

# Thermal Stabilization of Poly(3-hydroxybutyrate) by Poly(glycidyl methacrylate)

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**ABSTRACT:** Poly(3-hydroxybutyrate) (PHB)/poly(glycidyl methacrylate) (PGMA) blends with the PGMA content up to 30 wt % were prepared by a solution-precipitation procedure. The thermal decomposition of PHB/PGMA blends was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). The thermograms of PHB/PGMA blends contained a two-step degradation process, while that of pure PHB sample exhibited only one-step degradation process. This degradation behavior of PHB/PGMA blends, which have a higher thermal stability as measured by maximum decomposition temperature or residual weight after isothermal degradation for 1 h, is probably due to crosslinking reactions of the epoxide groups in the PGMA component with the carboxyl chain ends of PHB fragments during the degradation process, and the occurrence of such reactions can be assigned to the exothermic peaks in their DTA thermograms. An isothermal study of these blends at 200–250°C for 1 h indicated that the residual weight was directly correlated with the amount of epoxide groups in the PHB/PGMA blends. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2945–2952, 2002; DOI 10.1002/app.10318

**Key words:** blends; thermal properties; biopolymer; degradation

## INTRODUCTION

Biodegradable poly(3-hydroxybutyrate) (PHB) produced by a wide variety of bacteria is a thermoplastic crystalline polyester whose mechanical properties, except the elongational property, are comparable to those of isotactic polypropylene. This polyester has much potential in applications such as surgical sutures, long-term carriers for

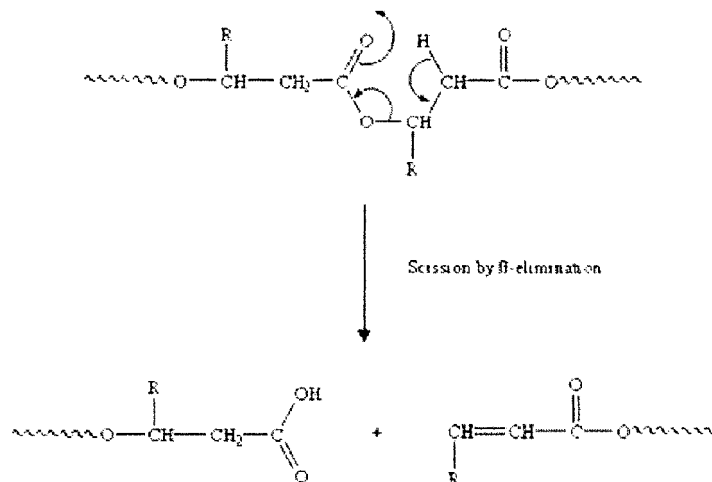
drugs, and degradable plastics. However, until now there has been no larger commercial application because PHB has a higher cost, narrow processability window (that is, PHB is easily decomposed at temperatures near its melting temperature), and brittleness (low impact resistance). In particular, the thermal instability of PHB in the melt prevents it from substituting the nonbiodegradable polymeric materials in commercial products.

The chain scission process in the thermal degradation of PHB is well known to occur by a cyclic  $\beta$ -elimination reaction as shown in Scheme 1.<sup>1–3</sup> The thermal degradation of PHB proceeds by a one-step process, which is known to involve a random, chain scission reaction of the ester

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Scheme 1

groups to form olefinic and carboxylic acid end groups. This type of scission reaction causes a gradual decrease in molecular weight of the polymer, and volatile products are formed when extensive polymer chain degradation occurs to yield oligomers.

