Improvement of the Thermal Stability of Polyhydroxybutyrates by Grafting with Maleic Anhydride by Different Methods: Differential Scanning Calorimetry, Thermogravimetric Analysis, and Gel Permeation Chromatography

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ABSTRACT: The crystallization and thermal degradation behaviors of polyhydroxybutyrate (PHB) grafted with maleic anhydride (MA) by different techniques were analyzed with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). The results of DSC, TGA, and GPC analyses indicated that the grafting method could affect the crystallization rate, crystallinity, and thermal stability of PHB because of changes in the molecular weight of PHB and the amount of MA grafted during the reaction. The reduction of the molecular weight of PHB that reacted during the processing followed this order of methods: melt grafting > solvent grafting > mechanical grafting. However, the grafting ratio of MA followed this order of methods: melt grafting > mechanical grafting > solvent grafting. All three grafting methods significantly improved the thermal stability, therefore increasing the crystallization rate and melting temperature of the as-received PHB. A grafting ratio of MA as low as 0.07 wt % could result in a significant improvement in the heat resistance of PHB. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2718–2726, 2008

Key words: biological applications of polymers; crystallization; degradation; differential scanning calorimetry (DSC); functionalization of polymers

INTRODUCTION

Polyhydroxyalkanoates (PHAs) produced by bacteria are attracting increasing attention because their biosynthetic nature can alleviate the problem of the surging price of oil-based synthetic polymers resulting from a possible shortage of oil. Of the various PHAs, polyhydroxybutyrate (PHB) has been mostly studied since its early introduction in the 1920s.[1–10] The practical usage and acceptance of PHB in industry can be expected because it has the lowest production cost of all PHAs and has unique biodegradation/biocompatibility properties, as long as its inherent serious shortcomings, brittleness and early thermal degradation, can be improved.

As is known, the brittleness of PHB is attributable to its high degree of crystallization and postcrystallization during storage. Processes such as annealing molded PHB at a high temperature, cold-drawing PHB, blending PHB with other thermoplastics, adding low-molecular-weight plasticizers, and incorporating different flexible constituents [e.g., 3-hydroxyvalerate (HV) and 3-hydroxyhexanoate (HHx)] into PHB have been demonstrated to effectively improve the flexibility and flexural strength of PHB.[4,8]

Among these methods, some can also promote the thermal stability of PHB simultaneously, such as blending PHB with a more stable thermoplastic polymer and adding HV and HHx to form PHB–HV and PHB–HHx copolymers. PHB–HV and PHB–HHx have a lower melting temperature (T_m) than PHB because of the smaller degree of crystallization and the presence of flexible chains. Henceforth, this copolymerization improves the thermal stability and broadens the processing window of PHB because of the use of a low molding temperature. Plasticizers have a similar effect, lowering the processing temperature of PHB. Despite this, the thermal degradation of PHB can also be retarded through the grafting of various unsaturated chemicals, such as acrylics (methyl methacrylate, 2-hydroxyethyl methacrylate, and acrylic acid) and styrene, onto PHB, possibly because of the hindrance of the degradation reaction.[11,12]

In general, these methods are promising routes to improving the thermal stability of PHB because it is

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well acknowledged that the thermal degradation of PHB cannot be effectively retarded by just the addition of conventional stabilizers or antioxidants that are usually used in stabilizing commodity thermoplastics. This is attributed to the fact that the thermal degradation reaction of PHB consists of nonradical, random chain scission and a cis elimination reaction of β-CH, including a six-membered ring transition.[13,14] In addition, this thermal degradation reaction is little changed in air, *in vacuo*, or in nitrogen.

In this article, the thermal resistance of PHB is shown to be significantly improved by the grafting of maleic anhydride (MA) to PHB with different methods. The uses of MA in modifying various properties of different thermoplastics have been widely investigated in the past. The nonisothermal crystallization and thermogravimetric analysis (TGA) of maleated PHB prepared by a solution reaction were also investigated by Chen et al.,[11,15,16] and they showed that the presence of MA would reduce the crystallization and nucleation rates but improve the thermal stability of PHB.[11,15,16] It is demonstrated here that the changes resulting from the use of three grafting methods are closely related to different crystallization and thermal degradation behaviors obtained from grafted PHBs.

