

# The Kinetics of the Thermal Decomposition of Poly(3-hydroxybutyrate) and Maleated Poly(3-hydroxybutyrate)

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**ABSTRACT:** The thermal decomposition mechanism of maleated poly(3-hydroxybutyrate) (PHB) was investigated by FTIR and  $^1\text{H}$  NMR. The results of experiments showed that the random chain scission of maleated PHB obeyed the six-membered ring ester decomposition process. The thermal decomposition behavior of PHB and maleated PHB with different graft degree were studied by thermogravimetry (TGA) using various heating-up rates. The thermal stability of maleated PHB was evidently better than that of PHB. With increase in graft degree, the thermal decomposition temperature of maleated PHB gradually increased and then declined. Activation energy  $E_a$  as a kinetic parameter of thermal decomposition was estimated by the Flynn-Wall-Ozawa and Kissinger methods, respectively. It could be seen that approximately equal values of activation energy were obtained by both methods. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1789–1796, 2002; DOI 10.1002/app.10463

**Key words:** poly(3-hydroxybutyrate); biodegradable; decomposition

## INTRODUCTION

Poly(3-hydroxybutyrate), aliphatic polyester obtained by bacterial fermentation, is known to degrade fully in the environment without any toxic products. Its biodegradable nature is very important from the reducing plastic waste point of view. PHB is also a thermoplastic polymer, and can be extruded or molded in same plants of synthesis polymer. Moreover, the industrial-scale fermentation production of PHB has taken on a large scale.<sup>1,2</sup> Therefore, PHB has attracted much industrial attention as an environmentally degrad-

able material. However, there are several shortcomings to its commercial use, one of which is that PHB may suffer thermal degradation when it is kept for a relatively long time at a temperature above its melting point. To overcome its shortcomings, PHB can be improved either by introducing various hydroxyalkanoate monomers to yield copolyesters or by blending PHB with other polymers.<sup>3–10</sup> Although both methods can reduce the crystallinity and the melting point of PHB, and improve its mechanical properties, its thermal stability has not been improved.

Some studies of the thermal decomposition of PHB and its copolymers have been reported. The possibility of melt-processing PHB was extensively studied in the 1950s and 1960s by Grace.<sup>11</sup> It was considered that the polymer was rather unstable at temperatures close to its melting point, and therefore, PHB was difficult to process by conventional melting routes. Further work<sup>12</sup> had confirmed that the polyester could suffer re-

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duction of molecular weight when maintained even at 170°C, i.e., about 10°C below its melting point. It was also reported that none of the conventional polyolefin stabilizers gave any significant improvement in the stability of PHB.<sup>13</sup> Mitomo et al.<sup>14–18</sup> reported the radiation grafting behavior of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), and styrene (St) onto PHB and its copolyester, and found that the thermal stability of the polyesters was obviously promoted. Recent work<sup>19</sup> within the authors' group has provided evidence that grafting a certain monomers onto PHB, for example, maleic anhydride, can remarkably enhance its thermal decomposition temperature.

In this article, we investigate the thermal decomposition mechanism of maleated PHB. The thermal decomposition behavior of pure PHB and maleated PHB with different graft degree at various heating-up rates are described. The kinetic parameter–activation energy is obtained by the Flynn-Wall-Ozawa method and the Kissinger method.

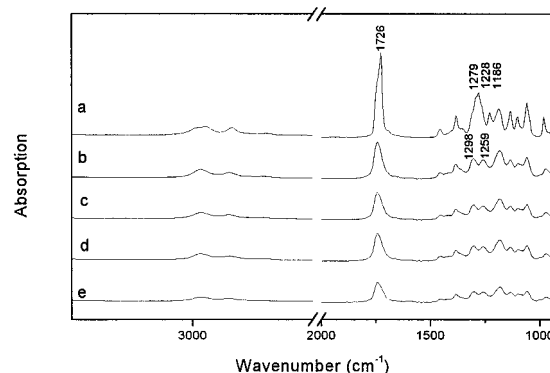
## EXPERIMENTAL

### Materials

PHB used in this study was provided by Beijing Institute of Biology, which was purified before used. Maleated PHB with different graft degree were prepared following the procedures described elsewhere.<sup>19</sup> Table I lists graft degree, molecular weight, glass transition temperature, and melting point of samples in this study. It needs to be noted in the table that, in the symbols (PHB-*g*-MA $\times\times$ ), PHB-*g*-MA, and  $\times\times$  stand for maleated PHB and its graft degree, respectively.

