Synthesis and Characterization of Maleated Poly(3-hydroxybutyrate)

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ABSTRACT: Graft copolymerization of maleic anhydride (MA) onto poly(3-hydroxybutyrate) (PHB) was carried out by use of benzoyl peroxide as initiator. The effects of various polymerization conditions on graft degree were investigated, including solvents, monomer and initiator concentrations, reaction temperature, and time. The monomer and initiator concentrations played an important role in graft copolymerization, and graft degree could be controlled in the range from 0.2 to 0.85% by changing the reaction conditions. The crystallization behavior and the thermal stability of PHB and maleated PHB were studied by DSC, WAXD, optical microscopy, and TGA. The results showed that, after grafting MA, the crystallization behavior of PHB was obviously changed. The cold crystallization temperature from the glass state increased, the crystallization temperature from the melted state decreased, and the growth rate of spherulite decreased. With the increase in graft degree, the banding texture of spherulites became more distinct and orderly. Moreover, the thermal stability of maleated PHB was obviously improved, compared with that of pure PHB. Its thermal decomposition temperature was enhanced by about 20°C. In addition, the introduction of the MA group promoted the biodegradability of PHB. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 659–668, 2003

Key words: poly(3-hydroxybutyrate); maleic anhydride; graft copolymers; biodegradable; crystallization

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a biodegradable and biocompatible thermoplastic polyester, and can be produced by many strains of bacteria as a storage medium. Its mechanical properties are similar to those of isotactic polypropylene. Consequently, PHB has attracted much attention as an environmentally degradable resin, which is useful for a wide range of agricultural, marine, and medical applications.[1–4] However, its main drawbacks are its brittleness and thermal instability. It is known that microbial PHB is a highly crystalline polymer, and the growth of cracks within the large spherulites of PHB is the origin of its brittleness. Moreover, PHB is thermally degraded easily during processing, which is of great disadvantage to its widespread commercial use.

To overcome the shortcomings of PHB, two methods have been extensively used to improve its physical properties and processibility. One method is to biosynthesize the copolyesters containing hydroxyalkanoate units other than 3-hydroxybutyrate (3HB) units. For example, 3HB copolyesters containing 3-hydroxyvalerate,[5,6] 4-hydroxyvalerate,[7] hydroxypropionate,[8] and hydroxyhexanoate[9] units can be produced by different microorganisms. The composition of monomer units in these copolyesters can be controlled by use of a mixture of different carbon sources in the culture medium. Depending on the chemical structure and the content of compositions, the properties of these copolyesters vary widely. The second method is to prepare the blends consisting of PHB and other polymers. The polymers that are miscible with PHB include poly(ethyleneoxide),[10,11] poly(vinyl acetate),[12] and poly(epichlorohydrin).[13] Poly(methyl methacrylate) (PMMA) is known to be incompatible with PHB at room temperature,[14] and compatible in the melted state.[15] Our work about those aspects has also been reported[16–18] previously. Although both methods can reduce the crystallinity and the melting point of PHB, and improve its mechanical properties, its thermal stability and the narrow processing window have not yet been solved.

Graft polymerization is a well-known method to modify the chemical and physical properties of polymers for specific applications. The typical method of graft polymerization is a radical reaction of various monomers initiated by chemical initiators,[19,20] plasma,[21] and electromagnetic and gamma radiation.[22]

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Out of these methods, chemical initiators have been extensively used for graft polymerization. Many polymers, including polyethylene,[23] polypropylene,[24] and poly(ethylene terephthalate),[25] have been used as a substrate for graft polymerization, and their properties, such as strength, color absorption, adhesion, hydrophilicity, and antistatic properties, have been improved. So far very little has been published on graft copolymerization of PHB. Yoshii et al.[26–30] reported the radiation graft behavior of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), and styrene (St) onto PHB and its copolymer, and found that the thermal stability or the biodegradability was obviously promoted; Lee et al.[31] studied graft copolymerization of acrylamide onto poly(hydroxybutyrate-*co*-hydroxyvalerate) film to test the application of grafted film on permselectivity. However, all work mentioned above is about the surface graft copolymerization of PHB, which means that grafting monomers chiefly modify its surface properties. On the other hand, all grafting monomers might produce long graft side chains by homopolymerization, so that these homopolymers might be left in the environment after PHB absolutely degrades, and cause new environmental problems.

To avoid those weaknesses, in this work, maleic anhydride (MA) was selected as the grafting monomer to be grafted onto the PHB chains because of its good reactivity and controllability in free-radical polymerization. On the basis of general graft copolymerization involving MA, it could be supposed that introducing a certain monomer onto PHB chains, such as MA, could disturb the regularity of PHB chains, then control the morphological structures and improve its properties. Furthermore, the introduction of MA favored its further modification. This study describes graft copolymerization of MA onto PHB by a solution polymerization method by use of benzoyl peroxide as initiator, which can control the homopolymerization of MA monomer. The effects of various polymerization conditions on graft degree were also investigated. In addition, the properties of maleated PHB, such as crystallization behavior, thermal stability, and biodegradability, were also studied.

EXPERIMENTAL

Materials

Poly(3-hydroxybutyrate) (PHB) was provided by Beijing Institute of Biology. Maleic anhydride (MA) and benzoyl peroxide (BPO) were purified by the recrystallization method before use. The other reagents were used as received.

Polymerization procedures

PHB was placed in a 250-mL polymerization vessel containing the monomer. The vessel was placed in an oil bath adjusted to the polymerization temperature. A BPO solution in the desired concentration was added and the reaction was carried out under nitrogen atmosphere. The reaction products were precipitated in acetone after a certain reaction time, and then filtered off. Finally, these products were Soxhlet extracted with acetone for at least 24 h, and the process entirely removed the unreacted monomer and residual initiator. The reaction products were then dried in vacuum at 60°C for 24 h.