EXPERIMENTAL

Grafting methods

The as-received PHB was biosynthesized from *Escherichia coli* with crude glucose as the medium [purity = 98%, weight-average molecular weight (M_w) = 605,000, polydispersity index (PDI) = 1.56, residual Ca^{2+} = 702 ppm, residual Mg^{2+} = 94 ppm; Nan-Tien Co., Nantong, China] and used without further purification. The residual Ca^{2+} and Mg^{2+} in PHB were measured by an EPA-certified laboratory with inductively coupled plasma atomic emission spectrometry (ICP-Optima 2000DV, PerkinElmer, Waltham, MA) and with the standard digestion and calibration methods. MA and benzoyl peroxide (BPO), used as an initiator, were purchased from Aldrich (St. Louis, MO) and used as-received. Three different grafting methods, melt, solvent, and mechanical grafting, were used in this study. The melt grafting was performed at 175°C with a Brabender PL-2000 plasticorder at a maximal torque of 5 kg m (1000 rpm) for 10 min. To prepare the solvent-grafting PHB specimens, PHB was dissolved in chloroform at 55°C to obtain 5 wt % solutions; subsequently, required MA and BPO were added, and the solutions were then stir-reacted at 55°C for 6 h. The grafted PHB was finally extracted with methanol, and then the solvent-grafted specimens were obtained by the drying of the extracted PHB on a

Petri dish at room temperature for 24 h. The mechanical grafting was performed through the grinding of PHB, MA, and BPO in a Restch type 51 ball mill (Rheinische, Germany) at 300 rpm for 10 h at room temperature. In all three methods, different amounts of MA and BPO were reacted together with 100 parts of PHB, but only the results from the representative grafted specimens prepared from 5 parts MA and 1 part BPO are shown here because the addition of more than 5 parts MA or more than 1 part BPO could not improve the thermal stability more significantly.[17] The unreacted residual MA and BPO were removed through the rinsing of the reacted PHB with acetone. The molecular weight distributions of the prepared specimens were measured with gel permeation chromatography (GPC) at 25°C. For GPC, PLgel 5-μ 10000A, 5-μ guard, and 5-μ mixed-C columns from Polymer Labs were used, along with an L-2490 refractive-index detector from Hitachi (Taipei, Taiwan) and a PU-980 intelligent high performance liquid chromatography (HPLC) pump from Jusco (Tokyo, Japan). Chloroform was used as the eluent at a flow rate of 1 mL/min with a PHB concentration of 20.0 mg/mL for GPC analysis. Polystyrene standards with different molecular weights (580–841,700 g/mol) were used to calibrate the GPC results. The prepared films were all stored in the refrigerator below the glass-transition temperature before analysis to avoid further crystallization during storage.

The unreacted MA removed during the acetone rinsing step was analyzed by gas chromatography, and from this, the amounts of unreacted MA were determined from gas chromatography calibration curves obtained from acetone solutions with different concentrations of MA; then, the amounts of MA that reacted were determined. The titration method was also used, but it could not accurately determine the amount of reacted MA because of acid groups that formed in the degraded PHB during the high-temperature melt-grafting procedure. The grafting ratio was defined as the ratio of the weight of reacted MA to the weight of used PHB.

Differential scanning calorimetry (DSC) analysis

A PerkinElmer DSC-7 was used to measure the endotherms and exotherms of different specimens. The thermogram was measured at a scanning rate of 10°C/min from −40 to 185°C (first scan); the specimens were kept at 185°C for 5 min to erase the thermal history, subsequently cooled to −40°C at a cooling rate of 10°C/min, and then reheated to 185°C at a scanning rate of 10°C/min (second scan) under a nitrogen environment (with a nitrogen flow rate of 40 mL/min). Three specimens prepared from hermetic aluminum (Al) pans were tested for each
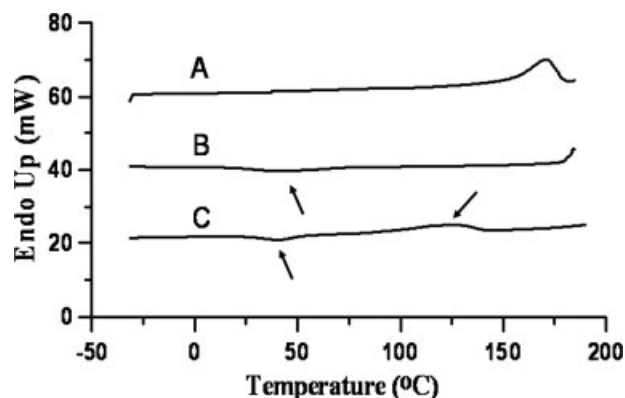
Figure 1 Representative DSC thermograms obtained from the as-received PHB by the (A) first heating scan, (B) cooling scan, and (C) second heating scan.

DSC measurement. The obtained thermograms were calibrated with the baseline obtained from the empty Al pan and an indium standard.

TGA

Different specimens were further analyzed with a PerkinElmer Pyris-1 thermogravimetric analyzer. The PHB specimens were pulverized with a Wig-L-Bug before TGA. The weight-loss behavior of each specimen was measured in a dynamic scanning mode. The specimen was scanned from room temperature to about 300°C at a heating rate of 10°C/min with a nitrogen flow rate of 40 mL/min. The peak temperatures of derivative weight-loss curves and weight-loss percentages were obtained from TGA thermograms.