**Table I** Characteristic Data of PHB and Various Maleated PHB

Sample	Graft Degree (%)	$M_w$ ( $\times 10^4$ )	$T_g$ (°C)	$T_m$ (°C)
PHB	—	73.1	1.0	173.2
PHB- <i>g</i> -MA21	0.21	17.4	2.0	174.1
PHB- <i>g</i> -MA44	0.44	12.8	1.9	173.9
PHB- <i>g</i> -MA56	0.56	12.9	2.4	173.9
PHB- <i>g</i> -MA73	0.73	8.19	1.6	172.9
PHB- <i>g</i> -MA118	1.18	8.16	1.7	172.3



**Figure 1** FTIR spectra of PHB-*g*-MA44; (a) at 25°C; (b) at 190°C; (c) at 190°C for 10 min; (d) at 190°C for 20 min; (e) at 190°C for 30 min.

### Experimental Conditions

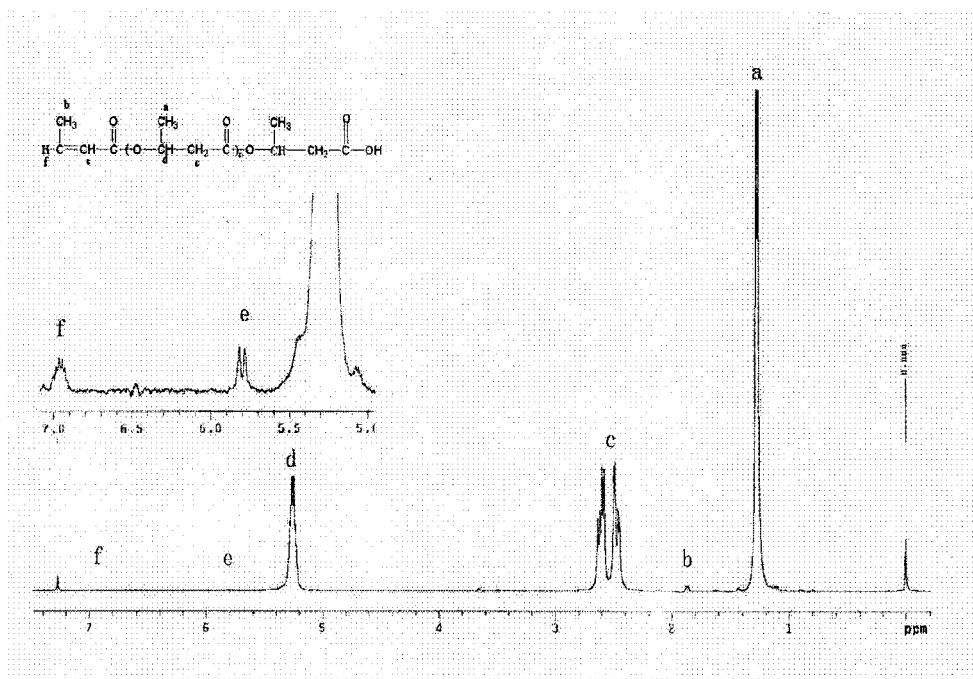
Infrared measurements were carried out with a Bio-Rad FTS-7 Fourier Transform Infrared Spectroscopy. The spectra were recorded with a resolution of 8 cm<sup>-1</sup>. A total of 16 scans were recorded. All spectra were baseline corrected. Thin films of samples were cast from the CHCl<sub>3</sub> solution onto KBr pellets. The films were dried at room temperature until CHCl<sub>3</sub> was removed completely.

<sup>1</sup>H-NMR analysis of samples was carried out on a UNITY-400 AMR spectrometer. The 400-MHz <sup>1</sup>H-NMR spectra were recorded at 20°C in CDCl<sub>3</sub> solution of polyester with 25 μs, 3164-Hz spectral width, 10 K data points, and 32 accumulation.

