

Effect of Nucleation Agents on the Crystallization of Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3/4HB)

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ABSTRACT: Boron nitride (BN), talc, hydroxyapatite (HA), and zinc stearate (ZnSt) were investigated as nucleation agents (NA) for nonfossil-based poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3/4HB) plastics. Nonisothermal crystallization behaviors of the P3/4HB/NA blends were examined by DSC. It revealed that BN is the most efficient nucleation agent to promote the crystallization rate, however, but not the crystallization degree. The lasting crystallization of P3/4HB was also removed. The nucleation effect was strengthened with increase of BN content up to 1% and then slackened deeply when further BN was added. Isothermal

crystallization analysis revealed that the addition of nucleation agent BN does not alter the crystal growth mode of P3/4HB, with maintaining the Avrami parameter n value around 2.40. Talc did enhance the crystallization of P3/4HB with however milder crystal growth rate. HA and ZnSt did not promote, but depressed the crystallization of P3/4HB plastics. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1116–1123, 2010

Key words: nucleation agent; P3/4HB; nonisothermal crystallization; isothermal crystallization; Avrami equation

INTRODUCTION

Polyhydroxyalkanoates (PHA), also known as bacterial polyesters, are a group of biodegradable polyesters accumulated by many bacteria, when an essential nutrient is limited.¹ Now, over 100 different types of PHA have been reported. Because of their renewability, biodegradability, and biocompatibility, PHA has become promising candidates as nonfossil-based commodity polymers and biomedical materials.^{2,3} Among them, poly(3-hydroxybutyrate) (PHB) is the most common short-chain-length PHA synthesized by various bacteria grown on different types of substrates.⁴ However, PHB has several inherent deficiencies that limit its applications, including its brittleness due to its high crystallinity and narrow processing window because of its thermal instability.^{5,6} To lower the crystallinity and melting temperature of PHB, the strategy to attain copolymers of 3-hydroxybutyrate (3HB) unit with 4-hydroxybutyrate (4HB) unit, i.e., poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3/4HB), has been successfully achieved by microbial fermentation.⁷ The chemical structure of P3/4HB is shown in Chart 1. As the PHB's sister copolymers, P3/4HB produced by *Ralstonia eutropha*, *Alcaligenes latus*, and *Comamonas acidovorans*, exhibits

much improved and adjustable mechanical and processing properties over PHB homopolymer, via changing the ratio of 3HB to 4HB content. These unique characters would make P3/4HB a promising candidate for large-scale application of PHA materials from soft elastomers to commodity plastics.^{8–10} Usually, when 4HB content is less than 10 mol %, the P3/4HB exhibits characteristic properties of plastics with the crystallization degree over 20 mol %. However, when the 4HB is more than 10 mol %, the P3/4HB will become less crystallized and softer, rubber-like, with the increase of 4HB, and eventually, it attains completely amorphous, highly elastic, and very tough gum like, when the 4HB content is increased up to 40 mol %. Thanks to the Tianjin Green Bioscience Materials Co. Ltd., who initiated a project for production of P3/4HB over 10k ton per year. This would promote the PHA from academic research to industrial applications at a real possibility.

Besides the biomedical applications of P3/4HB, our interest is focused on the P3/4HB as commodity polymer applications. Similar to most PHA materials, P3/4HB faces the drawbacks of slow crystallization and the lasting crystallization phenomena. This would cause the problems for processing instability and low efficiency. There were already a few investigations on the crystallization and even thermal degradation behaviors of P3/4HB.^{9,11–15} As the 4HB unit has one more backbone carbon atom than those of 3HB, 3-hydroxyvalerate (3HV), 3-hydroxyhexanoate

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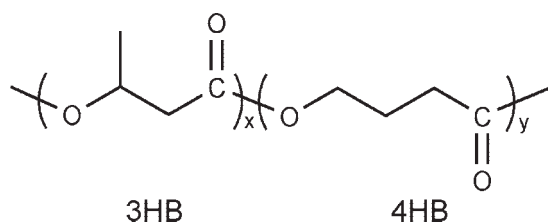


Chart 1 The chemical structure of P3/4HB.