RESULTS AND DISCUSSION

DSC analysis

Representative DSC thermograms of as-received PHB are shown in Figure 1. As shown in Figure 1(A), there is a clear endothermic peak, with the

peak T_m near 170.8°C and a melting heat of 81.5 J/g corresponding to a crystallinity of 55.8%, which is similar to those usually observed in room-temperature-stored PHB (see Table I).[18] After 5 min at 185°C, there is a noticeable broad exothermic peak near the relatively low value of 41.6°C, with an exothermic heat of approximately 30.4 J/g, during the cooling scan, as shown in Figure 1(B). This indicates that the as-received PHB after the first heating scan has a very low crystallization rate, which results in a small degree of crystallization due to insufficient time in the cooling run. As a result, a clear and small cold-crystallization peak is obtained from the second heating scan of this undercrystallized PHB [see Fig. 1(C)], with an exothermic crystallization peak around 40.5°C and a heat of crystallization of 16.1 J/g. In addition, the thermogram obtained from the second heating scan has a broad melting endotherm that begins below 100°C right after the cold-crystallization process with the peak T_m at 122.9°C and with a melting enthalpy (ΔH_m) of 48.9 J/g. Both melting characteristics are much lower than many of those published elsewhere.[15,19,20]

The low T_m value and small endotherm of the as-received PHB can be attributed to the drastic thermal degradation occurring during the high-temperature period in the first DSC heating scan. According to GPC analysis, M_w of the studied PHB significantly decreases from 605,000 g/mol (PDI = 1.56) before the DSC experiment to a low of 3878 g/mol (PDI = 1.76) after only 5 min of exposure at 185°C (see Table II). This great decrease in the molecular weight not only results in a low nucleation density and subsequently a long crystallization time but also causes the formation of small and imperfect crystallites that melt at a much lower temperature.[21] Henceforth, low T_m and heat values are obtained from the second DSC heating scan. The broad melting endothermic peak in Figure 1(C) also implies that the degraded PHB with a low M_w contains crystals of various particle sizes [confirmed by polarized mi-

TABLE I
Characteristic Data Obtained from the DSC Thermograms

| | DSC scan | | | | | |
| | First heating scan | | Cooling scan | | Second heating scan | |
PHB specimen	T_m (°C)[a]	ΔH_m (J/g)[b]	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
As-received	170.8	81.5 (55.8%)[c]	41.6	30.4 (20.8%)	122.9	48.9 (33.4%)
Melt-grafted	169.3	92.8 (63.5%)	105.3	80.0 (54.7%)	166.4	93.6 (64.1%)
Solution-grafted	171.4	101.8 (69.7%)	91.6	74.1 (50.7)	167.7	91.0 (62.3%)
Mechanically grafted	173.8	84.5 (57.8%)	112.1	83.0 (56.8%)	173.9	95.9 (65.6%)

ΔH_c = crystallization enthalpy.
[a] The standard deviation was smaller than 2°C.
[b] The standard deviation was smaller than 3 J/g.
[c] Percentage crystallinity based on PHB with 146 J/g of endotherm at 100% crystallinity.[18]

TABLE II
**Molecular Weights of the PHBs After Different Treatments**

	Condition			
	As-prepared		After the first DSC heating scan	
PHB specimen	M_w	PDI	M_w	PDI
As-received	605,000	1.56	3,878	1.76
Melt-grafted	62,000	2.21	15,930	2.31
Solution-grafted	252,000	2.29	236,000	3.45
Mechanically grafted	458,000	2.01	13,890	1.89

croscopy (not shown here)] and lamellar thicknesses.

The serious thermal degradation is also confirmed by TGA and FTIR analysis. In a TGA experiment, as-received PHB was heated at a rate of 10°C/min and isothermally kept at 185°C for 5 min in a nitrogen environment. This process was similar to that used in the first DSC heating scan. The heated PHB would have about a 5% weight reduction during this short exposure at 185°C (excluding the negligible amount of moisture absorbed), and this indicates serious early degradation. The change during thermal exposure can also be confirmed from FTIR spectra taken before and after exposure, as shown in Figure 2. It is obvious that the decreases in the intensities of the bands near 1724 and 1230 cm^{-1} and increases in the intensities at 3437 and 1629 cm^{-1} come from the as-received PHB after 5 min at 185°C. It is known that the degradation of PHB by a six-membered ring transition forms carboxylic acid and unsaturated groups that are responsible for emerging bands near 3437 and 1629 cm^{-1}, which are characteristic of increases in hydrogen-bonded groups and C=C bonds, respectively.[13,14] As described previously, the degradation also causes a decrease in the crystallinity, which leads to decreases in the intensities of the crystalline bands near 1724 and 1230 cm^{-1}.
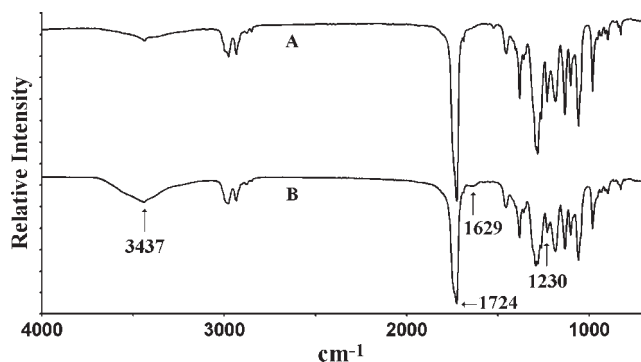
Figure 2 FTIR spectra obtained from the as-received PHB (A) before and (B) after exposure at 185°C for 5 min.
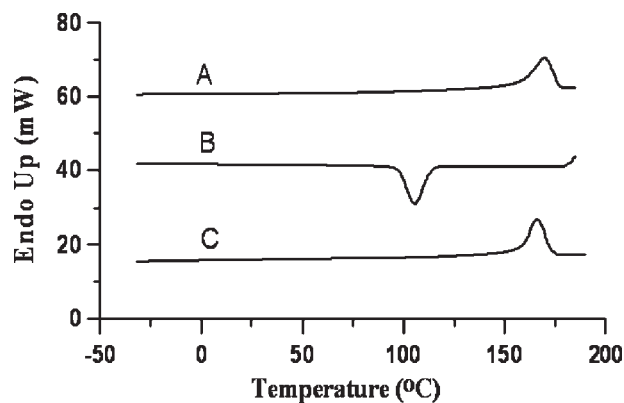
Figure 3 Representative DSC thermograms obtained from the melt-grafted PHB by the (A) first heating scan, (B) cooling scan, and (C) second heating scan.