The basic problem with PHB is that at its melting point its chain scission rate is too fast. In principle, this problem might be overcome either by reducing the crystalline melting point to lower the processing temperature, or by adopting some means of reforming links in the polymer, for example, by crosslinking. As an approach to low the processing temperature of PHB, copolymerization of 3-hydroxybutyrate with either 3-hydroxyvalerate or 4-hydroxybutyrate using the bacterial fermentation method has been developed. However, it is difficult to utilize these copolymers for diverse applications because the fermentation medium is rather limited and costly. Another approach to reduce the chain scission rate of PHB is blending with various additives or crosslinkers, which can repolymerize thermally fragmented polymer chains. Accordingly, some attempts<sup>4,5</sup> to increase the melt stability of PHB have been made by the use of additives, including various organic or inorganic compounds. The end groups

formed by the  $\beta$ -elimination reaction of PHB are a crotonyl moiety and a carboxylic acid, as depicted in Scheme 1. Holmes and his coworkers<sup>5</sup> have attempted the polymerization of the crotonyl groups using a number of combinations of free radical initiator and mono- or multifunctional unsaturated additives. However, most combinations were proven to be not effective because radicals produced by initiator are able to abstract hydrogen atoms from the polymer chain to yield the chain radicals capable of accelerating the polymer degradation as well as forming the crosslinks.

In our recent study,<sup>6,7</sup> it was found that poly(3-hydroxyalkanoate)s (PHAs) with epoxide pendant groups have a higher thermal stability owing to crosslinking reactions of pendant epoxide groups with the carboxyl chain ends fragmented. This suggests that end-group linking reactions using an epoxide group could be used effectively to repolymerize the thermally degraded polymer and then inhibit the rapid decrease in the molecular weight of PHB. The aim of this study is to develop a polymeric thermal stabilizer containing epoxide groups for PHB. For this, poly(glycidyl methacrylate) (PGMA) was blended up to 30 wt % with PHB, and thermal stability of PHB/PGMA blends was investigated by thermogravimetric analysis

Table I Molecular Characteristics and Code of the Polymers

Polymer	Code	$M_n$	$M_w/M_n$	$T_g$ (°C)	$T_m$ (°C)
Poly(3-hydroxybutyrate)	PHB	105,000	2.4	9	177
Poly(glycidyl methacrylate)	PGMA	93,000	2.5	58	—

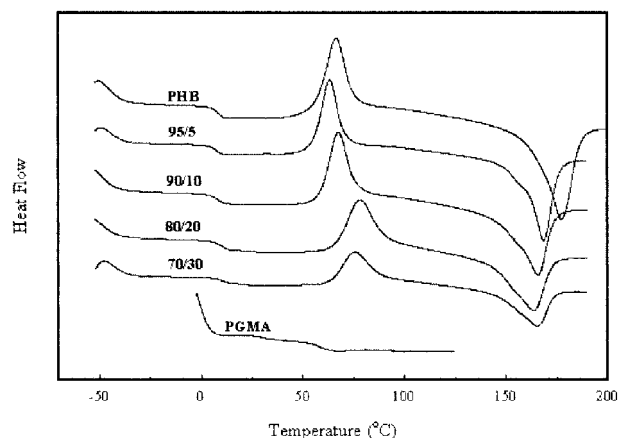


Figure 1 DSC thermograms of PHB/PGMA blends.

(TGA), differential thermal analyzer (DTA), and differential scanning calorimetry (DSC).

## EXPERIMENTAL

### Materials

Glycidyl methacrylate (GMA) (Aldrich Co.) was purified by distillation before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from absolute ethanol, dried under vacuum at 30°C. PHB, in a powder form, was supplied from the KOHAP Ltd. (Korea).

### Synthesis of Poly(glycidyl methacrylate)

PGMA was prepared by radical polymerization of GMA in benzene using 0.1% (w/v) AIBN as an initiator at 50°C. The polymer was precipitated in methanol, purified by reprecipitation in methanol from tetrahydrofuran (THF) solution, and dried in a vacuum oven at 30°C. IR(neat): 3435, 3001, 2947, 1732, 1485, 1450, 1390, 1342, 1259, 1149,

993, 906, 846, 760  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 4.38–3.72 (2H,  $\text{CH}_2\text{O}(\text{C}=\text{O})$ ), 3.21–3.24 (1H, CH of epoxy ring), 2.62–2.89 (2H,  $\text{CH}_2$  of epoxide ring), 1.91 (2H,  $\text{CH}_2$ ), 0.95–1.10 (3H,  $\text{CH}_3$ ). The characteristics of the polymer are summarized in Table I. Molecular weight and its distribution were determined by gel permeation chromatography (GPC) using THF as the eluent.