Thermogravimetry was performed with the Perkin-Elmer TGA 7 apparatus in nitrogen flow of 20 mL/min. The experiments were carried out at various heating-up rates ( $\Phi = 5, 10, 15, 20,$  and 40°C/min) using 6–8-mg samples. The temperature range was 25–800°C.

## RESULTS AND DISCUSSION

To investigate the thermal decomposition mechanism of maleated PHB, PHB-*g*-MA44 underwent for 30 min at 190°C was analyzed by FTIR, and the spectra were shown in Figure 1. When the sample was heated from 25 to 190°C, the bands at 1228 and 1279 cm<sup>-1</sup> disappeared, and the C=O stretching vibration at 1726 cm<sup>-1</sup> was shifted toward a higher frequency (1740 cm<sup>-1</sup>), whereas the band at 1186 cm<sup>-1</sup> was obviously intensified. These results are due to a change in crystallinity

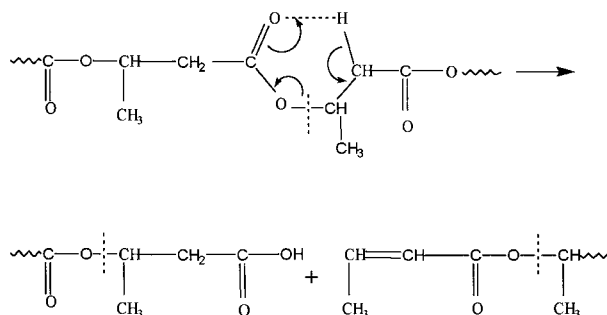


**Figure 2**  $^1\text{H-NMR}$  spectrum of the thermal decomposition of PHB-g-MA44 for 30 min at  $190^\circ\text{C}$ .

during the melting process.<sup>20</sup> For PHB, the carbonyl vibration consists of a peak centered at  $1726\text{ cm}^{-1}$  and a shoulder at  $1740\text{ cm}^{-1}$ , which are assigned to the vibrations of crystalline and amorphous carbonyl groups, respectively. When the sample was heated from  $25$  to  $190^\circ\text{C}$ , the crystal of the sample was melted so that the crystalline vibration disappeared. Therefore, the stretching vibration of amorphous carbonyl groups becomes a peak centered at  $1740\text{ cm}^{-1}$ . The bands at  $1228$ ,  $1279$ , and  $1186\text{ cm}^{-1}$  were crystalline-sensitive.<sup>21</sup> In the spectrum of crystalline PHB, the bands at  $1228$  and  $1279\text{ cm}^{-1}$  are very distinctly present, whereas they are not present at all in the spectrum of amorphous PHB. If the sample was cooled and then crystallized again, the bands at  $1228$  and  $1279\text{ cm}^{-1}$  can present again. Although the sample was isothermally treated for 30 min at  $190^\circ\text{C}$ , the peak of the double bonds was not detected. However, the spectrum became flat with the increase in time, which indicated that volatile products could be formed during the isothermal treatment process.

Pure PHB and PHB-g-MA44 were isothermally treated in nitrogen for 30 min at  $190^\circ\text{C}$ . After the treatment, the color of PHB became black, whereas the color of PHB-g-MA44 changed from white to brown, which was a direct evidence for

good thermal stability of maleated PHB. The 400-MHz  $^1\text{H-NMR}$  spectra of both isothermally treated samples were recorded, and their spectra were almost similar. Thus, Figure 2 only shows the spectrum of PHB-g-MA44. The chemical shift assignments of proton resonances are also shown in Figure 2, together with the expanded spectrum at 5–7 ppm. The strong proton resonances a, c, and d are assigned to the methyl, methylene, and methine proton resonances in 3-hydroxybutyrate units, respectively. The weak resonances e and f are assignable to the resonances of olefinic protons in the chain end unit of the oligomers, and