Regardless of the well-known thermal instability of PHB, PHB biosynthesized from *E. coli* has distinctly bad thermal stability, mostly because of lipase residues and/or inorganic metal compounds (used as the essential elements for the cultivation of microorganisms) present in the PHB product, which is not fully purified.[22–25] Amino–organic residues and considerable amounts of residual Ca^{2+} (702 ppm) and Mg^{2+} (94 ppm) are also present in the studied PHB.[17] The results here indicate that these small amounts of specific and powerful catalytic substances could cause serious degradation in the unpurified PHB. It has been confirmed in our study that the addition of this impurity to more stable purified PHB can result in accelerated early degradation.[17]

This early degradation and the corresponding changes in the thermal properties can be alleviated by the grafting of MA onto PHB molecules. DSC thermograms of PHB grafted with MA by the melt-grafting method are shown in Figure 3. During the first heating scan, a clear endothermic melting peak near 169.3°C with a melting heat of 92.8 J/g can be observed (see Table I). The PHB material experiences serious degradation during the melt-grafting process because of the long exposure to a high temperature and shear force environment in the Brabender. M_w of this PHB is greatly reduced to 62,000 g/mol with PDI near 2.21 after the grafting (see Table II). Yet the endotherm of this highly degraded PHB is similar to that from the as-received PHB shown in Figure 1(A). This indicates that the grafted PHB with M_w = 62,000 g/mol is able to effectively and quickly crystallize after the grafting process. This can be confirmed by the DSC cooling thermogram obtained right after the first heating scan, as shown in Figure 3(B).

A sharp exothermic peak near 105.3°C with a crystallization heat of 80.0 J/g [both values are significantly greater than those from the as-received PHB shown in Figure 1(B)] is shown in Figure 3(B). From

the much higher crystallization temperature (T_c) obtained, it is clear that the melt-grafted PHB has a much faster crystallization rate than the as-received PHB. In addition, the crystallinity of this MA-modified PHB during cooling is 54.8%, which is also much greater than that from the unmodified PHB. These results indicate that the grafted MA is beneficial to the crystallization of PHB despite the great decrease in M_w during the melt-grafting process. This helpful effect can be attributed to the role of MA in possibly changing the flexibility and packing and most importantly retarding the thermal degradation reaction of PHB. The decrease in the molecular weight during the time at 185°C after the first heating scan of this modified PHB (M_w = 15,930, PDI = 2.31) is much less than that of the as-received PHB (see Table II). As a result, the grafted MA can lessen the degradation reaction of PHB, with the cooling crystallization less affected.

The improvement of the thermal stability by grafted MA has also been confirmed by a separate test. In the test, blank PHB, that is, PHB without the addition of MA and BPO, was masticated in the Brabender under the same conditions used in the melt-grafting process. After processing, M_w of the as-received PHB drastically decreased to 30,000 (PDI = 1.58), which was much lower than the value of 62,000 g/mol for the melt-grafted PHB. Consequently, the MA-grafted PHB has better thermal stability. The effect of grafted MA on promoting the thermal stability of PHB can also be obtained from TGA results shown later.