### Preparation of PHB/PGMA Blends

PHB/PGMA blends (100/0, 95/5, 90/10, 80/20, 70/30, and 0/100, w/w) were prepared by coprecipitation from chloroform solution (2 wt %) with predetermined weight ratios. The resulting precipitates were dried under vacuum at 30°C.

### Sample Characterization

$^1\text{H-NMR}$  spectra were obtained with a Bruker AC-200 NMR spectrometer. Chloroform-*d* solutions of the polymer at concentration of 10 mg/mL were analyzed. The peaks were referenced to tetramethylsilane.

Differential scanning calorimetry (DSC) was conducted using a TA Instruments 2910 (duPont Co.), calibrated with standards. After a first scan up to 200°C, holding at 200°C for 1 min, and followed by rapid quenching to  $-80^\circ\text{C}$ , the DSC curves were recorded second at a heating rate of 20°C/min. The glass transition temperature ( $T_g$ ) was taken as the inflection point. The melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) were taken as the peak values of the respective endothermic and exothermic heats in the DSC curve.

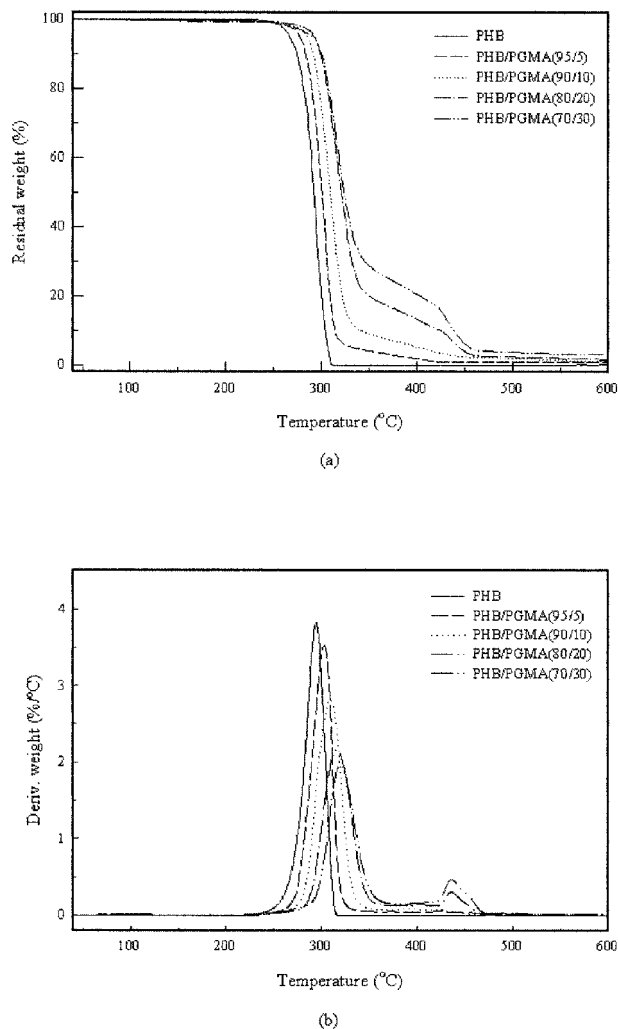
Thermogravimetric analysis (TGA) was conducted using a TA Instruments 2910 (duPont Co.) in a nitrogen atmosphere from 30 to 600°C at a heating rate of 20°C/min. Both the maximum and onset degradation temperatures are reported. Iso-

Table II Thermal Transitions of the PHB/PGMA Blends

Polymers	$T_g$ (°C) <sup>a</sup> (PHB)	$T_g$ (°C) <sup>b</sup> (PGMA)	$T_c$ <sup>a</sup> (°C)	$T_m$ <sup>a</sup> (°C)	$\Delta H_m$ <sup>a</sup> (J/g)
PHB	9	—	67	177	80
PHB/PGMA(95/5)	8	63	63	168	76
PHB/PGMA(90/10)	9	58	67	165	76
PHB/PGMA(80/20)	9	63	78	163	72
PHB/PGMA(70/30)	10	61	76	164	70

<sup>a</sup> Determined from the second scanned DSC thermograms.