Characterization of maleated PHB

The graft degree of maleated PHB can be determined by titration using phenolphthalein as indictor. Because the condition of titration is nonaqueous, a back titration for the specimens is necessary. First, maleated PHB was accurately weighed and completely dissolved in chloroform solvent. Second, excess 0.02*N* KOH alcohol solution was added, which made MA thoroughly react. Then, 0.02*N* HCl alcohol solution was titrated against KOH. Finally, KOH alcohol solution was added again to the titration end point. The reacted specimens without MA in the same conditions were also titrated to obtain blank values. Graft degree (*G*%) was calculated from the consumed quantity of KOH, by the following equation:

$$G\% = (V_{\mathrm{KOH}}N_{\mathrm{KOH}} - V_{\mathrm{HCl}}N_{\mathrm{HCl}} - M_0) \times 98.06/2W \times 100\%$$

where V is the volume (L), N is the normality (mol/L), M_0 is the blank value, and W is the specimen weight (g).

Viscosity measurements were carried out in an internal dilution Ubbelhode viscometer at 30°C in chloroform. The weight-average molecular weight (M_w) was determined by using the relation $[\eta] = 1.18 \times 10^{-4} M_w^{0.78}$.[32]

The ^{13}C-NMR analysis of the specimens was carried out on a Bruker DRS500 spectrometer (Bruker Instruments, Billerica, MA) in the pulse Fourier transform mode. The 125-MHz ^{13}C-NMR spectra were recorded at 27°C on a $CDCl_3$ solution of the specimens with 5.0-s pulse repetition.

Specimen preparation

The specimens for wide-angle X-ray diffraction (WAXD) measurement were molded and isothermally crystallized at 100°C for 24 h. Hot-pressed films for the biodegradation test were preheated at 180°C for 3 min and pressed at the same temperature for 1.5 min. Finally, the films were immediately cooled for 5 min by using a cold press.

Measurements

A Perkin–Elmer DSC-7 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) was used to study the glass-transition temperature (T_g) and melting and crystallization behavior of both pure PHB and maleated PHB. The specimens were heated from −50 to 190°C (first run) with a heating rate of 10°C/min and then maintained at 190°C for 2 min before rapid quenching to −70°C. The specimens were reheated to 190°C at a heating rate of 10°C/min (second run). The value of the midpoint of the transition was taken as the T_g. The specimens were cooled to −70°C at a rate of 10°C/min (third run) and finally reheated to 190°C at a heating rate of 10°C/min again (fourth run), which expressed the nonisothermal crystallization and the melting behavior. Melting temperature (T_m), crystallization temperature (T_c), and cold crystallization temperature (T_{cc}) were taken as the peak values of the respective endothermal and exothermal processes in DSC curves.

WAXD meaurements were performed with a Philips PW 1700 X-ray diffractometer (The Netherlands) using Cu–K_α X-ray at a voltage of 30 kV and a current of 20 mA.

The radial growth rate of PHB spherulites at 100°C was obtained by photographing from time to time during the isothermal crystallization process under an optical microscope. The radius growth rate ($R = dr/dt$) was calculated from the slope of the lines connecting the radius r and its time on an r versus t plot. The specimens on the hot stage were kept at 190°C for 2 min and then transferred as quickly as possible onto another hot stage at a prefixed 100°C.

The thermal decomposition of PHB and maleated PHB was investigated in the temperature range from 25 to 600°C using the Perkin–Elmer TGA 7 apparatus in air and nitrogen atmospheres. The experiments were carried out at a heating rate of 20°C/min using 10-mg specimens.

The biodegradation test[33] using *Penicillin* sp. was carried out at 28°C in phosphate buffer. The hot-pressed films (initial dimensions, 15 × 10 mm and ~ 0.1 mm thickness) were used. The biodegradation test was started by adding an aqueous solution including *Penicillin* sp., which was incubated at 28°C with shaking. After incubation time, the specimens were removed, washed with distilled water and methanol, and dried to constant weight *in vacuo* at 50°C. The weight loss of the films was calculated as the percentage decrease of the original film weight.

RESULTS AND DISCUSSION

Characterization and analysis of maleated PHB

From the polymerization procedure, it was known that the unreacted MA had been entirely removed. Hence, the amount of alkali consumed in the titration must be to react with MA grafted onto PHB chains. The fact can be used for the confirmation of graft copolymerization, and also for quantitative analysis of graft degree mentioned above.

The ^{13}C-NMR spectra for PHB and maleated PHB (PHB-*g*-MA) are shown in Figure 1. Through comparison of the spectrum of pure PHB with that of PHB-*g*-MA, the most striking characteristic in the spectrum of maleated PHB is that a small peak assigned to carboxylic carbon of MA is shown at about 166.5 ppm. Moreover, it contains the signals at δ = 43.7 ppm and δ = 29.8 ppm, which matches that of methine (δ = 43.2 ppm) and methylene (δ = 29.7 ppm) in the anhydride ring of the model compound hept-4′-yl succinic anhydride.[34] These are likely from single succinic anhydride rings that are formed when MA reacts with a tertiary radical site on the PHB backbone. The results demonstrate that graft copolymerization of MA onto PHB was successively achieved. In addition, there was an uncertain carbon signal (δ = 133.5 ppm) in the spectrum, attributed to the complexity of graft reaction. It is not the signal of MA monomer as a remnant compared with that of pure MA (its chemical shifts are δ = 164.8 ppm and δ = 137.0 ppm), and should be assigned to a different olefinic carbon. Unfortunately, there is no direct evidence to confirm it.

The relation between molecular weight and graft degree was investigated (shown in Fig. 2). Molecular weight decreases with the increase in graft degree and gradually levels off. The increase in graft degree is not correlated to the change of molecular weight, indicating that grafting sites are not the ends of molecular chains. Heinen et al.[34] used [2,3-$^{13}C_2$]MA to investigate the molecular structure of MA-grafted HDPE, *alt*-EPM, and iPP, and found that MA grafted onto the polymer backbone, chiefly in the form of single succinic anhydride rings. Therefore, the increase in graft degree should be attributable to the increase in grafting sites. It is speculated that the grafting site may be the methine carbon of PHB, given that the methine protons on the PHB chains are the most active acidic protons. They are easily abstracted from the backbones to generate the radicals initiating the graft polymerization. A tentative scheme for the graft polymerization, proposed on the basis of a speculative mechanism, is shown in Scheme 1. To explain deeply the mechanism of graft reaction, more explicit experimental evidences are needed to prove it.