The melting thermograms of two PHB specimens from the second heating scan can be objectively compared. In Figure 3(C), the melt-grafted PHB exhibits a sharp endothermic peak near 166.4°C with a melting heat of 93.6 J/g but no exothermic crystallization peak (also see Table I). The secondary crystallization occurring during the heating scan increases the heat from 80.0 J/g during the cooling scan to 93.6 J/g, and this is not observed in the as-received PHB because of the inferior small crystals and low crystallinity (as well as low crystallization rate) resulting from the severe degradation. Additionally, in comparison with those obtained from Figure 1(C), the results here indicate that the MA-grafted PHB has a much higher crystallinity and larger crystals with greater lamellar thickness than the unmodified PHB, even though it also has a relatively low molecular weight near 15,930 g/mol. This is consistent with what was concluded from the cooling scan.

Because of the unwanted degradation present in the melt-grafting process, a more benign solution-grafting method has been tested. As shown in Figure 4(A), the solution-grafted PHB has a melting endotherm different from those shown in Figures 1(A) and 3(A). A main melting peak near 171.4°C and an
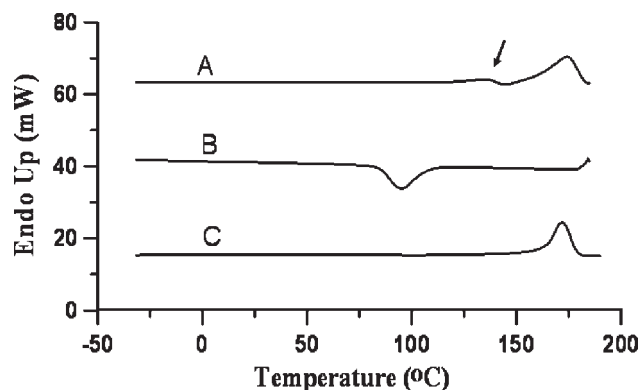
Figure 4 Representative DSC thermograms obtained from the solution-grafted PHB by the (A) first heating scan, (B) cooling scan, and (C) second heating scan.

additional small shoulder near 135.3°C were obtained (Table I). The multiple melting endotherms of PHB have been observed elsewhere.[26–29] In general, the multiple melting endotherms of crystalline polymers can be attributed to (1) melting, recrystallization, and remelting during the DSC scanning condition; (2) different forms of crystals; (3) crystals with different sizes, lamellar thicknesses, and perfections; (4) effects of physical aging and relaxation; and (5) crystals formed from different molecular weights.[30] In the case of PHB, factors 1 and 3 are usually responsible for generating multiple melting peaks in DSC thermograms.[26–29]

Henceforth, the small shoulder in Figure 4(A) is not a true independent melting peak but is attributable to the melting–recrystallization reaction of PHB crystals at a relatively high temperature. The concave downward region between two peaks is actually due to the exothermic recrystallization occurring after the melting of small and imperfect crystals at a low temperature. The low-temperature-melted crystals are formed during the recovery of the grafted PHB by the evaporation of the solvent after the solution-grafting reaction. As a result, the thermogram consists of one solvent–crystallization part with a lower T_m and a melting–recrystallization part with a higher T_m.

The solvent induced crystallization is different from the crystallization from the melt because the generation of crystalline nuclei is due to activated chain motion in the solution, which is different from that in the molten state.[31] The crystallization behavior of the polymer with the solvent is related to the amount of the solvent present in the resin. The concentration of the solvent present at the polymer/solvent interface and the solvent diffusion through the semicrystalline resin are key factors in determining the crystallization kinetics.[32] Henceforth, the amount of the solvent and the evaporation speed affect the crystallization kinetics and crystallinity of the

polymer.[33] It is because of these solvent-related effects that different DSC endotherms (the first heating scan) have been observed for the solvent-grafted and melt-grafted PHB specimens.

As shown in Figure 4(B), the solvent-grafted specimen also exhibits a clear exothermic crystallization peak similar to that observed in Figure 3(B) but with a lower peak temperature near 91.6°C and a small exothermic enthalpy of approximately 74.1 J/g during the cooling scan (see Table I). The result indicates that the solution-grafted PHB also has a crystallization rate and crystallinity much higher than those of the ungrafted PHB but lower than those of the melt-grafted PHB. The differences in the molecular weight and the amount of grafted MA among the specimens result in the discrepancy obtained.

As mentioned previously, the unmodified PHB has an M_w value too low after the thermal exposure to effectively crystallize during the cooling scan, whereas the grafted MA can improve the thermal stability of PHB and then lead to a material with a higher molecular weight and, consequently, a faster crystallization rate and larger crystallinity after the high-temperature exposure. The solution-grafted PHB has an M_w value of 252,000 g/mol (PDI ≈ 2.29) after the grafting reaction, which is much greater than that from the melt-grafted specimen because of the more mild grafting condition used in the solution reaction (see Table II). This M_w value also slightly decreases to 236,000 g/mol with a very broad PDI near 3.45 at the end of the first heating scan (see Table II). Although this M_w value is much higher than that of the melt-grafted PHB (M_w = 15,930 g/mol, PDI = 2.31), a lower crystallization speed and crystallinity have been obtained from the solution-grafted specimen. The result indicates that there could be factors other than the simple molecular weight, such as the grafting amount and the molecular weight distribution, that also significantly affect the crystallization behavior.

