends provides important information about the physical transition and thermal degradation mechanism and non-isothermal crystallization, respectively. The technique used for studying thermal properties is differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) provides valuable information for evaluating thermogravimetric kinetic parameters. The isoconversion model-free methods are used to determine reliable kinetic information from both isothermal and non-isothermal conditions (Sanchez *et al.,* 2009; Vyazovkin and Wight, 1999). Here, the isoconversion Flynn-Wall-Ozawa (FWO) model-free method was used to analyze thermal degradation kinetic parameters, and the reaction model was investigated using the master plot method.

MATERIALS AND METHODS

PBAT/S blends were supplied from Thantawan Industry PLC., Nakhon Pathom, Thailand. Differential scanning calorimetry (DSC) experiments were carried out using a differential scanning calorimeter (DSC 7; Perkin-Elmer; Waltham, MA, USA). The temperature and heat flow were calibrated with an indium standard under the same conditions for all samples. All samples were sealed in aluminum pans. The analyses were performed on 7–10 mg samples from 25 to 225 °C at four heating rates of 5, 10, 15 and 20 °C.min^{-1}. A nitrogen atmosphere with a constant flow rate of 20 mL.min^{-1} was applied. The melting temperature (T_m) was measured from the endothermic curve. Afterward, the samples were maintained at 225 °C for 5 min to erase the previous thermal history, followed by non-isothermal crystallization being performed at four cooling rates of 5, 10, 15 and 20 °C.min^{-1}. The crystallization temperature (T_c) was measured from the exothermic curve, and the crystallization enthalpy (ΔH_c) was determined from the area under the exothermic peak.

TGA experiments were carried out using thermogravimetric analysis (TGA7; Perkin-Elmer; Perkin-Elmer; Waltham, MA, USA) under a nitrogen atmosphere with a constant flow rate of 20 mL.min^{-1}. Each sample (thickness 44µm, weight 1.3 ± 0.2 mg) was placed in a platinum pan. Non-isothermal experiments were performed from 100–800 °C at five heating rates of 1, 2, 5, 10, and 15 °C.min^{-1}.

RESULTS AND DISCUSSION

Crystallization behavior

The non-isothermal DSC thermograms for the PBAT/S blends were recorded as a function of temperature (T) at four heating and four cooling rates. The DSC cooling curves are presented in Figure 1a which show only one exothermic peak of the non-isothermal crystallization which shifts to a lower temperature at a higher cooling rate. The melting temperatures are reported in Table 1 and show an increase with an increasing heating rate.

The crystallization temperature and crystallization enthalpy results are also reported in Table 1; T_c decreases, but ΔH_c increases as the cooling rate increases.

