INTRODUCTION

The increased amount of conventional plastic waste in recent years has caused severe environmental problems, which have motivated researchers to investigate biodegradable polymers (Muller et al., 1998; Zhao and Gan, 2006; Yoshioka et al., 2007). Nowadays, a number of biodegradable polymer materials, such as poly(lactic acid) (PLA), poly(butylene adipate-co-terephthalate) (PBAT) are commercially available. The crystallization behavior and thermal degradation of the polymers have been extensively studied, and were reported to exhibit comparable physical and chemical properties to low density polyethylene (LDPE), polypropylene (PP), etc. (Cranston, et al., 2003; Li and Huneault, 2007).

PBAT, an aliphatic-aromatic semi-crystalline copolyester, is a flexible material suitable for producing fibers, films and packaging materials. It shows high toughness, biodegradability and can be processed by conventional methods. However, there are some disadvantageous properties that prevent PBAT for extensive application in the market, such as its high price, high toughness and its thermal degradability at a temperature slightly above its melting point. In order to improve polymer properties, polymer blending has been

ABSTRACT

Thermal degradation of biodegradable poly(butylene adipate-co-terephthalate)/starch (PBAT/S) blends of 15 µm thickness was investigated by thermogravimetric analysis in a nitrogen atmosphere and in an air atmosphere at a flow rate of 20 mL.min⁻¹. The non-isothermal experiments were conducted at five constant heating rates (β = 1, 2, 5, 10 and 15 °C.min⁻¹) from 100 to 800 °C. The thermogravimetric curves showed two degradation stages in a nitrogen atmosphere and three degradation stages in an air atmosphere. The second stage occurred at temperatures from 366 to 418 and 369 to 421 °C respectively. Three models—namely, the model-free isoconversion methods of Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW) and Friedman (FR) were used to determine the dependence of the apparent activation energy $E_\alpha$. The results showed higher $E_\alpha$ values on conversion $\alpha$ in the nitrogen atmosphere. The average $E_\alpha$ levels were 172, 174 and 173 kJ.mol⁻¹ in the nitrogen atmosphere and 159, 159 and 160 kJ. mol⁻¹ in the air atmosphere for the KAS, OFW and FR methods, respectively. This confirmed that thermal degradation in an air atmosphere is faster than in a nitrogen atmosphere.

Keywords: poly(butylene adipate-co-terephthalate) /starch (PBAT/S), thermal degradation, apparent activation energy
used to obtain new materials for different needs (Shi et al., 2006; Ren et al., 2009).

Thermal degradation of thermoplastic biodegradable PBAT has been reported (Chivrac et al., 2006; Signori et al., 2009). In the present work, thermal degradation of PBAT/corn starch blends was investigated, and values for the thermal degradation activation energy in a nitrogen atmosphere and in an air atmosphere were determined by the model-free isoconversion method using the three models of Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW) and Friedman (FR).

**MATERIALS AND METHODS**

Poly(butylene adipate-co-terephthalate)/corn starch (PBAT/S) blends, in the Ecoflex® trademark of the international BASF company, were supplied from the Thantawan Industry Public Company, Nakhon Pathom. Thermal degradation was performed using a thermogravimetric analyzer (TGA7; Perkin-Elmer; Waltham MA, USA) in a nitrogen atmosphere and in an air atmosphere with a 20 mL.min⁻¹ constant flow rate. A sample of 15 µm thickness was measured by a micrometer, and approximately 1.3 ± 0.2 mg was weighed using a microbalance. Then, the sample was placed in a platinum pan and the non-isothermal experiment was carried out from 100 to 800 °C at five heating rates (β = 1, 2, 5, 10 and 15 °C.min⁻¹).

**Thermal degradation kinetic analysis**

Thermal degradation of PBAT/S can be determined from the mass loss of the thermogravimetric (TG) curves. The conversion α can be determined in terms of the mass loss from the TG curves using Equation 1:

\[ \alpha = \frac{m_0 - m}{m_0 - m_\infty} \]  

where \( m_0 \), \( m \) and \( m_\infty \) are the initial mass, the actual mass at temperature \( T \) and the final mass of the degradation process, respectively.