<sup>b</sup> Determined from the first scanned DSC thermograms.



**Figure 2** TGA (a) and DTG (b) thermograms of PHB/PGMA blends.

thermal TGA was conducted at 200–250°C for 1 h. Differential thermal analysis (DTA) was conducted using a TG-DTA 2000S (MAC Science Co.)

**Table III** Parameters Evaluated from the  $T_g$  and DTG Thermograms of PHB/PGMA Blends

Polymers	$T_i^a$ (°C)	$T_{max1}$ (°C)	$T_{max2}$ (°C)	Wt(%) at 400°C <sup>b</sup>
PHB	267	295	—	~0
PHB/PGMA(95/5)	278	302	421	2
PHB/PGMA(90/10)	285	308	427	5
PHB/PGMA(80/20)	293	317	436	13
PHB/PGMA(70/30)	290	317	435	21

<sup>a</sup> Values determined at 5% weight loss on TGA curve.

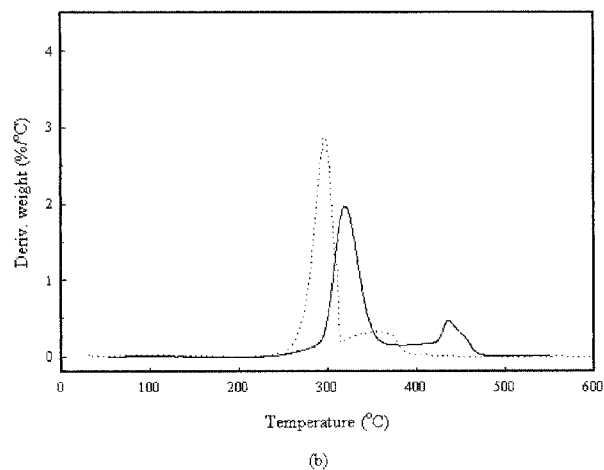
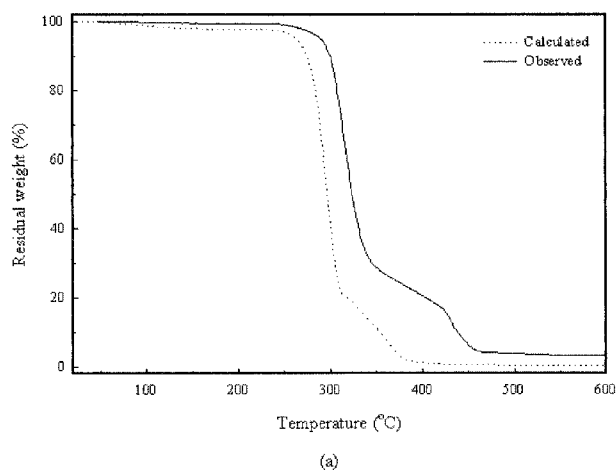
<sup>b</sup> Residual weight at 400°C.

in a nitrogen atmosphere from 30 to 600°C at a heating rate of 20°C/min.