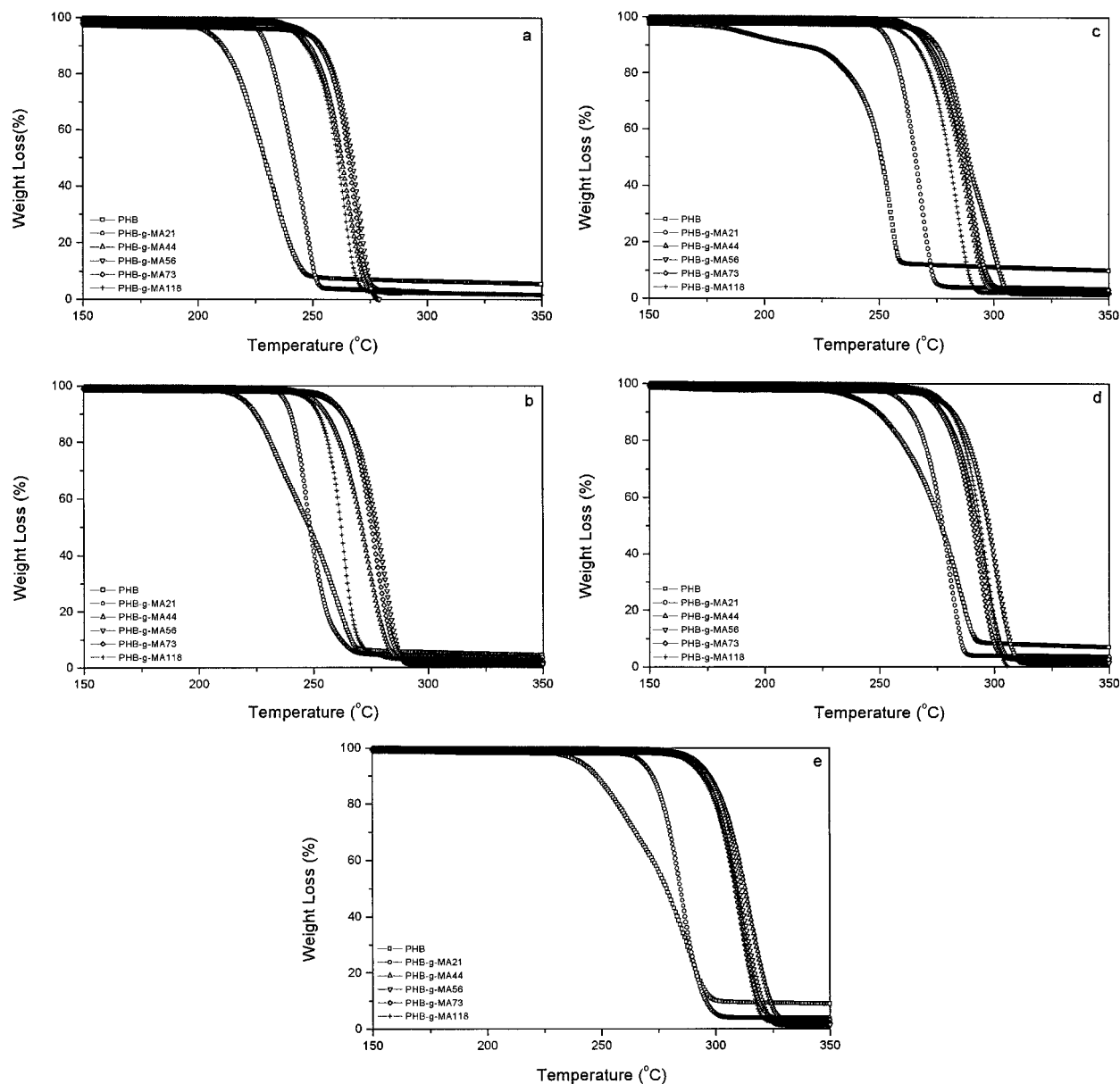


**Figure 3** The random chain scission of PHB by a six-membered ring ester decomposition process during the thermal decomposition process.

the weak resonance b at 1.87 ppm is assigned to the resonance of the methyl proton in the chain end unit. The results conclude that the thermal decomposition of maleated PHB obeys the six-membered ring ester decomposition process that can give an olefinic end, as shown in Figure 3.