For many degradation processes, the rate of reaction, \( \frac{d\alpha}{dt} \), can be expressed as Equation 2 (Arbelaiz et al., 2006):

\[ \frac{d\alpha}{dt} = A \exp \left( \frac{-E_\alpha}{RT} \right) f(\alpha) \]  

where \( A \) is the pre-exponential factor, \( E_\alpha \) is the apparent activation energy, \( R \) is the gas constant (8.3136 J.(mol K)⁻¹) and \( f(\alpha) \) is the differential reaction model.

For non-isothermal conditions at a constant heating rate \( \beta = \frac{dT}{dt} \), Equation 2 can be rewritten as Equation 3:

\[ \frac{d\alpha}{dT} = \frac{1}{\beta} A \exp \left( \frac{-E_\alpha}{RT} \right) f(\alpha) \]  

where the conversion rate \( \frac{d\alpha}{dt} \) can be determined by the derivative of Equation 1 from the TG curve.

The integral form of the reaction model \( g(\alpha) \) can be obtained by integrating Equation 3 as shown in Equation 4:

\[ g(\alpha) = \int_0^\alpha f(\alpha) \frac{A}{\beta} \exp \left( \frac{-E_\alpha}{RT} \right) dT \]  

where \( T_0 \) is the initial temperature.

There are several analytical methods that can be applied to estimate the apparent activation energy \( E_\alpha \). The method used here is the model-free isoconversion method. This method assumes the conversion function \( g(\alpha) \) to be constant for all values of conversion \( \alpha \) at different heating rates \( \beta \).

The first isoconversion method was proposed by Kissinger-Akahira-Sunose (KAS). Based on the Coats-Redfern approximation (Jankovic, 2008), the KAS equation is in the following form (Equation 5):

\[ \ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{A_u R}{E_\alpha g(\alpha)} \right) - \frac{E_\alpha}{RT} \]  

From thermograms recorded at different heating rates \( \beta \), a series of measuring temperatures...
corresponding to a fixed value of conversion $\alpha$ can be obtained. Plotting of $\ln(\beta/T^2)$ versus $1/T$ should give a straight line, whose slope is $-E_\alpha / R$, and the intercept is $\ln[A_\alpha R / E_\alpha g(\alpha)]$.

The second isoconversion method was proposed by Ozawa-Flynn-Wall (OFW). Using Doyle’s approximation for the temperature integral, the OFW equation (Jankovic et al., 2006) is shown in Equation 6:

$$
\ln \beta = \ln\left(\frac{A_\alpha E_\alpha}{R g(\alpha)}\right) - 5.331 - 1.052 \frac{E_\alpha}{RT}
$$

For a fixed value of $\alpha$ at different heating rates $\beta$, plotting of $\ln \beta$ versus $1/T$ should give a straight line, whose slope can be used to evaluate the apparent activation energy $E_\alpha$.

The third method was proposed by Friedman which was based on Equation 3. The Friedman (FR) equation expressed the logarithmic form of the conversion rate $d\alpha / dT$ as a function of the reciprocal temperature at different heating rates $\beta$ (Zou et al., 2009) as shown in Equation 7:

$$
\ln \left[\beta \left(\frac{d\alpha}{dT}\right)\right] = \ln \left[A_\alpha f(\alpha)\right] - \frac{E_\alpha}{RT}
$$

If the differential conversion function $f(\alpha)$ is constant for a particular value of $\alpha$, then $\ln \left[A_\alpha f(\alpha)\right]$ is also constant. For a fixed value of $\alpha$ at different heating rates $\beta$, plotting $\ln \left[\beta \left(\frac{d\alpha}{dT}\right)\right]$ versus $1/T$ should give a straight line, whose slope is $-E_\alpha / R$, and the intercept is $\ln \left[A_\alpha f(\alpha)\right]$.

RESULTS AND DISCUSSION

Thermal degradation

The TG curves and the corresponding derivative mass loss $d\alpha / dt$ curves or DTG curves of PBAT/S performed in the nitrogen atmosphere and in the air atmosphere at five different heating rates ($\beta = 1, 2, 5, 10$ and $15 \text{ °C.min}^{-1}$) are shown in Figure 1. The TG curves and DTG peaks moved to higher temperatures with increased heating rate $\beta$; that is, the temperature increased as the heating rate increased.