It is well recognized that a polymer with a molecular weight too low or too high would adversely affect the crystallization and lower the crystallinity. The maximum crystallization can be obtained from a polymer with an optimal molecular weight.[34] A short-chain polymer is too mobile to fit in the crystalline structure (large negative entropy), whereas a very long chain polymer is too viscous to arrange itself in a regular pattern. For example, linear polyethylene with maximal crystallinity has a molecular weight in the range of 10,000–100,000.[32] Polyethylenes with molecular weights in other regions all have lower crystallinity. As for PHB, a similar effect could also be present but more complicated because of the considerable differences in the PDI and the amount of MA attached.

TABLE III
### Grafting Ratios of MA Obtained from Different PHBs

	PHB specimen		
	Melt-grafted	Solution-grafted	Mechanically grafted
Grafting ratio of MA[a] (%)	1.54	0.07	0.12

[a] Weight of grafted MA/Weight of PHB.

As described, the amount of MA that reacts can affect the crystallization behavior because the grafted MA will introduce irregularity into the molecular chain and add hindrance to retard crystallization.[11] The solution-grafted PHB has a grafting ratio of MA near 0.07%, whereas that of the melt-grafted PHB is higher at 1.54% (Table III). As for these two specimens, it is believed that the effect of the grafted MA interacts with the effect of the molecular weight on the crystallization (see Tables I and II). The adverse effect on the crystallization from the mobile chains with a low molecular weight is compensated by the irregularity and hindrance from the grafted MA, and then this interaction results in the fast crystallization obtained from the melt-grafted PHB. A similar effect has also been observed for the mechanically grafted PHB (shown later).

Despite the difference obtained during cooling, the solution-grafted PHB has a thermogram similar to that of the melt-grafted PHB obtained from the second heating scan. From Figure 4(C), an endothermic peak near 167.7°C and an enthalpy of approximately 91.0 J/g have been obtained. No clear exothermic peak like that shown in Figure 4(A) can be observed because of the better formed crystal and higher crystallinity produced during the cooling scan. However, the relatively broad melting peak indicates that the crystals from the solution-grafted PHB may have a broader distribution of lamellar thicknesses (or crystal sizes), which can be attributed to the relatively large distribution of molecular weights (large PDI) after the thermal exposure. As expected, a larger secondary crystallization has also been obtained (91.0–74.1 = 16.9 J/g) because of the lower crystallinity that formed during the cooling run (see Table I).

A third method, mechanical grafting, is also used to react MA with PHB to prevent the severe degradation encountered in the melt grafting but improve the low grafting ratio obtained from the solvent-grafting method. From the first heating thermogram shown in Figure 5(A), it was expected that mechanically grafted PHB would have a melting endotherm similar to that in Figure 1(A) from the unmodified PHB because of their similar thermal histories. Nonetheless, the mild mechanical grinding
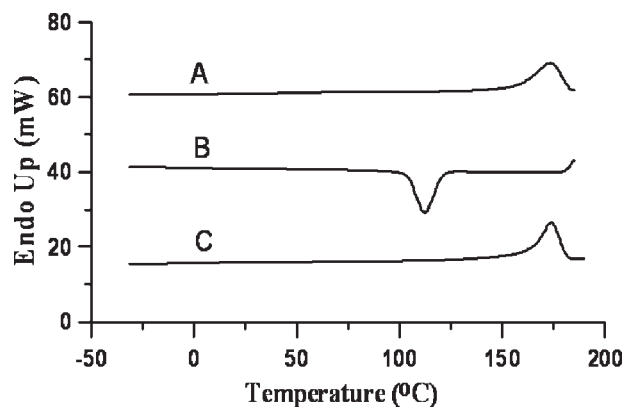
Figure 5 Representative DSC thermograms obtained from the mechanically grafted PHB by the (A) first heating scan, (B) cooling scan, and (C) second heating scan.

conditions used still generate some heat and shear force, and this anneals and stretches the molecules and then results in a small increase in T_m and ΔH_m in comparison to those shown in Figure 1(A) (see Table I). The mild heat and shear also result in a small reduction of M_w from 605,000 to 458,000 g/mol with a PDI of approximately 2.01 after the grafting reaction (Table II).

Similar to the other grafted PHBs, the mechanically treated PHB also has a faster crystallization rate and higher crystallinity than the unmodified PHB. This is shown in Figure 5(B): an exothermic peak near 112.1°C and an enthalpy of approximately 83.0 J/g were obtained during cooling. As expected, M_w of this mechanically grafted PHB also drastically drops to 13,890 g/mol (PDI = 1.89) after the first heating scan but is still significantly higher than that of the unmodified PHB (Table II).