The nonisothermal thermogravimetric curves of all samples, obtained at the heating-up rates of 5°C/min, 10°C/min, 15°C/min, 20°C/min, and 40°C/min, are shown in Figure 4(a)–(e), respectively. In each case, weight loss occurs in one step between 200 and 350°C. The sign of weight loss of

pure PHB appears earliest, while weight loss of various maleated PHB occurs at higher temperature, which may indicate that maleated PHB is fairly stable. The result is in accordance with the isothermally treated phenomenon. Table II lists some characteristic temperatures of PHB and various maleated PHB at the heating-up rate of 10°C/min.  $T_{5\%}$ ,  $T_{50\%}$ , and  $T_{90\%}$  represent the temperatures at which weight loss is 5, 50, and 90%, respectively. For example  $T_{5\%}$ , it can be seen from the table that  $T_{5\%}$  of maleated PHB is almost 20°C higher than that of pure PHB, although



**Figure 4** TGA curves of pure PHB and various maleated PHB at different heating-up rates of (a) 5°C/min; (b) 10°C/min; (c) 15°C/min; (d) 20°C/min; (e) 40°C/min.

**Table II** Characteristic Temperatures for the Thermal Decomposition of PHB and Various Maleated PHB at the Heating-Up Rate of 10°C/min

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)
PHB	219.3	248.1	266.1
PHB-g-MA21	238.1	258.6	271.8
PHB-g-MA44	250.7	270.8	281.4
PHB-g-MA56	256.6	277.7	284.9
PHB-g-MA73	257.6	275.3	283.7
PHB-g-MA118	247.7	261.9	269.3

graft degree is very small (0.21%). With the increase in graft degree,  $T_{5\%}$  gradually increases and then declines. Furthermore, when the heating-up rate increases, the thermal decomposition ranges of PHB obviously increases compared with that of maleated PHB, which indicates that pure PHB is more sensitive to the change of temperature. When MA group is grafted onto PHB chains, grafted MA in a certain degree disturbs the regularity of PHB chains, increases the steric hindrance of PHB, inhibits the forming of six-member ring on the chains, and reduces the probability of cyclization that is necessary to thermal decomposition. In a word, the introduction of MA group plays an important role in retarding the random chain scission of the polyester at the ester groups according to a  $\beta$ -hydrogen elimination, resulting in that the thermal stability of PHB-g-MA is obviously improved.

The DTG curves of pure PHB and various maleated PHB obtained at a heating-up rate of 5°C/min are shown in Figure 5. As seen, the peaks of maleated PHB are shifted to higher temperature compared with that of pure PHB. The width of half height ( $\Delta T_{1/2}$ ) for pure PHB is 28°C, while  $\Delta T_{1/2}$  for maleated PHB is in the range from 20 to 14°C. The thermal decomposition range evidently decreases after grafting MA, which implies that the decomposition rate of maleated PHB is quicker. During maleated PHB decomposition process, the existence of MA group enhances its temperature of thermal decomposition so that the beginning of thermal decomposition of maleated PHB occurs at higher temperature than that of PHB. The higher temperature is the primary factor resulting in the increase in the decomposition rate of maleated PHB. The values of the peaks for all samples at various heating-up rates are listed in Table III.

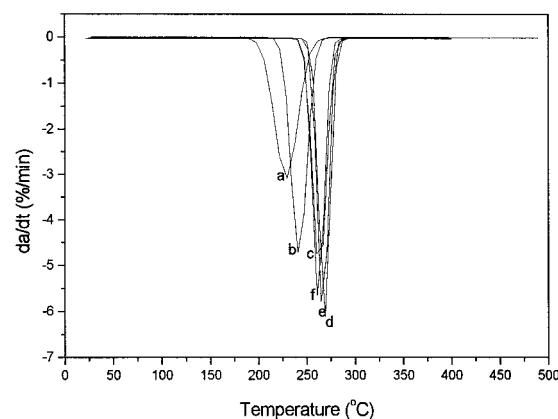
For the purpose of further explanation of PHB and maleated PHB thermal decomposition, it is necessary to know the kinetic parameter—activation energy, which is a subject of the investigations in this article.