Figure 1  Thermogravimetric (TG) and derivative mass loss $d\alpha / dT$ (DTG) curves at five different heating rates: (a) in nitrogen atmosphere; and (b) in air atmosphere.
There were two and three degradation weight loss stages in the nitrogen atmosphere and the air atmosphere, respectively. The peak temperatures: \( T_{p1} \), \( T_{p2} \), \( T_{p3} \), the final 100% degradation temperature \( T_f \) and the degradation content (%) of corn starch (S), PBAT and ash (A) obtained from TG curves at various heating rates are reported in Table 1.

The lower peak temperature \( T_{p1} \) and higher peak temperature \( T_{p2} \) from the thermal degradation curves of PBAT/S in the nitrogen atmosphere occurred at similar temperatures to those reported in the literature (Mano et al., 2003; Mohanty and Nayak, 2010). They were due to thermal degradation of corn starch and PBAT, respectively.

The three degradation peak temperatures in the air atmosphere occurred at similar temperatures to those reported by Li et al. (2006). The first two lower peak temperatures \( T_{p1} \) and \( T_{p2} \) were due to thermal degradation of corn starch (S) and thermal degradation of PBAT, respectively, from high molecular weight macromolecules into smaller chain fragments; the third peak temperature \( T_{p3} \) was due to thermal oxidized degradation of small molecular weight polymer fragments (PBAT,\( O_2 \)).

The model-free isoconversion methods of KAS, OFW and FR were used to determine the apparent activation energy for PBAT/S in the nitrogen atmosphere and in the air atmosphere. Figures 2–4 show linear fitting plots of \( \ln (\beta / T^2) \) versus \( T^{-1} \), \( \ln \beta \) versus \( T^{-1} \) and \( \ln [\beta(d\alpha / dT)] \) versus \( T^{-1} \), at a fixed value for \( \alpha = 0.1-0.9 \) of the three methods, respectively. The straight lines fitted by the KAS and OFW methods are nearly parallel, which implies that the two methods are applicable to PBAT/S. From Figures 2 and 3, degradation of PBAT/S for \( \alpha = 0.2-0.8 \) or 20–80% degradation of PBAT/S in the nitrogen and air atmospheres consumed nearly the same amount of activation energy \( E_\alpha \). Values for the apparent activation energy \( E_\alpha \) calculated from the slopes are summarized in Table 2.

The correlation coefficient \( r \) for different conversion \( \alpha \) reported in Table 2 was determined from the straight line using Equation 8:

\[
r = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 \sum_{i=1}^{n} (y_i - \bar{y})^2}}
\]

The values for the average activation energy \( E_{\alpha, \text{av}} \) in the nitrogen and air atmospheres determined from the KAS, OFW and FR methods (Table 2) were consistent; \( E_{\alpha, \text{av}} = 172, 174 \) and

<table>
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<th>Atmosphere</th>
<th>( \beta ) (°C.min(^{-1} ))</th>
<th>( T_{p1} ) (°C)</th>
<th>( T_{p2} ) (°C)</th>
<th>( T_{p3} ) (°C)</th>
<th>( T_f ) (°C)</th>
<th>S (%)</th>
<th>PBAT (%)</th>
<th>PBAT,( O_2 ) (%)</th>
<th>A (%)</th>
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<td>N(_2)</td>
<td>1  298</td>
<td>366</td>
<td>-</td>
<td>513</td>
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<td>73.0</td>
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<td>2  300</td>
<td>373</td>
<td>-</td>
<td>565</td>
<td>25.6</td>
<td>72.9</td>
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<td>388</td>
<td>-</td>
<td>617</td>
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<td>10 335</td>
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<td>15 332</td>
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<td>-</td>
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<td>15 334</td>
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<td>28.1</td>
<td>63.9</td>
<td>8.4</td>
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**Figure 2** Kissinger-Akahira-Sunose (KAS) model plots of $\ln(\beta/T^2)$ versus $T^{-1}$ for polybutylene adipate-co-terephthalate /starch (PBAT/S) blends: (a) in nitrogen atmosphere; and (b) in air atmosphere.

**Figure 3** Ozawa-Flynn-Wall (OFW) model plots of $\ln(\beta/T^2)$ versus $T^{-1}$ for polybutylene adipate-co-terephthalate /starch (PBAT/S) blends: (A) in nitrogen atmosphere, and (B) in air atmosphere.