Effects of polymerization conditions

The sorts of graft polymerization media play an important role in the graft reaction. For investigating the effect of different solvents, two solvents, chloroform and chlorobenzene, were used in the polymerization.

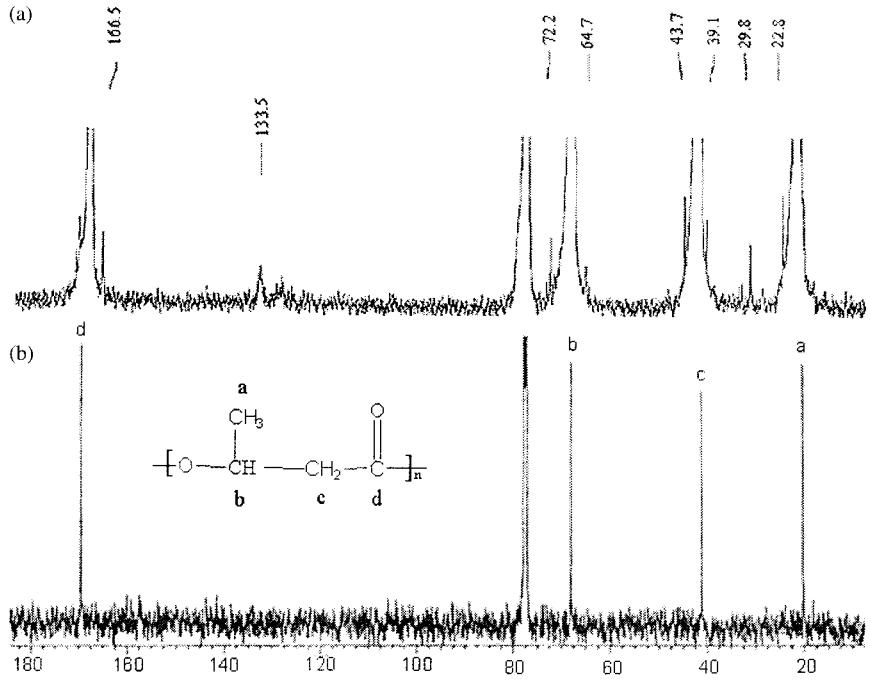


Figure 1 ^{13}C-NMR spectra of PHB (a) and maleated PHB (b).

When the medium was the chloroform solvent, the reaction temperature was very low, only about 70°C, which was not the most effective temperature for graft copolymerization. Hence, graft degree in chloroform is very low. Chlorobenzene was inert for the graft reaction and could also drive the reaction carried out in higher temperature; thus, graft degree in the chlorobenzene was better. In the rest of the study, chlorobenzene was used as the solvent in the polymerization.

The effect of monomer concentration on graft degree was investigated by the experiments carried out at different MA concentrations. The data are shown in Figure 3. Graft degree gradually increases with the increase in MA concentration. When the monomer concentration is less than 2%, the graft degree is small, within 0.4%. However, it reaches the highest value, 0.85%, when the MA concentration is increased to 3%. Above 3%, the graft degree declines and gradually levels off. Under this reaction condition, it is not easy for the homopolymerization of MA to take place for its special molecular structure.[34] Therefore, MA may attach to the PHB backbone in the form of single succinic anhydride rings, and graft degree is mainly decided by the number of macroradicals initiated by BPO. By increasing the MA concentration, the chances of PHB macroradicals reacting with MA are enhanced, and consequently graft degree increases. When MA is excessive, undesired reactions (e.g., the cage effect) would easily take place, resulting in the decline in graft degree.

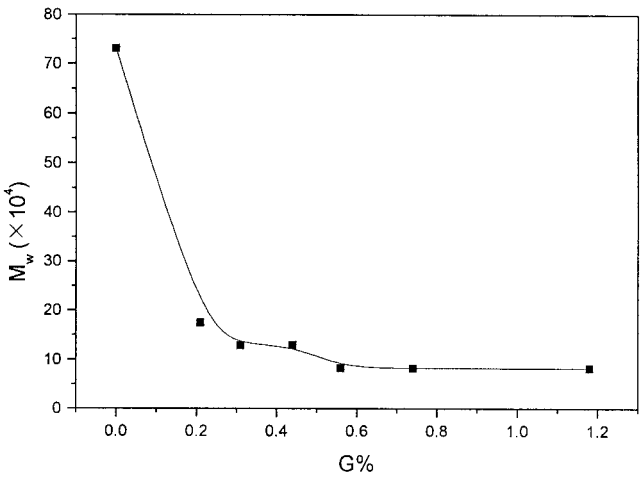
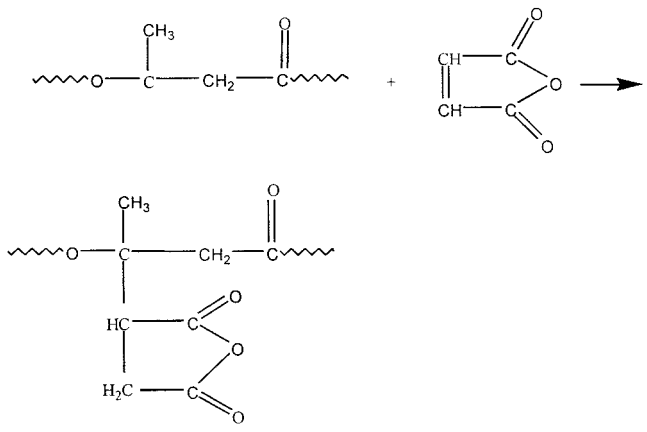


Figure 2 Weight-average molecular weight (M_w) of PHB as a function of graft degree.