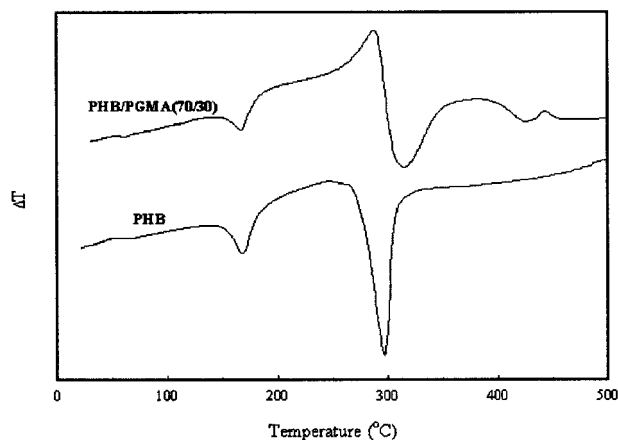
## RESULTS AND DISCUSSION

### Miscibility of PHB/PGMA Blends

Figure 1 shows the DSC thermograms of pure blend components PGMA and PHB, which was quenched from the melt. PGMA has only a glass transition occurred at 58°C, while from the second scan the DSC curve of PHB shows the glass transition ( $T_g = 9^\circ\text{C}$ ), followed by cold crystallization (peak maximum at  $T_c = 67^\circ\text{C}$ ) and melting ( $T_m = 177^\circ\text{C}$ ). Table II shows  $T_g$ ,  $T_m$ , and  $T_c$  values obtained from the first or second scanned



**Figure 3** TGA (a) and DGT (b) thermograms for PHB/PGMA(70/30) blend: solid line, observed; and dotted line, calculated.



**Figure 4** DTA thermograms for (a) pure PHB and (b) PHB/PGMA(70/30) blend.

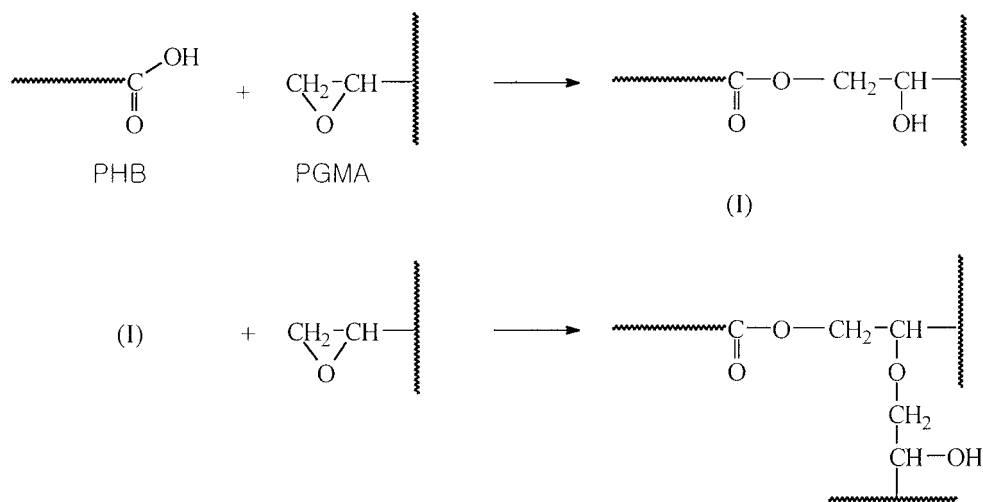
DSC curves of PHB/PGMA blends with the PGMA content up to 30 wt %. The glass transition temperatures of PHB and PGMA components were almost constant, independent of the blend composition, indicating the immiscibility of the two blend components in the range of blend compositions investigated (the miscibility of PHB/PGMA for the overall composition range is under study and will be the subject of a forthcoming article). From the values reported in Table II it is evident that the presence of PGMA would slightly affect the enthalpy of fusion of PHB, as well as the crystallization temperature and the enthalpy of crystallization.