The crystallization behaviors of the grafted PHBs are affected by various factors. It is clear that the crystallization rates and crystallinities obtained from the cooling scans of the three grafted specimens follow the order of mechanical grafting > melt grafting > solvent grafting. Yet the molecular weights (and PDI) obtained after the first heating scan (i.e., at the start of the cooling scan) follow the reverse order of solvent grafting ≫ melt grafting > mechanical grafting, although the MA grafting ratios are in the order of melt grafting (1.54%) > mechanical grafting (0.12%) > solvent grafting (0.07%) and have a different trend than that mentioned previously (see Table III). The results imply that regardless of the complicated interaction effect involved, MA-modified PHB with a smaller molecular weight and a narrower PDI would have a faster crystallization rate and greater crystallinity. This is consistent with what has been mentioned previously.

MA is grafted to the polyester primarily through the individually attached succinic anhydride rings in the presence of abundant tertiary hydrogens.[35,36] In

a study of grafting MA to PHB in the solution phase, Chen et al.[15] showed that the formation of single succinic anhydride rings can be found as MA reacts with a tertiary radical site on the PHB backbone. In this study, a similar NMR result has been obtained from three different MA-grafted PHBs. This can be confirmed from the representative ^{13}C-NMR spectrum obtained from the melt-grafted PHB and shown in Figure 6, in which small peaks near δ = 43.5 ppm and δ = 30.5 ppm, characteristic of methine and methylene in the attached anhydride ring, respectively, are present. Many other NMR signals are also similar to those obtained in Chen et al.'s study.
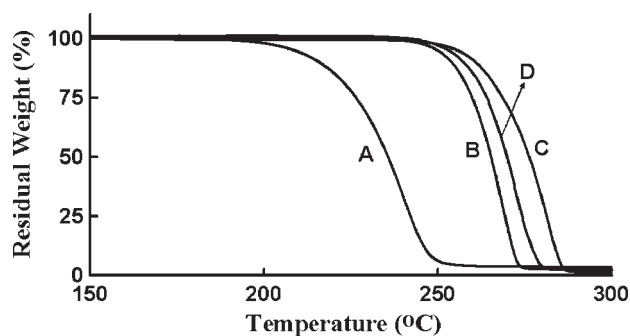
It can be concluded that PHB grafted with MA has better thermal stability and consequently a higher crystallization rate and crystallinity than ungrafted PHB, and the modified PHB with the fastest crystallization rate and greatest crystallinity will also have the highest value of T_m. This is confirmed in Figure 5(C): a T_m value near 173.9°C and an enthalpy of approximately 95.9 J/g have been obtained from the second heating scan of the mechanically grafted specimen (Table I). These values are the highest among the three grafted PHBs. In addition, T_m is almost the same as that from the first heating scan (173.8°C). The results indicate that the crystallization of the mechanically grafted PHB is least affected during the high-temperature period and repeated heating procedures used in the DSC experiment. This can be attributed to the least amount of degradation occurring during the mechanical-grafting reaction and the best MA/M_w interaction effect on the crystallization.

TGA

The enhancement of the thermal stability by grafted MA can be confirmed by TGA. It is shown in Figure 7 and Table IV that all three grafted PHBs have a
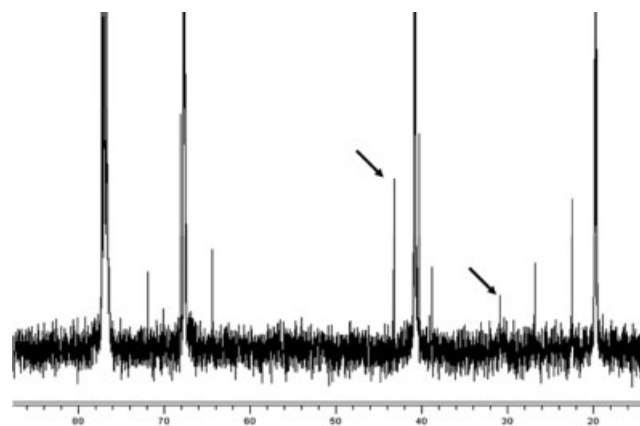
Figure 6 Representative ^{13}C-NMR spectrum obtained the melt-grafted PHB.

Figure 7 Representative TGA thermograms obtained from the (A) as-received, (B) melt-grafted, (C) solution-grafted, and (D) mechanically grafted PHBs.

degradation temperature much higher than that of the as-received PHB. The onset temperatures (Ti) of weight loss from the as-received, melt-grafted, solution-grafted, and mechanically grafted PHB begin at 189.8, 236.4, 237.7, and 243.4°C, respectively, and follow the order of as-received $\ll$ melt-grafted $\sim$ solution-grafted $<$ mechanically grafted (see Table IV). A significant delay of the onset temperature ($>50°C$) has been obtained from the grafted PHBs.

The weight losses from the as-received, melt-grafted, solution-grafted, and mechanically grafted specimens before 150°C, shown in Figure 7, are 0.15, 0.24, 1.38, and 0.11%, respectively. The small losses from the absorbed water (mainly in the as-received, melt-grafted, and mechanically grafted specimens) and residual solvent (in the solution-grafted specimen) are finished before 100°C. These small losses would not affect the major degradation reaction and characteristics obtained from different specimens.