**Figure 4** Friedman plots of $\ln [\beta(d\alpha / dT)]$ versus $T^{-1}$ for polybutylene adipate-co-terephthalate / starch (PBAT/S) blends: (a) in nitrogen atmosphere, and (b) in air atmosphere.
173 kJ/mol in the nitrogen atmosphere and $E_{\alpha, av} = 159, 159$ and 160 kJ/mol in the air atmosphere for the KAS, OFW and FR methods, respectively. The average apparent activation energy in the nitrogen atmosphere was higher than that in the air atmosphere, which confirms that thermal degradation in oxygen is faster than in a nitrogen atmosphere.

The dependence of the apparent activation energy $E_{\alpha}$ on the conversion $\alpha$ calculated from the three methods, in nitrogen and in air atmospheres, are shown in Figure 5. It can be seen from Figures 5A and 5B that there are two different regions in the $E_{\alpha}$ versus $\alpha$ curves in the nitrogen atmosphere. First, $E_{\alpha}$ decreased slightly for $\alpha = 0.1\text{–}0.3$, then increased slowly for $\alpha = 0.4\text{–}0.9$. However, there exist three different regions in the air atmosphere. First, $E_{\alpha}$ increased rapidly for $\alpha = 0.1\text{–}0.3$; second, it decreased slightly for $\alpha = 0.3\text{–}0.5$; then it increased slowly for $\alpha = 0.5\text{–}0.9$.

The variation of the apparent activation energy $E_{\alpha}$ on conversion $\alpha$ obtained from the FR method was different from the KAS and OFW methods. This was due to the differential form (Equation 7), in the FR method (Jankovic et al., 2007).

Table 2  Apparent activation energy $E_{\alpha}$ determined from Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW) and Friedman (FR) methods and correlation coefficient $r$ for for polybutylene adipate-co-terephthalate /starch (PBAT/S) blends in nitrogen ($N_2$) atmosphere and in air atmosphere.

<table>
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<tr>
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<th>KAS ($E_{\alpha}$ (kJ.mol$^{-1}$))</th>
<th>$r$</th>
<th>OFW ($E_{\alpha}$ (kJ.mol$^{-1}$))</th>
<th>$r$</th>
<th>FR ($E_{\alpha}$ (kJ.mol$^{-1}$))</th>
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CONCLUSION

Thermogravimetric analysis was applied to investigate the thermal degradation of PBAT/S of 15 µm thickness. Five heating rates ($\beta = 1, 2, 5, 10,$ and $15 \, {^\circ}\text{C.min}^{-1}$) in a nitrogen and in an air atmosphere at a 20 mL.min$^{-1}$ flow rate were applied over a temperature range of 100 to 800 $^\circ$C.

There were two degradation weight loss stages during the thermal degradation of PBAT/S in the nitrogen atmosphere. The lower peak temperature $T_{p1}$ that occurred at 298–335 $^\circ$C was due to the degradation of corn starch, while the higher peak temperature $T_{p2}$ that occurred at 366–418 $^\circ$C was due to the degradation of PBAT.

There were three thermal degradation stages of PBAT/S in the air atmosphere. The lower peak temperature $T_{p1}$ that occurred at 307–334 $^\circ$C was due to the degradation of corn starch, while the higher peak temperature $T_{p2}$ that occurred at 369–421 $^\circ$C was due to thermal degradation of PBAT from high molecular weight macromolecules into smaller chain fragments; the third peak temperature $T_{p3}$ that occurred at 437–507 $^\circ$C was due to thermal oxidized degradation of small molecular weight polymer fragments.

The apparent activation energy was determined from the Kissinger-Akahira-Sunose, Ozawa-Flynn-Wall (OFW) and Friedman (FR) methods.
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Dependence of the apparent activation energy $E_\alpha$ on conversion $\alpha$ in the nitrogen atmosphere and in the air atmosphere calculated from the KAS method was similar to the OFW method and was lower than $E_\alpha$ obtained from the FR method. The values of average activation energy $E_\alpha$ were 172, 174, 173 kJ.mol$^{-1}$ in the nitrogen atmosphere; and 159, 159, 160 kJ.mol$^{-1}$ in the air atmosphere for the KAS, OFW and FR methods, respectively. The value of the apparent activation energy in nitrogen was higher than that in the air atmosphere. This confirmed that thermal degradation in oxygen is faster than in a nitrogen atmosphere.

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LITERATURE CITED