Scheme 1

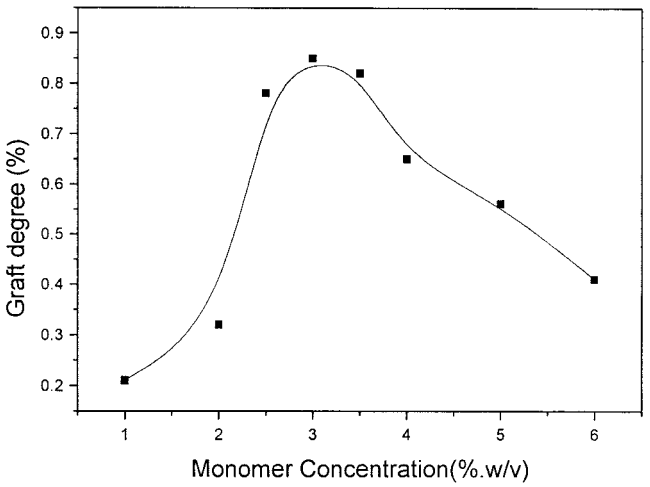


Figure 3 Graft degree as a function of monomer concentration. Reaction conditions: PHB = 5 g; BPO = 0.2% (w/v); chlorobenzene = 100 mL; time = 4 h; temperature = 130°C.

Figure 4 shows the effect of initiator concentration on graft degree. As seen in the figure, graft reaction is very sensitive to initiator. When the initiator concentration increases from 0.1 to 0.2%, graft degree rapidly increases up to the highest value, 0.85%. The increase in BPO concentration can enhance the chance of hydrogen abstraction from the PHB backbone. More free radicals from the dissociation of BPO could produce more active sites on the PHB backbones, thus facilitating graft reaction. However, when the initiator concentration continuously increases, graft degree rapidly decreases to 0.5%. Excess initiator can cause the free-radical species to give a termination reaction with PHB macroradicals, or combination reaction between them, resulting in the decrease in graft degree. On the other hand, excess initiator can cause PHB to depolymerize, and further cause molecular weight acute reduction. Therefore, BPO concentration is taken about 0.2% from those results.

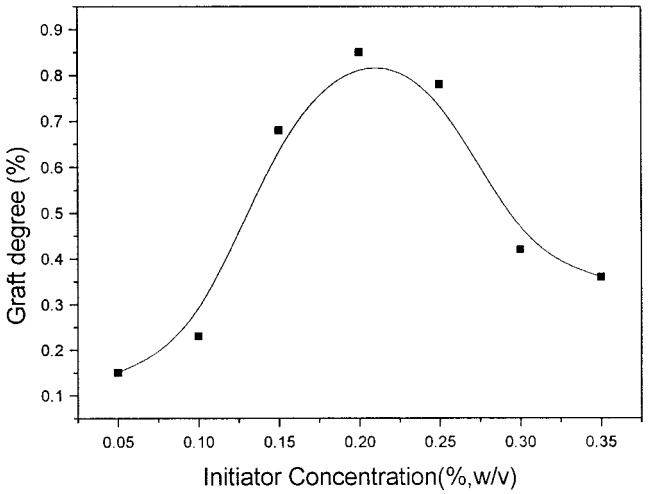


Figure 4 Graft degree as a function of initiator concentration. Reaction conditions: PHB = 5 g; MA = 3% (w/v); chlorobenzene = 100 mL; time = 4 h; temperature = 130°C.

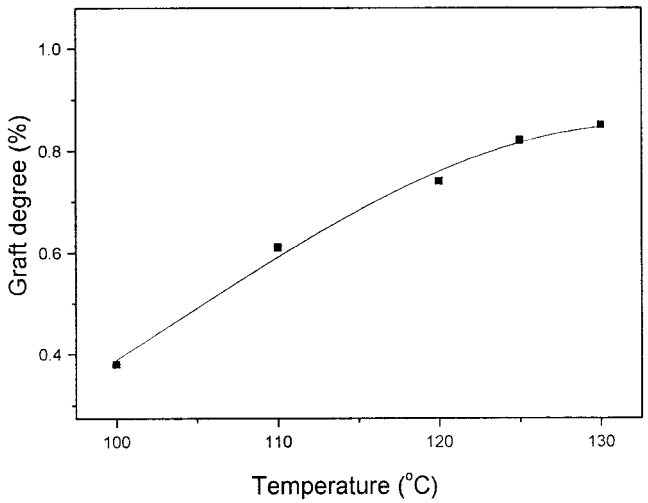


Figure 5 Graft degree as a function of reaction temperature. Reaction conditions: PHB = 5 g; MA = 3% (w/v); BPO = 0.2% (w/v); chlorobenzene = 100 mL; time = 4 h.

Graft copolymerization of MA onto PHB was studied over various temperatures, ranging from 100 to 130°C (shown in Fig. 5). Graft degree continuously increases as the temperature heightens, which indicates that a higher temperature is advantageous to graft copolymerization. However, above 120°C, the tendency slows down. The maximum graft degree is obtained at 130°C. Under higher temperature conditions, the activity of the macroradicals, together with the dissociation of BPO and the production of free radicals, is greatly improved. Moreover, MA may transfer to the active state of $MA^{+}\cdots{}^{-}MA$ under the influence of BPO,[35] and tend more easily to drive a free-radical reaction.

Reaction time is of great importance to graft copolymerization. The polymerization cannot be finished in a shorter period because the dissociation of BPO and the production of macroradicals must consume time, whereas the radicals would have lost their activity when the reaction time is too long. The effect of reaction time on graft degree is presented in Figure 6. Graft degree gradually increases with reaction time, and slows down about 4 h, implying that graft copolymerization is almost finished.