(3HHx), and 3-hydroxypropionate (3HP) units, it was found that P3/4HB copolymer shows unique crystallization behaviors.^{16–18} These studies showed that the 4HB units acted as crystal defects in the copolymer, and with increasing 4HB composition both the crystallization degree and the crystallization rate decrease. However, from open report, we do not find the information on how to increase the crystallization rate of P3/4HB and make the crystallization go to completion as soon as possible. To achieve the practical use, i.e., efficient processing of P3/4HB plastics, the slow crystallization and the lasting crystallization behaviors must be solved. Under these circumstances, we performed the investigation on the nucleation agents to circumvent the slow crystallization difficulty of the P3/4HB materials. The P3/4HB with 4HB content 7.63 mol % was chosen as typical sample of P3/4HB plastics to investigate the crystallization behavior by blending with four kinds of chemical agents, i.e. boron nitride (BN), talc, hydroxyapatite (HA), and zinc stearate (ZnSt). Both nonisothermal and isothermal crystallization behaviors of P3/4HB blends were studied with differential scanning calorimeter (DSC). This article wishes to report the results.

EXPERIMENT

Materials

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3/4HB) was obtained by bacterial fermentation and supplied by Tianjin Green Bioscience Co., Ltd. (Tianjin, China), $M_n = 9.38 \times 10^5$, $M_w/M_n = 1.29$, estimated by GPC; 4HB content 7.63 mol % calculated by ^1H NMR analysis. The chemical agents boron nitride (BN), talc, hydroxyapatite, and zinc stearate powder were provided by Guangzhou Qianhui Co., Ltd. (Guangdong, China), the average particle sizes of them were 2, 4, 10, and 6 μm , respectively. The chemical agents and other reagent grade chemicals were used as received without further purification.

Sample preparation

About 2 g of P3/4HB powder was first dissolved in 80 mL of chloroform at 70°C. After that, an appro-

prate amount of the above chemical agent particles was added to the P3/4HB solution. The mixtures were magnetically stirred at the same temperature for 3 h, and this was followed by 5 min of sonication in a water bath. Subsequently, the mixing solution was poured onto a glass dish (9 cm in diameter). After evaporation of the chloroform, the resultant films were dried in vacuum for 2 day to constant weight and placed at a glass desiccator for at least 2 week before tested. The obtained P3/4HB blend was ready for further characterizations.

Characterization of P3/4HB blends

Thermal transitions of the P3/4HB blends were characterized by differential scanning calorimetry (DSC) performed on TA Instruments Q100 (TA Instrument) calibrated using indium and measurement was conducted under nitrogen atmosphere (50 mL/min). All samples were weighted about 2 mg and wrapped in an aluminum pan. Two different procedures, including nonisothermal crystallization and isothermal crystallization, were employed to study the crystallization behaviors of the P3/4HB blends.

For nonisothermal crystallization, the samples were heated to 180°C at a rate of 50°C/min and held for 3 min to melt the residual crystals, and then the samples were cooled from 180 to -50°C at various cooling rates of 5, 10, 15, 20°C/min, respectively, then reheated to 180°C at a heating rate of 10°C/min. The cool scan and the second heat run of the DSC curves were used to analyze the thermal property. The crystallization onset temperature (T_o) and crystallization peak temperature (T_c) were obtained from the cool scan. The melting temperature (T_m) and melting enthalpy (ΔH_f) were determined from DSC endothermal peaks at the second heat run. The lasting or cold crystallization temperature (T_{cc}) and cold crystallization enthalpy (ΔH_c) were determined from the DSC corresponding exothermal peaks at the second heat run.

For isothermal crystallization, the sample was heated to 180°C at a rate of 20°C/min and held for 3 min to remove prior thermal histories. It was then cooled to the appropriate crystallization temperature (T) at a rate of 80°C/min. The tested temperature was maintained at (T) until the crystallization was well finished. The isothermal crystallization kinetics was analyzed through the Avrami equation.

RESULTS AND DISCUSSION

Nonisothermal crystallization

Four kinds of chemical agents, i.e., BN, talc, hydroxyapatite, and zinc stearate were chosen to

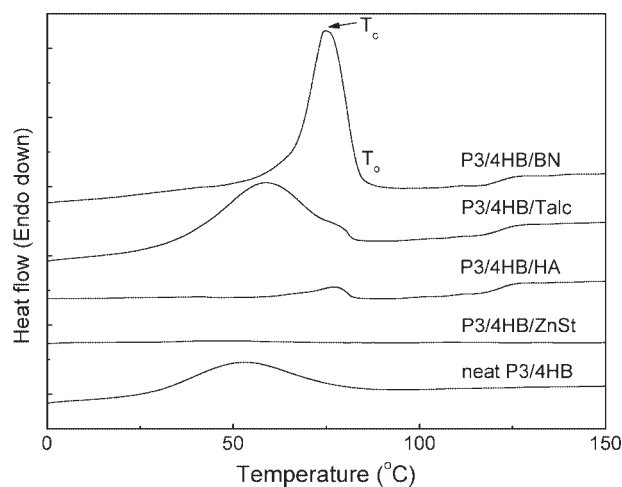


Figure 1 The DSC thermograms of P3/4HB blended with different chemical agents (0.5 wt %) (cool scan at 10°C/min).