The methods of calculating the activation energy can be divided into two groups: single heating-rate method and multiple heating-rate method. Because multiple heating-rate method considers the effect of heating-up rates, activation energy of thermal decomposition of pure PHB and various maleated PHB is estimated by using one of multiple heating-rate methods—the Flynn-Wall-Ozawa method. The Flynn-Wall-Ozawa method<sup>22,23</sup> is an approximate integral method similar to the Doyle method. Moreover, it is more widely applicable to the random scission in the main chains of polymers.<sup>24</sup> The expression of  $E_a$  with the Flynn-Wall-Ozawa method is shown as follows:

$$E_a = -R/b[d(\log\Phi)/d(1/T)] \quad (1)$$

where  $E_a$  is the activation energy, J/mol;  $R$  is the gas constant,  $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ;  $T$  is the temperature at constant conversion amount, K;  $\Phi$  is the heating-up rate, K/min;  $b$  is the constant ( $\approx 0.457 \pm 0.03$  for  $20 < E_a/RT < 60$ ).

A typical plot by the Flynn-Wall-Ozawa method at various heating-up rates is shown in Figure 6. The individual lines correspond to differently chosen conversion amounts (from 5 to 90%). Those isoconversion lines are parallel or unparallel as conversion amount varies. The



**Figure 5** DTG curves of pure PHB and various maleated PHB obtained at a heating-up rate of 5°C. Samples: (a) PHB; (b) PHB-g-MA21; (c) PHB-g-MA44; (d) PHB-g-MA56; (e) PHB-g-MA73; and (f) PHB-g-MA118.

**Table III** Temperatures at Maximum Rate of Weight Loss ( $T_{\max}$ ) for the Thermal Decomposition of PHB and Various Maleated PHB at Various Heating-Up Rates

Sample	$T_{\max}(\text{°C})$				
	5(°C/min)	10(°C/min)	15(°C/min)	20(°C/min)	40(°C/min)
PHB	232.4	259.8	264.3	274.6	277.2
PHB-g-MA21	247.2	267.6	278.8	281.0	285.8
PHB-g-MA44	264.6	274.1	288.8	295.3	315.2
PHB-g-MA56	270.5	281.7	290.1	301.1	312.2
PHB-g-MA73	267.9	277.3	289.6	293.7	310.5
PHB-g-MA118	263.8	278.0	293.6	297.5	312.2

value of the derivative expression in eq. (1),  $[d(\log\Phi)/d(1/T)]$ , is determined on the basis of the slope of the lines in Figure 6, and then  $E_a$  can be determined from eq. (1). The data of activation energy of all samples are shown in Figure 7. Generally,  $E_a$  of pure PHB gradually declines with the increase in conversion amount and finally levels off. The tendency can be explained by the fact that the thermal decomposition of PHB is an autocatalytic reaction. Its thermal decomposition product, for example, crotonic acid, can catalyze the reaction and make its activation energy smaller. Similar results have been reported by Kopinke et al. and Luderwald et al. in the literature.<sup>25,26</sup> Unlike pure PHB,  $E_a$  of maleated PHB is approximately constant throughout the whole conversion range when graft degree of samples is less than 0.44%, whereas  $E_a$  of samples with graft degree above 0.56% is slightly enhanced as conversion amount is between 5 and 40%. After that, they slowly decline. This is probably due to the result that there is an esterification among MA group, the end group of polyester and its oligomers. It can also be found in Figure 7 that  $E_a$  gradually increases with the increase in graft de-

gree. When graft degree reaches 0.56%,  $E_a$  achieves the maximum value, and then declines slowly. The various tendencies of activation energy for different samples indicate that PHB thermal decomposition is a complex process, and also that the amount and the kinds of grafting monomer have an important influence on activation energy of decomposition. Therefore, it is quite possible for the decomposition process of PHB grafting various monomers to exhibit the differently decomposed behavior.

To check and compare the results obtained by the Flynn-Wall-Ozawa method, activation energy was calculated by the Kissinger equation based on various DTG curves.<sup>27</sup> The Kissinger equation is shown as follows:

$$\ln(\Phi/T_m^2) = \ln[nRA(\alpha_m^{n-1})/E_a] - E_a/RT_m = I - E_a/RT_m \quad (2)$$

where  $E_a$  is the activation energy, J/mol;  $\Phi$  is the heating-up rate, K/min;  $T_m$  is the temperature at the maximum rate of weight loss, K;  $n$  is the reaction factor;  $R$  is the gas constant, 8.314 J ·