It is also shown in Figure 8 that the peak temperatures of weight loss (T_p's; i.e., the temperatures at the maximal rate of weight loss) from the four specimens are in the order of as-received (239.7°C) $\ll$ melt-grafted (267.9°C) $<$ mechanically grafted (273.0°C) $<$ solution-grafted (280.5°C) (Table IV). The differences in T_p and T_i also confirm the significant effects of the grafted MA (or the grafting method) on changing the degradation kinetics and increasing the stability of PHB. The changes in the degradation kinetics of various grafted PHBs have also been confirmed in the study with a TGA

TABLE IV
Degradation Temperatures Obtained from the TGA Thermograms of the PHBs

	PHB specimen			
	As-received	Melt-grafted	Solution-grafted	Mechanically grafted
T_i (°C)	189.8	236.4	237.7	243.4
T_p (°C)	239.7	267.9	280.5	273.0

The standard deviation was smaller than 2°C.
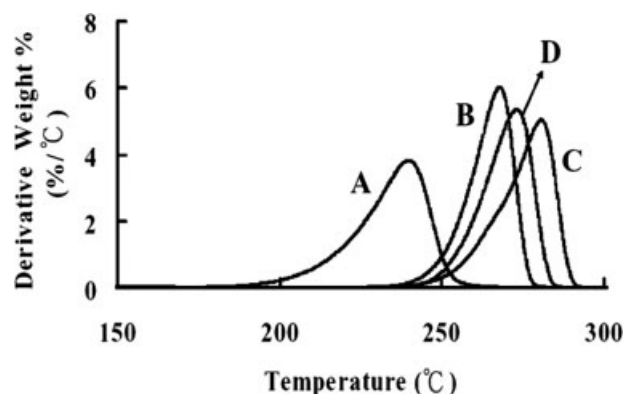
Figure 8 Representative TGA derivative thermograms obtained from the (A) as-received, (B) melt-grafted, (C) solution-grafted, and (D) mechanically grafted PHBs.

dynamic scanning method, with which changes in degradation speeds and kinetic parameters have been obtained.[17]

Additionally, the temperature ranges of degradation, as shown in Figure 8, are in the order of as-received $>$ solution-grafted $>$ mechanically grafted $>$ melt-grafted. The rates of weight loss at T_p follow the reverse order because of similar total weight loss percentages of the four specimens. This trend is expected because the molecular weight of PHB should decrease to a certain low value before volatile degraded products are lost. The large molecules require more time to downsize to evaporate. As a result, the as-received PHB, which had the largest M_w at the beginning of the TGA experiment, was found to have the broadest temperature range, whereas the melt-grafted and mechanically grafted PHBs, which had smaller M_w values after the grafting reaction, were found to have a narrower temperature range of degradation.

There are several factors that could have affected the thermal stability of the studied PHBs: the catalytic impurities, grafted MA, and thermal degradation during the grafting reaction. These factors could also have resulted in the different TGA (and DSC) characteristics obtained. For example, the melt-grafted PHB degrades seriously during the high shear melt processing, but it has the largest amount of grafted MA because of the efficient melt-grafting process; henceforth, although it starts with the smallest M_w, it still has promising thermal stability in dynamic TGA (see Tables II and III). As described previously, MA grafted onto PHB molecules retards the formation of six-member cyclic rings by contributing steric hindrance through the bulky MA molecules; consequently, all MA-grafted PHBs have much better thermal stability than the as-received PHB.[16,37] It is reasonable that the as-received PHB has the worst thermal stability because of the

presence of catalytic impurities and absence of grafted MA.

The effect of a possible reaction of MA with impurities containing Ca and Mg elements on degradation has also been tested. The values of T_p (238.4°C) and T_i (188.6°C) obtained from the purified PHB with the addition of MA-reacted impurities (with similar mechanical and solution-grafting procedures) are similar to those from the as-received PHB. This indicates that the improvement of the thermal stability of the MA-grafted PHB is not due to the reaction of MA with impurities. In addition, the concentrations of Ca and Mg impurities in the mechanically grafted and melt-grafted PHB specimens were almost unchanged after the rinsing step, and this implies that these impurities could not be removed by acetone. Consequently, the observed enhancement of the thermal stability of MA-grafted PHBs is not from the reaction of MA with impurities or the loss of Ca and Mg impurities.

CONCLUSIONS

The crystallization and thermal degradation properties of PHB grafted with MA by different techniques have been obtained. It has been shown that the crystallization rate, crystallinity, and thermal stability of grafted PHB are significantly affected by the grafting method because of the different reductions of the molecular weight of PHB and different amounts of MA attached during the grafting reaction. All three grafting methods improve the thermal stability and increase the crystallization rate and T_m of PHB. A small amount of grafted MA could significantly improve the thermal stability and crystallization of PHB.

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