Crystallization behavior and morphology of PHB and maleated PHB

DSC data of PHB and maleated PHB with various graft degrees in the second and third heating runs are listed in Table I. It was found that T_{cc} values of maleated PHB from the glass state are enhanced by about 10°C, whereas their T_c values from the melted state decrease by about 15°C. The results indicate that the

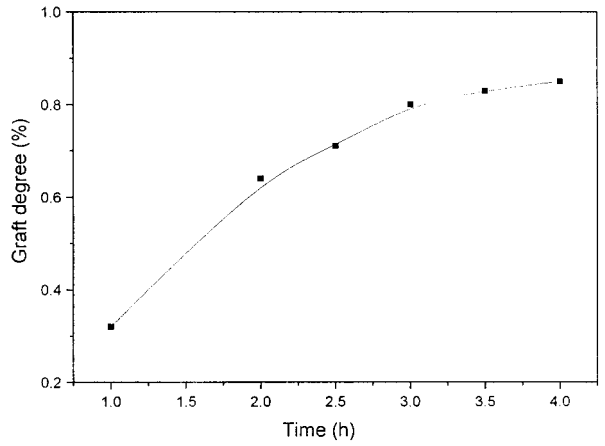


Figure 6 Graft degree as a function of reaction time. Reaction conditions: PHB = 5 g; MA = 3% (w/v); BPO = 0.2% (w/v); chlorobenzene = 100 mL; temperature = 130°C.

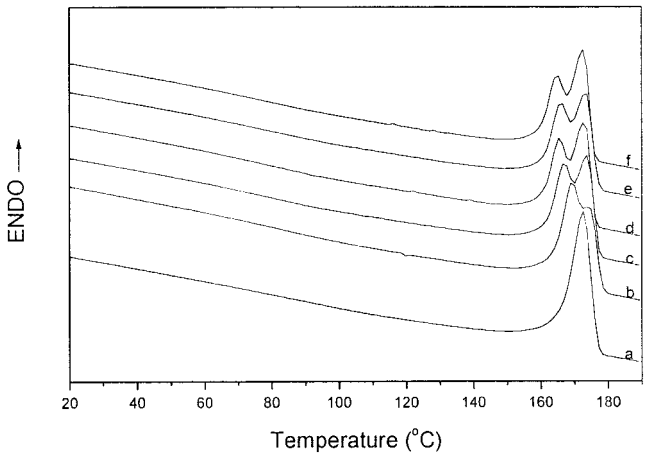


Figure 7 DSC curves recorded during the fourth heating run of PHB and different PHB-*g*-MAs. (a) PHB; (b) PHB-*g*-MA21; (c) PHB-*g*-MA44; (d) PHB-*g*-MA56; (e) PHB-*g*-MA73; (f) PHB-*g*-MA118.

introduction of MA can hinder the crystallization of PHB because the regularity of PHB chains is, to a certain degree, disturbed after grafting MA; moreover, the MA group intensifies the interaction among PHB chains. However, the T_g values of maleated PHB are not affected by the MA group: they remain at about 1°C, almost the same value as that of pure PHB. The result may be attributed to the effect of two reverse factors. On the one hand, the molecular weight of maleated PHB remarkably decreases, and the segmental mobility is improved, resulting in the decline in T_g values. On the other hand, the intensified interaction among the chains can result in an increase in T_g values. Consequently, there is little movement in T_g under the influence of both factors. From the data in Table I, it is found that T_m values of all samples in the second run are scarcely changed, although the crystallization enthalpy (ΔH_c) in the third run slightly decreased with the increase in graft degree, which implies that after grafting MA, the crystallinity of PHB declines.

DSC melting curves of maleated PHB with various graft degrees in the fourth run show multiple melting peaks, whereas the DSC melting curve of pure PHB shows only a simple peak (shown in Fig. 7). Moreover, it can be seen that the relative areas of two melting peaks vary with graft degree, that is, the larger the graft degree, the stronger the higher temperature peak; thus, the double melting peaks of maleated PHB should be attributed to the lower temperature peak in the melting of crystals formed during the cooling process, whereas the higher temperature peak is attributed to crystals recrystallized during the DSC heating process. As known, PHB can crystallize completely at a lower cooling rate; thus, a simple peak during the reheating process is a normal phenomenon for pure PHB. The crystallization ability of maleated PHB becomes weak because the introduction of MA can hinder the crystallization of PHB. Consequently, maleated PHB may obtain different imperfect crystals during the cooling process, and the amount of imperfect crystals increases with the increase in graft degree. When reheated, the imperfect crystals may melt at a lower temperature, with the result that the melting peak of the existing crystals for maleated PHB transfers to a lower temperature. Meanwhile, the amount of recrystallization will increase with the increase in graft degree because there are more chances for the melting of imperfect crystals and recrystallization, resulting in the change of the areas of melting peaks.

TABLE I
Graft Degree and DSC Results of PHB and Different PHB-*g*-MAs

Specimen	Graft degree (%)	M_w ($\times 10^4$)	T_g (°C)	T_{cc} (°C)	T_m (°C)	T_c (°C)	ΔH_c (J/g)
PHB	0	73.1	1.0	37.4	173.2	100.1	73.7
PHB-*g*-MA21[a]	0.21	17.4	2.0	46.8	174.1	89.6	71.5
PHB-*g*-MA44	0.44	12.8	1.9	46.4	173.9	86.5	69.9
PHB-*g*-MA56	0.56	12.9	2.4	47.2	173.9	85.3	68.4
PHB-*g*-MA73	0.73	8.19	1.6	45.7	172.9	85.8	69.1
PHB-*g*-MA118	1.18	8.16	1.7	45.2	172.3	85.2	68.2

[a] PHB-*g*-MA21, maleated PHB whose graft degree is 0.21%.

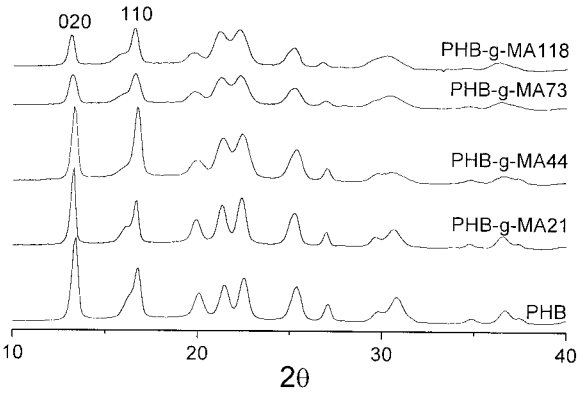


Figure 8 WAXD profiles of PHB and different PHB-*g*-MAs isothermally crystallized at 100°C.