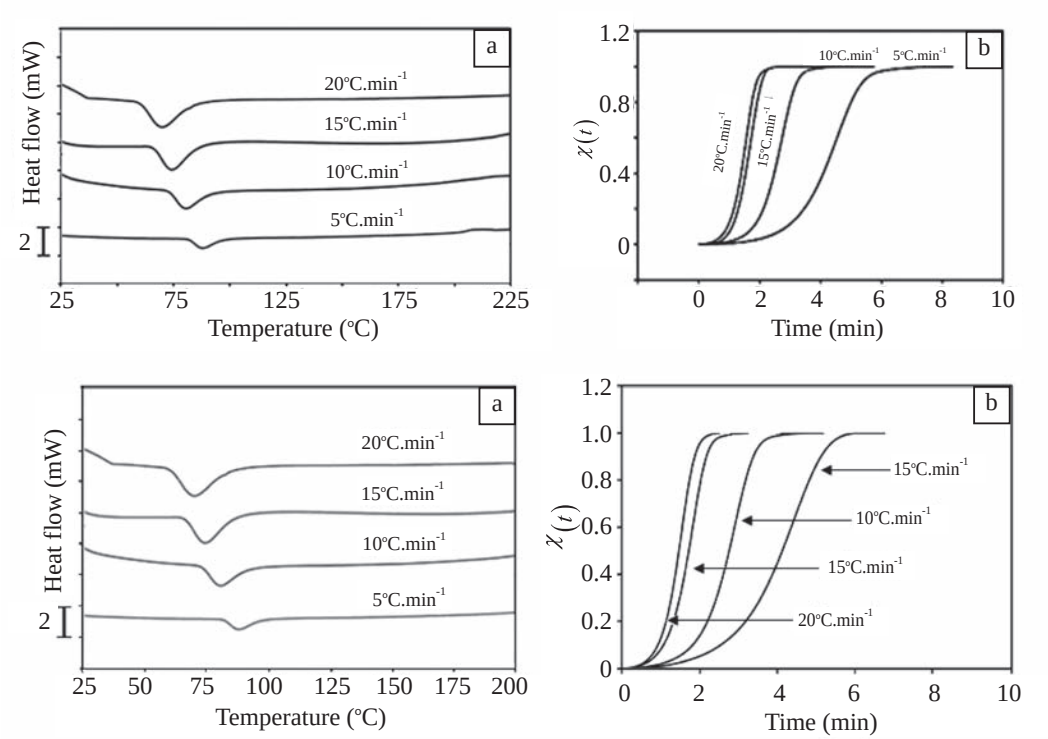

Figure 1 (a) Differential scanning calorimetry thermograms; and (b) Relative crystallinity $\chi_{(t)}$ of the non-isothermal crystallization at four cooling rates for poly (butylene adipate-co-erephthalate)/ starch blends.

Table 1 Melting temperature (T_m), crystallization temperature (T_c), and crystallization Enthalpy (ΔH_c) at rate of changing temperature (φ) for poly (butylene adipate-co-terephthalate)/starch blends.

φ ($^oC.min^{-1}$)	T_m (^oC)	T_c (^oC)	ΔH_c ($J.g^{-1}$)	$\tau_{1/2}$ (min)
5	141.9	97.9	10.8	4.3
10	140.6	91.7	11.3	2.6
15	140.2	86.4	11.7	1.6
20	140.0	83.6	12.0	1.5

The relative crystallinity $\chi(T)$ at temperature T can be determined from Equation 1:

$$\chi(T) = \frac{\Delta H_c}{\Delta H_\infty} \quad (1)$$

where ΔH_c is the total enthalpy released during crystallization at temperature T and ΔH_∞ is the complete crystallization enthalpy.

The relative crystallinity $\chi(t)$ at time t can be determined conversely from the relative crystallinity $\chi(t)$ at temperature T using Equation 2:

$$t = (T_0 - T) / \varphi \quad (2)$$

where T_0 is the initial crystallization temperature and φ is the cooling rate.

The relative crystallinity as a function of time determined from the $\chi(T)$ curve and Equation 2, as described by Trivijitkasem *et al.* (2008), is presented in Figure 1b. The non-isothermal

crystallization half time ($\tau_{1/2}$) determined from Figure 1b is reported in Table 1, which shows a longer crystallization half time at a lower cooling rate.

Thermogravimetric measurement

Thermal degradation of the PBAT/S blends recorded as a function of temperature at five heating rates is shown in Figure 2a. The TG curve shifts to a higher temperature at a higher heating rate. There were two weight loss stages: the first one appeared at a lower temperature between 309 and 342 °C and represented the degradation of corn starch, while the second one at a higher temperature between 375 and 420 °C showed the degradation of PBAT (Mano *et al.*, 2003; Mohanty and Nayak, 2010).

The conversion α can be determined from the weight loss TG curves using the following equation:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} \quad (3)$$

where w_0, w and w_∞ are the initial weight, the actual weight at temperature T and the final weight of the degradation process, respectively.

The derivative weight loss $d\alpha/dT$ curves or DTG curves shown in Figure 2b were determined from the TG curves. There were two peaks for each heating rate.

The two peak temperatures, the final complete degradation temperature and the degradation content for corn starch, PBAT and ash obtained from the TG and DTG curves at various heating rates are reported in Table 2. The three characteristic temperatures increased with an increased heating rate.

Thermal degradation kinetics

The thermal degradation kinetics for the non-isothermal process can be analyzed from various methods. Here the isoconversion Flynn-Wall-Ozawa (FWO) model-free method was used as shown in Equation 4 (Chiangga *et al.*, 2012):

$$\ln \beta = \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_\alpha}{RT} \quad (4)$$

where β is the heating rate, A_α is the apparent pre-exponent factor, E_α is the apparent activation energy, R is the gas constant (8.3136 J.mol^{-1} K^{-1}), $g(\alpha)$ is the integral form of the reaction model and T is the temperature.