#### Dynamic TGA Study of PHB/PGMA Blends

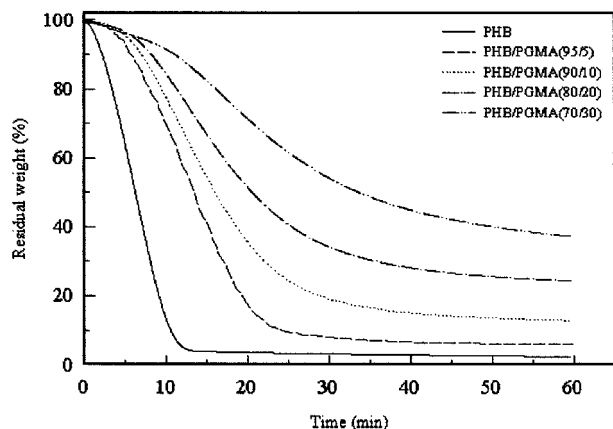
Figure 2(a) shows the TGA thermograms of PHB/PGMA blends containing the PGMA content (ep-

oxide content) up to 30 wt %. The thermal degradation of pure PHB proceeds by a one-step process with a maximum decomposition temperature at 295°C. However, the thermal decomposition patterns of blends followed a considerably different pattern from the single-step reaction of the PHB, and as the PGMA content in blends increased up to 30 wt %, their thermal stability as measured by first maximum decomposition temperature also increased from 295 to 317°C. The thermograms for blends contained two separated degradation steps, or stages, with two maximum rate peaks as shown clearly in the corresponding DTG curves. Figure 2(b) shows the DTG thermograms of PHB/PGMA blends with the PGMA content. As the epoxide content of blends increased, the new second maximum decomposition peaks increased in size without positional change ( $T_{\max 2} = 430 \pm 5^\circ\text{C}$ ), whereas the first ones shifted gradually to higher temperatures (295 to 317°C) with decrease in the peak area. The second decomposition peak, which was obtained with all of the PGMA-containing blends around 430°C, are believed to be caused by thermal crosslinking reaction during the degradation process. Table III shows the initial and maximum degradation temperatures for PHB/PGMA blends, together with the residual weights at 400°C. It was noticeable that the residual weights for PHB/PGMA blends at 400°C increased up to 21% with increasing the PGMA content, while that for pure PGMA was only 4% at that temperature.

Figure 3 compares the observed TGA and DTG curves (solid line) of a PHB/PGMA(70/30) blend with the corresponding calculated curves (dotted

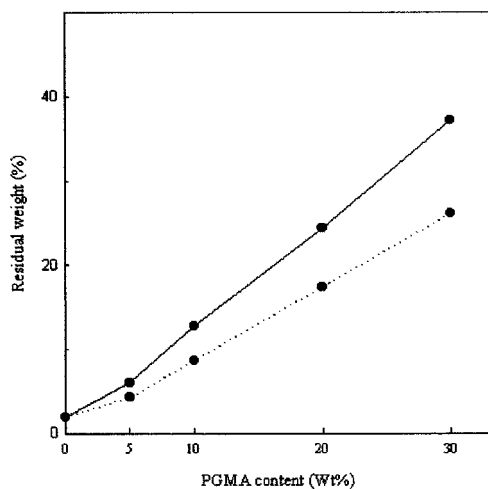


**Scheme 2**

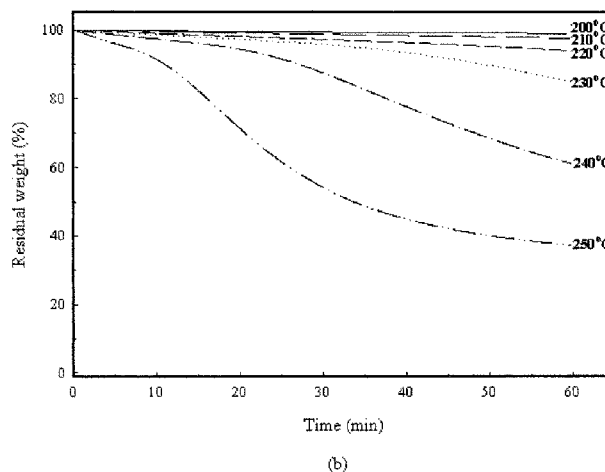
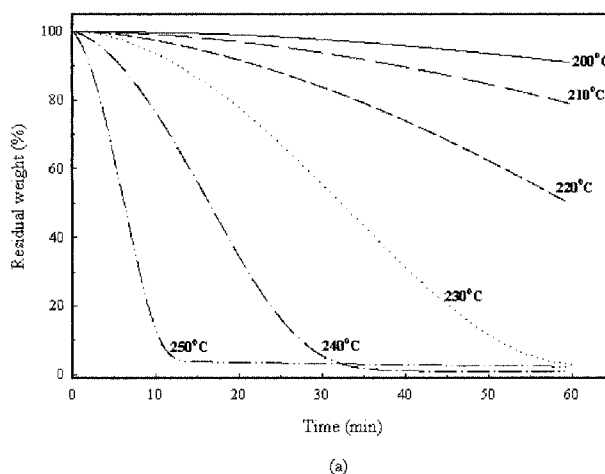