Studies on the structure of the crystallized PHB and maleated PHB were also carried out with WAXD. The X-ray diffraction results are shown in Figure 8. A comparison of the spectrum of pure PHB with that of maleated PHB shows that the *d*-spacing values are constant for all crystallographic planes, which indicates that the PHB unit cell is not changed after grafting MA. Hence, it can be concluded that the MA group is not introduced to the crystalline regions of PHB. However, with the increase in graft degree, the intensities of the crystalline peaks of maleated PHB obviously decrease and their widths clearly increase. These results confirm that the crystalline integrity of maleated PHB declines with the amount of MA, which is in agreement with the DSC data. It needs to be pointed out that crystallite growth of PHB varies in different directions. The ratio values of I_{110}/I_{020} for PHB and maleated PHB are shown in Figure 9. When the graft degree is 0.21%, the I_{110}/I_{020} ratio value is almost the same as that of pure PHB, although the I_{110}/I_{020} ratio value gradually increases as graft degree exceeds 0.44%. Research on the crystalline structure of

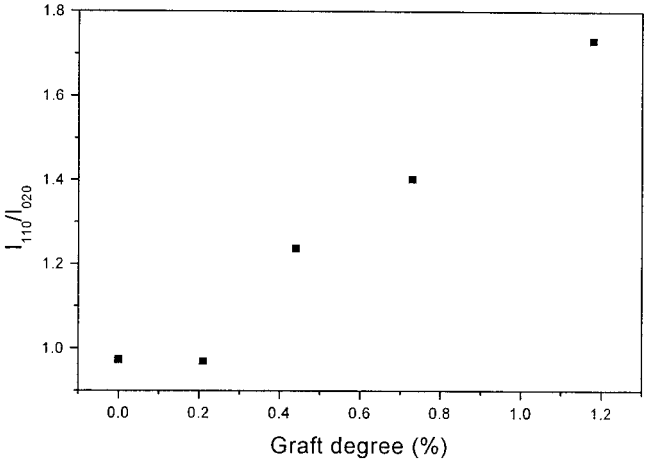


Figure 9 The ratio of I_{110} to I_{020} for PHB and different PHB-*g*-MAs.

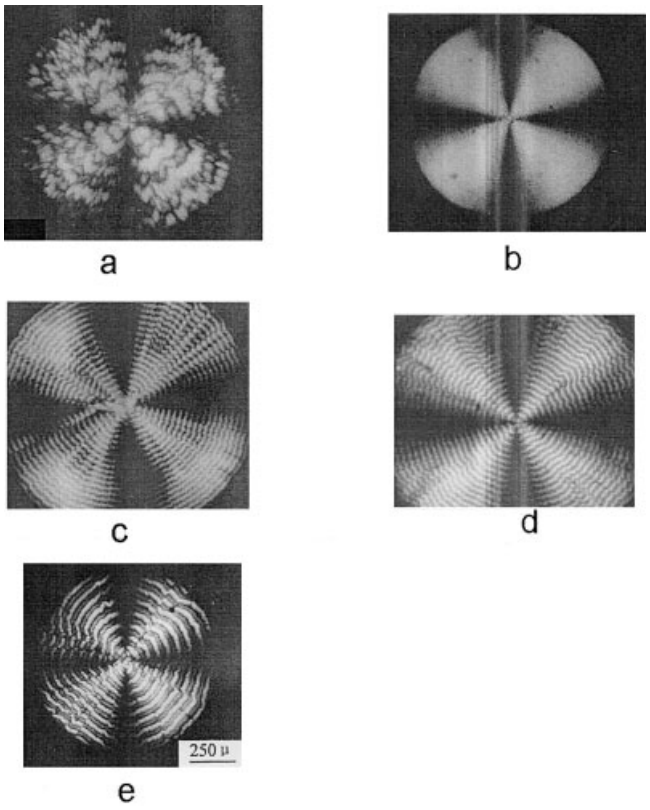


Figure 10 Photographs of PHB and different PHB-*g*-MA spherulites isothermally crystallized at 100°C. (a) PHB; (b) PHB-*g*-MA21; (c) PHB-*g*-MA44; (d) PHB-*g*-MA73; (e) PHB-*g*-MA118.

PHB[36,37] confirmed that parameter *a* of the unit cell might be easily changed if the crystallization conditions were different, which indicated that the crystallite growth of PHB along the direction of the *a* axis was more sensitive than that along other directions. Consequently, the difference in I_{110}/I_{020} ratio values could be explained by more restriction in the movement of the segment for (020) after grafting MA, leading to limited growth of crystallites in the (020) direction.

Figure 10 shows the photographs of PHB and maleated PHB spherulites isothermally crystallized at 100°C. The spherulites exhibit the familiar Maltese cross–birefringent pattern and concentric extinction bands. After grafting MA, the banding texture of PHB becomes more distinct and orderly. At a constant crystallization temperature, the band spacing of PHB-*g*-MA21 is so minuscule that it cannot be clearly distinguished. However, the band spacing for other maleated PHBs gradually increases with the increase in graft degree, the maximum value of which is 25 μm.

The radial growth rates of spherulites (R) for pure PHB and maleated PHB were determined by observation with a polarizing optical microscope when the specimens were isothermally crystallized at 100°C. It was observed that the spherulite radius r linearly increased in time up to the point of impingement, indi-

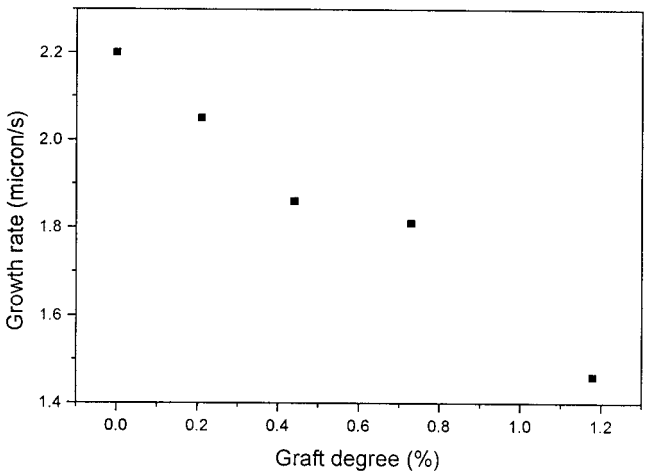


Figure 11 Spherulitic growth rate as a function of graft degree for PHB and different PHB-*g*-MAs isothermally crystallized at 100°C.

cating a constant growth rate throughout the crystallization process. The relation between R and graft degree is shown in Figure 11. As seen, the radial growth rate of spherulites linearly decreases with the increase in graft degree. During crystallization, the MA group is excluded from the crystal lattice by the WAXD results so that the crystallization of maleated PHB must take more time than that of pure PHB. Moreover, with the increase in graft degree, R becomes slower.