explore their nucleating effect on P3/4HB plastics. The crystallization results of the P3/4HB blends from the cool scan of DSC determination (at a cooling rate of 10°C/min) were shown in Figure 1 and the nonisothermal parameters were listed in Table I. The crystallization onset temperature T_o and crystallization peak temperature T_c were obtained from the cool scans. And the value of $(T_o - T_c)$ was used to evaluate the nonisothermal crystallization rate, namely, at the same cooling rate, the lower value of $(T_o - T_c)$, the faster of crystallization rate.¹⁹ Low $(T_o - T_c)$ value means high crystallization rate and higher T_o indicates that the polymer could crystallize more easily at a relatively lower under-cooling process. As shown in Figure 1 and Table I, the crystallization peak from cool scan of P3/4HB/BN blend was the narrowest, i.e., lowest $(T_o - T_c)$ value 9°C, and shifted to highest crystallization temperature T_o . It indicates that BN is the most efficient nucleating agent on P3/4HB to increase both the crystallization easiness and the rate, similar results were reported by some forerunner researchers on PHBV/BN blend systems.^{20–22} Though the talc gave the higher T_o at 83.1°C, which was higher than that of neat P3/4HB, however, it displayed a larger $(T_o - T_c)$ value 24.2°C. These suggest that talc was a good nucleation agent to initiate P3/4HB crystallization but in a

slower rate. On the other hand, the change of the crystallization enthalpy (ΔH_c) also supported the earlier results. The P3/4HB/BN and P3/4HB/talc systems have the crystallization enthalpy of 34.29, 30.60 J/g, which are much higher than that of neat P3/4HB (18.51 J/g) and means the much higher crystallization degree in these two systems during the cooling experience. The other two chemical agents hydroxyapatite and zinc stearate exhibit no nucleating effect on the P3/4HB crystallization, even depress the crystallization as shown in Figure 1 and Table I. A NA with fine particle sizes has a high tendency to form more nuclei. It is understood that good NA can form a fine dispersion of small crystals of a thin crystalline layer absorbed on another substance.²³ The hydroxyapatite used in this study is too large and depress the crystallization of P3/4HB. Zinc stearate is a low molecular weight lubricant, which would reduce the crystallization ability of P3/4HB. Although BN and talc have nucleating effect on P3/4HB crystallization, the BN show better nucleating effect as the highest crystallization rate were obtained. These nucleation results of BN and talc on P3/4HB were quite similar to those of BN and talc on PHB and PHBV as reported by Inoue.²¹

In general, the addition of nucleating agent may be effective for acceleration of the crystallization of polymers.²⁰ By adding a nucleating agent, the nucleating density increases and the spherulite size decrease so that the crystallization rate is increased. An effective nucleating agent should decrease the surface fold energy. Usually, a good nucleating agent provides a surface that reduces the free energy barrier to the primary nucleation, and, thus, the nucleation density is increased. BN acted as the heterogeneous nucleation agent by lowering the energy barrier toward nucleation. Low molecular nature and suitable particles size of BN dispersed in the molten acting as heterogeneous species to initiate the crystal growth and hence increase crystallization rate. The diversity of crystalline morphologies (such as size of the spherulites and lamellar thickness) becomes narrower and the perfection of the spherulites goes to higher. Heterogeneous nucleation increases the nucleation rate in the high-temperature region, hence resulting in a shifting of the crystallization temperature (T_c) value (Fig. 1 and Table II) to

TABLE I
Nonisothermal Parameters of Neat P3/4HB and the P3/4HB Blends

NAs	Wt %	T_o (°C)	T_c (°C)	$T_o - T_c$ (°C)	ΔH_c (J/g)
None	–	79.9	53.0	26.9	18.51
Zinc stearate	0.5	/	/	/	/
Hydroxyapatite	0.5	/	/	/	/
Talc	0.5	83.1	58.9	24.2	30.60
Boron nitride	0.5	83.7	74.7	9.0	34.29