**Figure 5** Isothermal TGA thermograms obtained at 250°C for PHB and PHB/PGMA blends: (a) PHB; (b) PHB/PGMA(95/5); (c) PHB/PGMA(90/10); (d) PHB/PGMA(80/20); and (e) PHB/PGMA(70/30).

line) for the same blend, which are obtained by addition of the thermogravimetric traces of pure polymers. Calculated curves correspond to the thermal degradation of a blend (PHB/PGMA, 70/30) with no interaction between the two components during the thermal degradation. From the TGA curves it can be seen that the weight loss of the blend was retarded in the temperature range of 270–470°C with respect to that expected on the basis of an additive rule. The observed DTG curves also show that the temperature of the maximum degradation rate of PHB was shifted toward higher temperatures, while the degradation temperature of PGMA was inversely affected



**Figure 6** Residual weight after isothermal degradation at 250°C as a function of PGMA content in blends: solid line, observed; dotted line, calculated.



**Figure 7** Time dependence of weight loss for PHB and PHB/PGMA(70/30) under isothermal condition in the temperature range of 200–250°C.

by the PHB. Because the weight loss initiated at approximately 290°C in the PHB/PGMA blend is mainly associated with the ester cleavage of the PHB component by  $\beta$ -elimination reaction, this retarded degradation indicates that the reactions between two polymers take place during the initial degradation process, and then PHB are more stabilized in the blend. To investigate whether crosslinking reactions occurred during the degradation of PHB/PGMA blends, the DTA analyses were conducted up to 600°C. Figure 4 shows the DTA thermograms for pure PHB and PHB/PGMA(70/30) blend. The DTA thermogram of the blend sample shows an endothermic peak at 315°C and two exothermic peaks at 381 and 442°C, in contrast to the DTA thermogram of the

**Table IV Residual Weight (%) and Degradation Rate (%/min) of PHB and PHB/PGMA(70/30) under Isothermal Conditions**

Temperature (°C)	PHB		PHB/PGMA(70/30)	
	wt% at 1 h	Degradation Rate	Wt% at 1 h	Degradation Rate
200	91	0.2	99	~0
210	79	0.4	98	~0
220	50	1.0	94	0.1
230	3	2.3	85	0.4
240	1	3.8	61	0.9
250	2	10.4	37	1.9

pure PHB sample, which showed only a single endothermic decomposition peak at 296°C. The exothermic peaks at 381 and 442°C on the DTA thermogram also increased with the PGMA content in blends (not shown). The exothermic peaks following the endothermic decomposition peak can be ascribed to a thermal crosslinking reaction of the epoxide groups of PGMA with carboxylic acid groups, which are formed by the random chain scission of the PHB component, and with hydroxyl groups formed as a result of a former reaction. The reaction of the epoxide groups of PGMA with carboxylic acid groups leads to ester linkages, while that of epoxide groups with hydroxyl groups results in ether linkage. As reported for the epoxy-rich/anhydride curing system,<sup>8,9</sup> ester formation reaction is faster than ether formation, as shown below:

The two polymers are immiscible in the composition range studied, and the blends result in a biphasic structure. However, the PHB oligomers with carboxylic acid ends formed in the initial decomposition stage could diffuse from the PHB phase to the PGMA one, due to the enhanced miscibility of the two polymer components caused by thermal degradation of PHB, and could react rapidly with the epoxide groups of PGMA to form new interchain bonds, resulting in retarding the

degradation of blend. Therefore, the second maximum peaks on DTG thermogram (Fig. 2) may be ascribed to decomposition of newly formed inter-chain bonds.