Thermal stability of PHB and maleated PHB

PHB is easily degraded, if it is kept for a relatively long time at a temperature slightly close to its melting temperature. Hence, it can be molded and extruded satisfactorily only within a narrow processing range and in a short time. Thermal stability of PHB is of great importance to its commercial application.

Table II shows the TGA data of pure PHB and maleated PHB decomposed in air and nitrogen atmospheres. It can be seen that the temperature of decomposition (T_d) of PHB is obviously enhanced after grafting MA. For example, it was found that $T_{5\%}$ was enhanced by about 20°C, although the graft degree was lower (0.21%). When graft degree exceeded 0.44%, $T_{5\%}$ was enhanced about 30°C, which means that grafting MA can greatly widen its processing range. For pure PHB, its thermal stability in nitrogen is much better than that in air, whereas there is little difference for maleated PHB in two atmospheres. The results imply that PHB has greater reactivity in air, and the presence of MA can, to a certain extent, depress the decomposition of PHB resulting from the oxygen. Many studies in the literature[38–41] about the mechanism of thermal decomposition of PHB have been published. It is now widely accepted that the degradation occurs almost exclusively by way of a random chain-scission mechanism involving a six-member ring transition, as shown in Scheme 2. Consequently, the improvement in thermal stability of maleated PHB may be attributed to two factors: (1) The labile hydrogen abstracted from the tertiary carbon atom is replaced by MA at the generated site. The introduction of MA increases the steric hindrance of PHB, inhibits the formation of a six-member ring on the chains, and thus enhances its thermal stability. (2) The stronger interaction among the chains of maleated PHB restricts the mobility of the segment so that the cyclization process involving the MA group becomes very difficult, thus reducing the probability of cyclization.

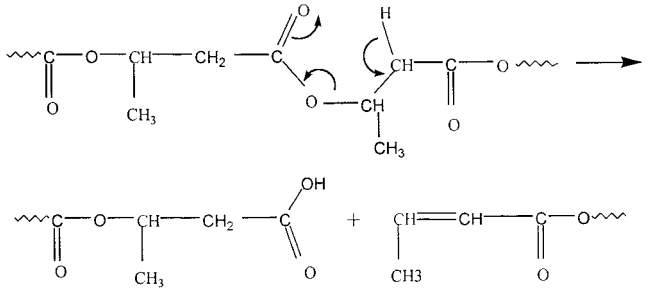
TABLE II
TGA Results of PHB and Different PHB-*g*-MAs

	T_d[a]		$T_{5\%}$[b]	
Specimen	Air	N_2	Air	N_2
PHB	246	252	228	239
PHB-*g*-MA21	260	268	252	259
PHB-*g*-MA44	273	281	268	272
PHB-*g*-MA56	274	287	270	276
PHB-*g*-MA73	276	281	267	272
PHB-*g*-MA118	274	286	265	276

[a] T_d, temperature of decomposition.
[b] $T_{5\%}$, temperature when the weight loss is 5%.

Biodegradability of PHB and maleated PHB

Biodegradation is an important characteristic of maleated PHB. If its biodegradability is destroyed after modification, the advantage of PHB as an environmentally degradable resin will be seriously weakened. Figure 12 shows the weight loss curves of pure PHB and maleated PHB with various graft degrees for the biodegradation test. The treatment time is fixed to 50 h. The weight loss value of pure PHB is about 8.5% after treatment, whereas the weight loss value for maleated PHB is much higher than that of pure PHB. With the increase in graft degree, the weight loss value gradually increases, indicating that the biodegradability of maleated PHB can be promoted by the amount



Scheme 2

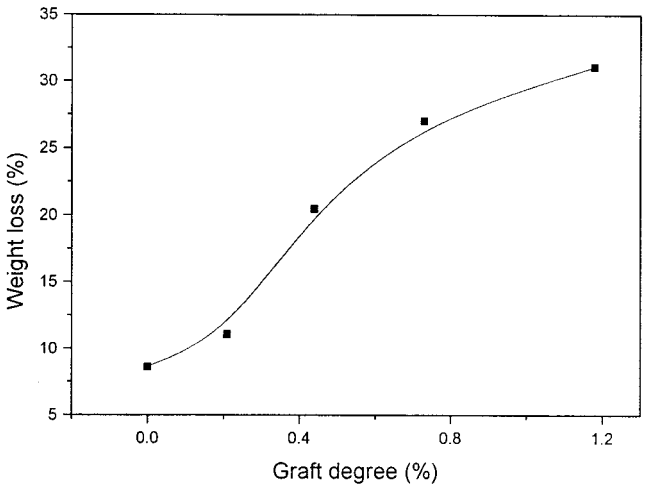


Figure 12 Weight loss as a function of graft degree for PHB and different PHB-*g*-MAs. Biodegradation conditions: fungi, *Penicillin* sp.; time, 50 h; temperature, 28°C.

of MA. An important reason is that PHB becomes more hydrophilic attributed to grafting MA. Therefore, wettability of films of maleated PHB with enzyme solution is clearly improved, resulting in the promotion of biodegradability.

CONCLUSIONS

Although PHB has the inactive chemical structure, maleic anhydride was successfully grafted onto PHB chains by free-radical graft copolymerization, which can be proved with chemical titration and ^{13}C-NMR. The effects of various polymerization conditions on graft degree, such as solvents, monomer concentration, initiator concentration, reaction temperature, and time, were also investigated. The results show that the monomer and initiator concentrations play an important role in graft copolymerization, and graft degree initially increases with the increase in monomer and initiator concentrations, and then plateaus above a certain level. By changing the reaction conditions, graft degree can be controlled in the range from 0.2 to 0.85%.