**Table IV** Activation Energies by the Kissinger Method and Average Activation Energies by the Flynn-Wall-Ozawa Method for PHB and Various Maleated PHB

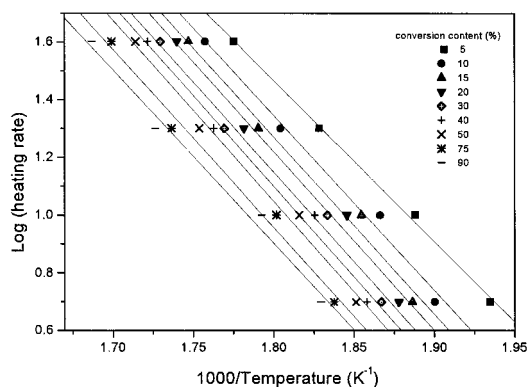
Sample	I	$B^* \times 10^3$ (K)	$E_a$ (kJ/mol) (Kissinger)	$E_a$ (kJ/mol) (Flynn-Wall-Ozawa)
PHB	11.519	9.59	79.73	86.14
PHB-g-MA21	14.65	13.12	109.08	101.13
PHB-g-MA44	14.68	13.70	113.90	108.09
PHB-g-MA56	14.31	13.92	115.73	116.51
PHB-g-MA73	14.29	13.81	114.82	111.26
PHB-g-MA118	9.09	13.05	108.49	110.62

$$B^* = E_a/R$$

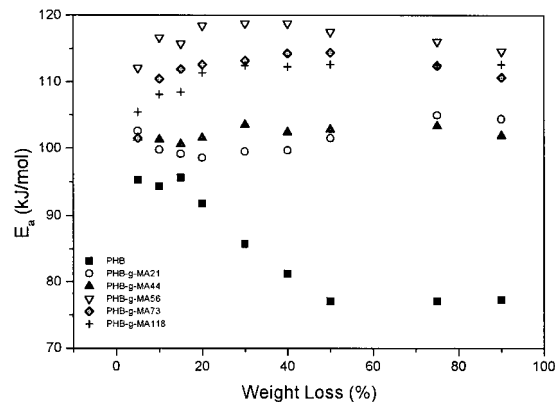
$\text{mol}^{-1} \cdot \text{K}^{-1}$ ;  $A$  is the preexponential factor; and  $\alpha_m$  is the weight of the sample at the maximum rate of weight loss. In this case, the temperatures of the DTG peaks are taken as  $T_m$  values. The  $E_a$  values can be obtained from the slope of the linear relationships between  $\ln(\Phi/T_m^2)$  and  $1/T_m$ ; the activation energy values of all samples are evaluated by using the data listed in Table III, and the results are listed in Table IV, together with the average  $E_a$  obtained by the Flynn-Wall-Ozawa method. The table shows that by using both methods approximately equal values of activation energy are obtained for the whole conversion range.

## CONCLUSIONS

The isothermal treated products of PHB and maleated PHB at 190°C were investigated with FTIR and  $^1\text{H-NMR}$ , and the results indicated that the thermal decomposition of maleated PHB obeyed the six-membered ring ester decomposition process. The thermal decomposition behavior of PHB and maleated PHB with different graft degree were studied by thermogravimetry using various heating-up rates. PHB and maleated PHB are mainly thermally decomposed in the temperature range from 200 to 350°C in a one-step process. The thermal decomposition temperature of maleated PHB is obviously higher than that of pure PHB. It can be concluded that grafting MA on PHB chains may effectively improve its thermal stability. The range of thermal decomposition for PHB becomes narrower after grafting MA monomer, implying that the decomposition rate of mal-



**Figure 6** The Flynn-Wall-Ozawa method applied to calculate activation energy of thermal decomposition for PHB-g-MA56.



**Figure 7** Activation energies obtained by the Flynn-Wall-Ozawa method at various heating-up rates.

ated PHB increases. Activation energy defined by the Flynn-Wall-Ozawa method exhibits the different tendencies with the change in graft degree and conversion amount. It may be the result that there is an esterification involving MA group and the end group of PHB and its oligomers. For comparison, activation energy is also calculated by the Kissinger method, and the results are approximately equal to the average values of activation energy for the whole conversion range by the Flynn-Wall-Ozawa method.

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