TABLE II
Nonisothermal Parameters of P3/4HB and P3/4HB/BN Blend

P3/4HB/BN	T_c (°C)	ΔH_c (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
100/0.0	53.0	16.56	53.0	30.26	-3.5	113.2	127.9	39.69
99.9/0.1	56.0	23.04	51.3	8.58	-3.0	114.9	128.6	37.27
99.7/0.3	64.3	33.80	/	/	-2.8	118.3	131.0	38.74
99.5/0.5	74.7	34.52	/	/	-3.0	121.7	133.8	37.05
99.0/1.0	73.4	32.62	/	/	-3.1	121.2	133.5	32.30
98.5/1.5	77.7	33.24	/	/	-3.6	122.6	134.6	34.16
98.0/2.0	78.8	32.46	/	/	-3.4	123.1	134.7	33.91
95.0/5.0	79.7	32.10	/	/	-3.2	123.6	135.1	29.03

a high temperature. While talc probably dissolved in the molten and the surface hydroxyl groups reacted with the polyester chain by transesterification; then, the *in situ* formed substrates acted as the "true" nucleating agents, so lowering the energy barrier toward nucleation.²¹ This would be helpful in understanding the P3/4HB crystallization behavior in the existence of talc.

The effect of different cooling rates on P3/4HB crystallization was shown in Figure 2. As the cooling rate increases, the crystallization temperature (T_c) becomes lower. The crystallization temperature was decreased gradually from 84.2 to 63.2°C when cooling rate rose from 5 to 20°C/min. These results were attributed to the shorter experienced crystallization time as the cooling rate increases. When the cooling rate is lower, the samples have enough time to form the necessary nuclei and the polymer chains have enough time to move to pack together into better crystalline domains. The crystallization temperature would be getting higher. However, when the cooling rate was higher, the motion of P3/4HB chains cannot follow the cooling process, resulting in the lower crystallization temperature detected.

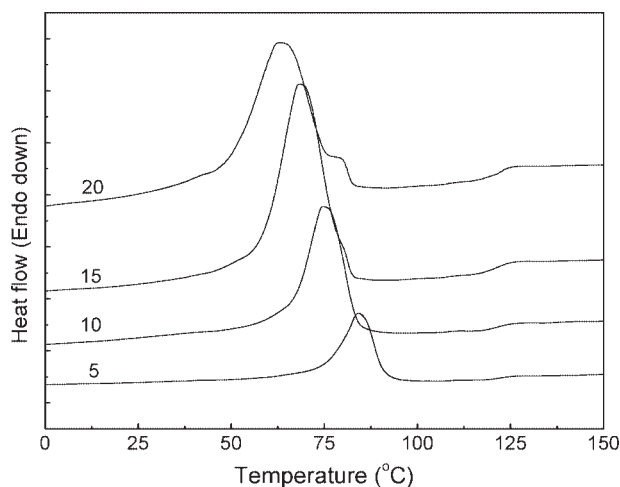


Figure 2 The nonisothermal crystallization of P3/4HB/BN (99.5/0.5) blend at different cooling rates (DSC, cool scan).

The melting behavior of the P3/4HB/BN (99.5/0.5) blend was investigated by reheating the nonisothermal crystallized samples, which were obtained after different cooling rate experiences. The reheating rate was 10°C/min, and the endothermic curves are shown in Figure 3. The endothermic curve became broadening with the previous cooling rate increase. According to these DSC thermograms, the melting profile contained two melting peaks termed T_{m1} and T_{m2} from low to high temperatures, respectively. The lower melting temperature (T_{m1}) was attributed to the melting of the primary crystallites formed during previous cool scan. Some of these crystals experienced melting-recrystallization or crystal rearrangement during the DSC heating scan, and these would melt again at the higher melting temperature (T_{m2}).^{20,24} The shape and area of the T_{m1} curve became broaden and smaller with previous cooling rate increase, indicating that the crystals did not go to completion when the previous cooling experience was fast. However, the shape and area T_{m2} peak became broaden and larger with the previous cooling rate increase, demonstrated that the amount of imperfect crystals formed increased, and the