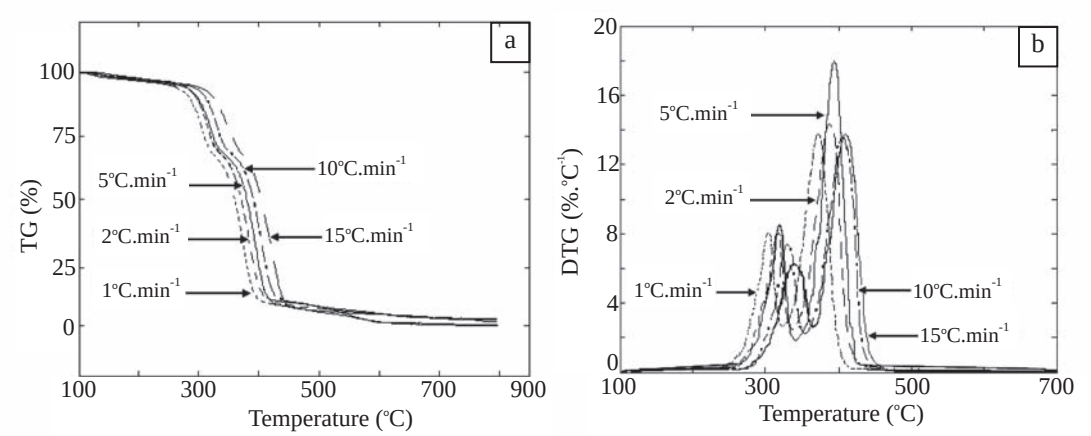

Figure 2 (a) Thermal degradation (TG); and (b) Derivative weight loss (DTG) curves for poly (butylene adipate-co-terephthalate)/starch blends.

Table 2 Characteristic temperatures for peak 1 (T_{p1}) and peak 2 (T_{p2}) and the degradation content for corn starch (S), poly (butylene adipate-co-terephthalate)/starch blends(PBAT) and ash (A) at different heating rates(β).

β ($^oC.min^{-1}$)	T_{p1} (^oC)	T_{p2} (^oC)	T_f (^oC)	S (%)	PBAT (%)	A (%)
1	309	375	428	25.7	72.2	0.9
2	318	387	460	24.0	74.1	0.9
5	320	398	489	24.6	72.9	0.8
10	333	417	501	25.4	72.6	0.9
15	342	420	527	27.2	70.0	0.8

According to Equation 4, plotting ln β versus 1/T, using the data obtained from the TG curves for the different heating rates (β) and fixed values of α, provides a straight line. The slope ($-1.052\,E_\alpha/R$), can be used for evaluating the apparent activation energy and the intercept ($\ln[A_\alpha E_\alpha/Rg(\alpha)]$) can be used for evaluating the logarithm apparent pre-exponent factor ($\ln A_\alpha$).

The FWO plots for PBAT/S for the conversion values α = 0.1, 0.2,…, 0.9 are shown in Figure 3. The linear correlation was greater than 0.99. The apparent activation energy and the linear correlation coefficient for each conversion α value were determined from the slope and the deviation of the lines, respectively, and are reported in Table 3.

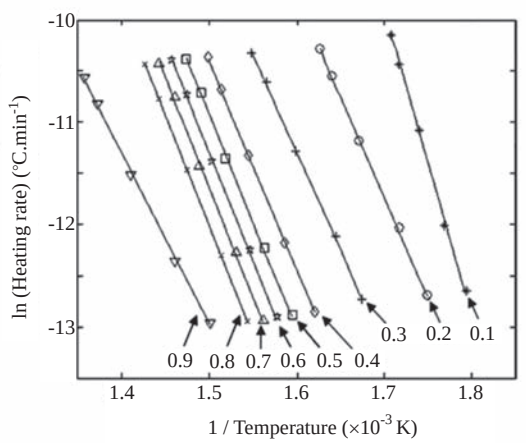

Figure 3 Plots of natural logarithm of the heating rate (β) versus the reciprocal of temperature (T^{-1}) for poly (butylene adipate-co-terephthalate)/starch blends.

Table 3 Apparent activation energy (E_α) and logarithm apparent pre-exponent factor ($\ln A_\alpha$) for poly (butylene adipate-co-terephthalate)/starch blends at different values of conversion (α).

α	E_α ($kJ.mol^{-1}$)	$\ln A_\alpha$ (min^{-1})
0.1	214.4	30.63
0.2	261.2	36.10
0.3	262.6	36.75
0.4	269.6	36.82
0.5	275.6	38.43
0.6	276.3	38.55
0.7	277.4	38.80
0.8	278.1	38.93
0.9	280.0	39.05
Mean	266.1	37.12

The variation of the apparent activation energy (E_α) as a function of conversion α for the PBAT/S blends is shown in Figure 4. E_α increased as the conversion α was increased. The apparent activation energy was 214 kJ.mol^{-1} at α = 0.1 and increased rapidly to 261 kJ.mol^{-1} at α = 0.2, then increased slowly to 280 kJ.mol^{-1} at α = 0.9. The increase in E_α with conversion α implies a multi-step degradation mechanism of the PBAT/S blends. The average apparent activation energy was 266 kJ.mol^{-1}. A greater activation energy indicates higher thermal stability.