The crystallization behavior, the morphology, and the thermal stability of PHB and maleated PHB with various graft degrees were studied by DSC, WAXD, optical microscopy, and TGA. For maleated PHBs, T_{cc} values obviously increase and T_c values distinctly decrease. The results indicate that the introduction of MA disturbs the regularity of PHB chains, intensifies the interaction among the chains, and greatly hinders their crystallization. However, the apparent T_g values of maleated PHB are not affected by the MA group. During the DSC melting heating process, multiple melting peaks for maleated PHB are observed that are caused by the recrystallization process and are related to graft degree. Hence, the peak on the lower temperature side is the melting of the crystals formed during the cooling process of maleated PHB. Although grafted MA does not affect the crystalline structure of PHB, as shown by the WAXD results, the relative intensities of the I_{110}/I_{020} plane for maleated PHB are enhanced with the increase in graft degree because of more restriction in the movement of segments for the (020) direction. In addition, it was found that the morphology of maleated PHB isothermally crystallized at 100°C is strongly affected by graft degree. The banding textures of PHB become more clear and orderly after grafting MA. Moreover, the larger the graft degree, the slower the growth rate of spherulites. Thermal stabilities of PHB and maleated PHB were investigated in air and nitrogen atmospheres. PHB is more stable in nitrogen than in air, and a small amount of MA can greatly retard the thermal decomposition of PHB. The biodegradability of PHB is promoted after grafting MA because of the improvement in the wettability of PHB with the enzyme solution.

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References

1. Doi, Y. Microbial Polyester; VCH: New York, 1990.
2. Chiellini, E.; Solaro, R. Adv Mater 1996, 8, 4.
3. Zhang, L. L.; Deng, X. M. Polym Bull 1994, 1, 1.
4. Sharma, R.; Ray, A. R. J Macromol Sci Rev Macromol Chem Phys 1995, C35, 327.
5. Holmes, P. A.; Wright, L. F.; Collins, S. Eur. Pat. Appl. 0052459, 1981.
6. Doi, Y.; Kunnioka, M.; Nakamura, Y.; Soga, K. Macromolecules 1987, 20, 2988.
7. Doi, Y.; Segawa, M.; Kunika, M. Int J Biol Macromol 1990, 12, 106.
8. Nakamura, S.; Kunnioka, M.; Doi, Y. Macromol Rep 1991, A28, 15.
9. Shiotani, T.; Kobayashi, G. Jpn. Pat. JP 93,049, 1993.
10. Avella, M.; Greco, P.; Martuscelli, E. Polymer 1991, 32, 1647.
11. Avella, M.; Martuscelli, E.; Raimo, M. Polymer 1993, 34, 3234.
12. Greco, P.; Martuscelli, E. Polymer 1989, 30, 1475.
13. Sadocco, P.; Canetti, M.; Seves, A. Polymer 1993, 34, 3368.
14. Yoon, J. S.; Choi, C. S.; Maing, S. J. Eur Polym J 1993, 29, 1359.
15. Lotti, N.; Pizzoli, M.; Ceccorulli, G. Polymer 1993, 34, 4935.
16. Xing, P. X.; Dong, L. S. Macromolecules 1997, 30, 2726.
17. Xing, P. X.; Ai, X.; Dong, L. S. Macromolecules 1998, 31, 6898.
18. An, Y. X.; Li, L. X.; Dong, L. S. J Polym Sci Part B: Polym Phys 1999, 37, 443.
19. Sacak, M.; Pulat, E. J Appl Polym Sci 1989, 38, 539.
20. Sanli, O.; Pulat, E. J Appl Polym Sci 1993, 47, 1.
21. Heieh, Y.; Pugh, C. J Appl Polym Sci 1984, 29, 2547.
22. Memetea, T.; Stannett, V. Polymer 1979, 20, 465.
23. Wang, Y. L.; Ji, D. Q.; Yang, C. L. J Appl Polym Sci 1994, 52, 1411.
24. Severini, F.; Fanti, N. Polymer 1999, 40, 7059.
25. Sacak, M.; Sertkaya, F.; Taul, M. J Appl Polym Sci 1992, 44, 1737.
26. Mitomo, H.; Watanabe, Y.; Yoshii, F. Radiat Phys Chem 1995, 46, 233.

27. Bahari, K.; Mitomo, H.; Taro, E. Polym Degrad Stab 1998, 61, 245.
28. Bahari, K.; Mitomo, H.; Enjoji, T. Angew Makromol Chem 1997, 250, 31.
29. Mitomo, H.; Enjoji, T.; Watanabe, Y. J Macromol Sci Pure Appl Chem 1995, A32, 429.
30. Mitomo, H.; Sasaoka, T.; Yoshii, F. Sen'i Gakkaishi 1996, 52, 623.
31. Lee, H. S.; Lee, T. Y. Polymer 1997, 38, 4505.
32. Akita, S.; Einaga, Y.; Miyaki, Y. Macromolecules 1976, 9, 774.
33. Chen, S.; Xia, H. M. Mycosystema, to appear.
34. Heinen, W.; Rosenmoller, C. H.; Wenzel, C. B. Macromolecules 1996, 29, 1151.
35. Bickford, W. K. J Am Chem Soc 1948, 53, 33.
36. Skrbic, Z.; Divjakovic, V. Polymer 1996, 37, 505.
37. Bluhm, T. L.; Hamer, G. K. Macromolecules 1986, 19, 2871.
38. Keith, H. D.; Padden, F. J. Polymer 1984, 25, 28.
39. Grassie, N.; Murray, E. J. Polym Degrad Stab 1984, 6, 47.
40. Grassie, N.; Murray, E. J. Polym Degrad Stab 1984, 6, 95.
41. Grassie, N.; Murray, E. J. Polym Degrad Stab 1984, 6, 127.