A similar type of melt reaction was proposed by Grassie and coworkers, who suggested that, in the initial stages of the thermal degradation of PHB, terminal hydroxyl end groups on original polymer chains can react with carboxylic acid groups formed by chain scission.<sup>2</sup> Reactions of this type during the thermal degradation of polymers have also been reported previously for hydroxy-terminated siloxanes<sup>10–12</sup> and polyamides,<sup>13</sup> although the extent of this reaction would be limited due to a low concentration of terminal hydroxyl chain ends.

#### Isothermal TGA Study of PHB/PGMA Blends

Figure 5 shows the isothermal TGA curves obtained at 250°C for PHB and PHB/PGMA blends. At that temperature the PHB sample was almost completely degraded and volatilized within 10 min, while the residual weight of blends was in the range of 6–37% after isothermal degradation for 1 h. The relationship between the PGMA content in blends and the residual weight (observed and calculated) after isothermal degradation at

**Table V Second Scanned DSC Results for Pure PHB and PHB/PGMA(70/30) Blend after Isothermal Degradation for 1 h at 200, 210, and 220°C**

Temperature (°C)	PHB			PHB/PGMA(70/30)		
	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)
200	-1	60	153	13	—	—
210	-6	71	134	11	—	—
220	-15	—	—	8	—	—

250°C is shown in Figure 6. The calculated residual weights for PHB/PGMA blends could be obtained by using the residual weight (87%) of the PGMA homopolymer after isothermal degradation at 250°C for 1 h. The residual weight is directly related to the amount of PGMA in blends in a linear manner. It was also noticeable that the observed residual weights (%) showed higher values up to ~11% (for PHB/PGMA, 70/30) than the calculated ones. This indicates that most, if not all, of the epoxide groups of PGMA may have participated in the thermal crosslinking reactions, as described above. Figure 7 shows the time dependence of weight loss for PHB and PHB/PGMA(70/30) under the isothermal condition in the temperature range of 200–250°C. The degradation rate calculated from the slope of the linear dependence of weight loss is expressed in %/min and listed in Table IV. Both weight loss (%) and degradation rate (%/min) of PHB/PGMA(70/30) show much lower values than those of the pure PHB. It was noticeable that the degradation rate of pure PHB was faster up to about 10 times than that of the PGMA-containing blend. Considering the commercially investigated processing conditions of PHB, this thermal stability of the PHB/PGMA blend was so improved and desirable.

#### Properties of Thermally Degraded PHB/PGMA Blends

To investigate the difference in thermal properties of pure PHB and PHB/PGMA(70/30) blend degraded isothermally in TGA sample chamber, DSC measurement was conducted by a second heating. Table V shows the second scanned DSC results for pure PHB and PHB/PGMA(70/30) blend, which were isothermally degraded for 1 h at 200, 210, and 220°C. In the case of pure PHB, the glass transition decreased gradually from 9 to –15°C as the PHB sample was degraded at a higher temperature. The crystalline melting temperature of PHB also decreased significantly and disappeared for the sample degraded at 220°C for 1 h, indicating that the chain length of the PHB sample degraded at 220°C is too short to form a crystalline domain. For PHB/PGMA(70/30), one

glass transition only occurred on a second scanned DSC curve without melting transition of PHB. The disappearance of melting transition in this blend might be due to a crosslinking reaction, which could restrict crystallization of the PHB chain during the thermal degradation of PHB.

Although the pure PHB sample degraded isothermally at 200–250°C was immediately soluble in its solvents, the samples of PHB/PGMA blends after the isothermal study were not soluble, and showed very little swelling in chloroform, THF, acetone, and methylene chloride, which strongly supports the proposed occurrence of crosslinking reactions during the degradation process.

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