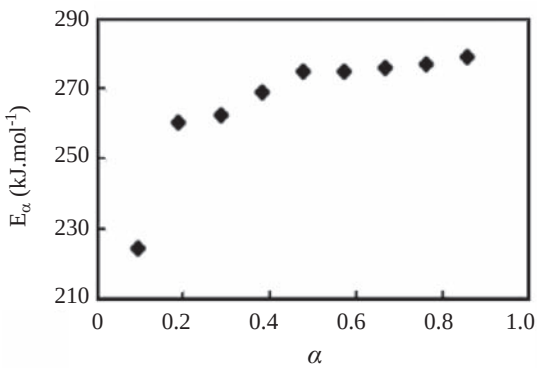

Figure 4 Dependence of the apparent activation energy (E_α) on conversion α for poly (butylene adipate-co-terephthalate)/ starch blends.

Determination of reaction model

The integral form of the reaction model $g(\alpha)$ is defined in Equation 5 (Jankovic *et al.*, 2007):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T} \exp(\frac{-E_\alpha}{RT})dT \qquad (5)$$

where $f(\alpha)$ is the differential form of reaction model and T_0 is the initial temperature. Equation 5 can be transformed into Equation 6 using $x = E_\alpha / RT$ and Equation 7:

$$g(\alpha) = \frac{AE_\alpha}{R\beta}\int_x^\infty \frac{\exp\ (-x)}{x^2}dx = \frac{AE_\alpha}{R\beta}\, p(x) \qquad (6)$$

where $$p(x) = \int_x^\infty \exp\frac{(-x)}{x^2}dx \qquad (7)$$

At a reference point, α = 0.5, Equation 6 is then modified to Equation 8:

$$g(0.5) = \frac{AE_a}{R\beta}\, p(x_{0.5}) \qquad (8)$$

where $x_{0.5} = E_\alpha / RT_{0.5}$ and $T_{0.5}$ is the temperature at conversion α= 0.5.

Dividing Equation 6 by Equation 8, produces Equation 9:

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(x)}{p(x_{0.5})} \qquad (9)$$

There is no analytical solution for $p(x)$, so the approximate formula for $p(x)$ with high accuracy was used as shown in Equation 10:

$$p(x) = \frac{\exp(-x)}{x}\cdot\left(\frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}\right) \qquad (10)$$

The values of $p(x)$and $p(x_{0.5})$can be calculated from Equation 10 using the experimental data of E_α from Figure 3 at different heating rates of β.

Utilizing the master-plot method, the reaction model $g(\alpha)$ can be investigated (Ramis *et al.*, 2004; Saha and Ghoshal, 2007). Figure 5 shows the theoretical master plots of various $g(\alpha)/(0.5)$ functions versus α: 1) phase-boundary controlled reaction (contracting area), R2; 2) two-dimensional diffusion (bidimensional particle shape), D2; 3) Avrami-Erofeev (m = 2), A2; 4) Avrami-Erofeev (m = 3), A3; 5) first-order (Mampel), F1; and 6) power 3, P3. The experimental master plots of $p(x)/p(x_{0.5})$ versus α are also shown in Figure 5.

For a given conversion α, the experimental values of $p(x)/p(x_{0.5})$ and theoretically calculated values of $g(\alpha)/(0.5)$ are equivalent when an appropriate reaction model is used. Hence, it

can be concluded from Figure 5 that the best fit reaction model $g(\alpha)$ for describing the thermal degradation process for PBAT/S blends is the reaction model R2, where

$$g(\alpha) = [1-(1-\alpha)^{1/2}] \quad (11)$$

Determination of logarithm apparent pre-exponent factor

The logarithm apparent pre-exponent factor ($\ln A_\alpha$) can be determined from the intercept of the straight line in Figure 3. By substituting the values of E_α from Table 3, and the values of $g(\alpha)$ from Equation 11 into the expression $\ln [A_\alpha E_\alpha / Rg(\alpha)]$, $\ln A_\alpha$ can be determined from the intercept of the line. The results are reported in Table 3. Figure 6 shows the variation of the logarithm pre-exponent factor as a function of conversion α, which increased with increasing conversion α. The logarithm apparent pre-exponent factor was 30 min^{-1} at $\alpha = 0.1$ and increased rapidly to 36 min^{-1} at $\alpha = 0.2$, then increased slowly to 39 min^{-1} at $\alpha = 0.9$. The average value of logarithm apparent pre-exponent factor $\overline{\ln A_\alpha}$ was 37 min^{-1}.

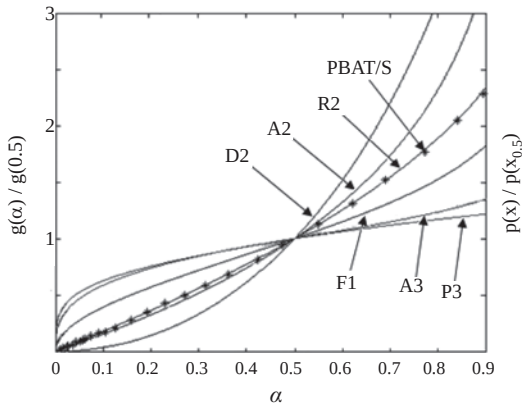

Figure 5 Master plots of experimental data for $p(x)/p(x_{0.5})$ and some theoretical reaction models $g(\alpha)/(0.5)$ versus α for poly (butylene adipate-co-terephthalate)/ starch blends.

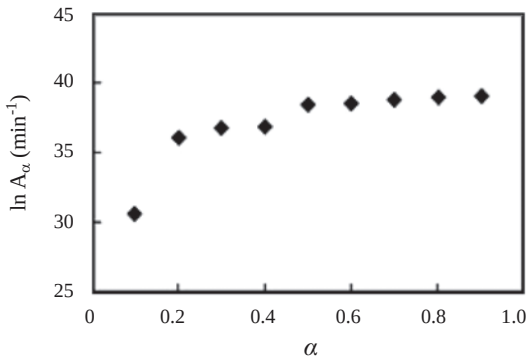

Figure 6 Dependence of logarithm pre-exponent factor ($\ln A_\alpha$) on conversion α for poly (butylene adipate-co-terephthalate)/ starch blends.

CONCLUSION

Non-isothermalcrystallization of biodegradable poly(butylene adipate-co-terephthalate)/starchblends was studied using differential scanning calorimetry from 25 to 225 °C at four cooling rates of 5, 10, 15 and 20 °C.min^{-1}. A nitrogen atmosphere of 20 mL.min^{-1} flowing rate was applied. There was only one crystallization peak in the exothermic experiment which shifted to a lower temperature as the cooling rate was increased.

The crystallization temperature varied from 98 to 84 °C and the enthalpy varied from 11 to 12 J.g^{-1} as the cooling rate was varied from 5 to 20 °C.min^{-1}; the crystallization temperature decreased, but the crystallization enthalpy increased with an increasing cooling rate. The relative crystallinity as a function of time showed a longer crystallization time at a lower cooling rate. The crystallinity half time decreased with an increasing cooling rate (variation from 4 min to 2 min),which resulted in a shorter crystallization half time at a higher cooling rate.

Thermal degradation of the PBAT/S blends was studied using thermogravimetric analysis from 100 to 800 °C, at five heating rates of 1, 2, 5, 10 and 15 °C.min^{-1}. The TGA curves showed two thermal degradation weight

loss stages. The derivative weight loss curves determined from the TG curves showed two peaks for each heating rate. The lower peak temperature occurred at 309–342 °C, as the heating rate was varied from 1 to 15 °C.min^{-1} and was due to the degradation of the corn starch, while the higher peak temperature occurred at 375–420 °C as the heating rate was varied from 1 to 15 °C.min^{-1} and was due to the degradation of PBAT.

The thermal degradation kinetic parameters were determined from the isoconversion Flynn-Wall-Ozawa model-free method. Both the apparent activation energy and the logarithm apparent pre-exponent factor increased with increased conversion α. The average apparent activation energy and the average logarithm apparent pre-exponent factor for $\alpha = 0.1 – 0.9$ were 266 kJ.mol^{-1} and 37 min^{-1}, respectively.

The reaction model $g(\alpha)$ determined from the master plot method for PBAT/S was a phase-boundary controlled reaction, where $g(\alpha) = [1– (1– \alpha)^{1/2}]$.

ACKNOWLEDGEMENT

This work was financially supported by the Kasetsart University Research and Development Institute (KURDI).

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