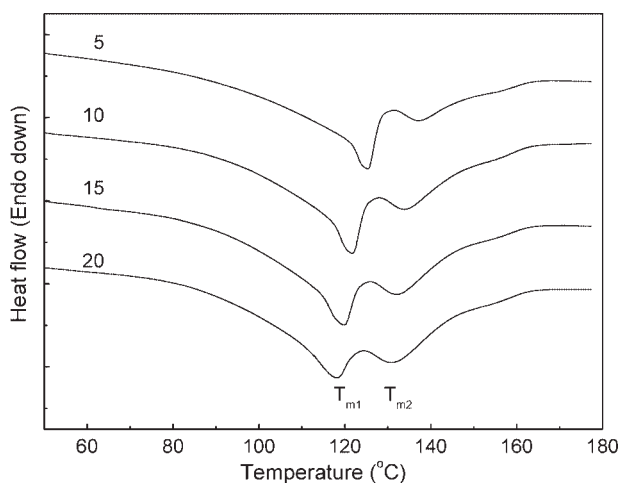


Figure 3 The DSC thermograms (second heat run at 10°C/min) of P3/4HB/BN (99.5/0.5) blend after cool scan at different cooling rates.

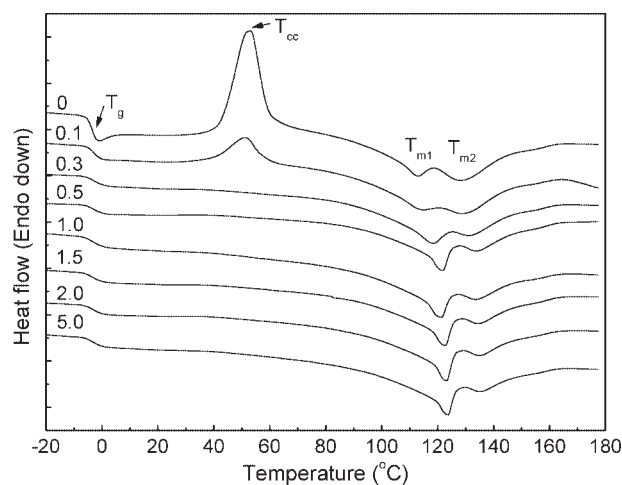


Figure 4 The DSC thermograms of neat P3/4HB and P3/4HB/BN blends with different amount of BN (second heat run at 10°C/min).

crystal rearrangement also increased with previous cooling rate increase.

The effect of different amount of nucleation agent BN on the melting behavior of P3/4HB was studied by the DSC second heat run after the previous cooling rate of 10°C/min (Fig. 4). The melting profiles contained two melting peaks also, i.e., T_{m1} and T_{m2} , as discussed before. The area ratio of peak T_{m1} to peak T_{m2} increases greatly with the addition of BN, which suggest that the nucleation agent enhance the formation of primary crystallites, and, however, depress the imperfect crystals and the crystal rearrangement. Thus, nucleation agent BN would make the crystals more perfect. It was also noted that T_{m1} and T_{m2} of the BN nucleated P3/4HB were higher than those of the neat P3/4HB (Table II), indicative of more perfected crystal (larger lamellar thickness) formed in the nucleated P3/4HB. The better the nucleation effect, the higher the melting point T_{m1} was revealed. All these results indicated that the addition of BN increases not only the crystallization rate but also the crystal perfection. From Table II, it was noted that with the addition of BN, the melting enthalpy ΔH_m does not increase, but decreases gradually. It revealed that the nucleation agent BN does not increase the overall crystallization degree of P3/4HB plastics. Comparison with the crystallization enthalpy ΔH_c in Table I, it can be seen that without BN, neat P3/4HB gives a lower ΔH_c value 18.52 J/g and much higher ΔH_m value 39.69 J/g, which means the crystallization did not go to finish during the cool scan and much following on crystallization occurred. With the addition of nucleation agent BN, the ΔH_c and ΔH_m have the quite similar values, which means the crystallization went very fast and almost no following on crystallization occurred. From the DSC thermograms (Fig. 4), it was also

observed that when BN was more than 1 wt %, the melting profiles of the P3/4HB crystals did not change too much. Therefore, for practical applications, 0.5–1.0 wt % BN might be the appropriate content.

Nonisothermal crystallization behaviors of neat P3/4HB and the P3/4HB/BN blends were also examined by DSC cooling scan, from melt at a cooling rate of 10°C/min (Fig. 5, Table II). All the crystallization temperature (T_c) shifted to a much higher temperature region and its crystallization peak becomes sharper until BN content up to 1 wt %, indicating that the crystallization became faster and the diversity of crystalline morphologies (such as size and perfection of the spherulites, and lamellar thickness) became narrower with the introduction of BN.²¹ However, when the BN was more than 1 wt %, no further significant change was observed. For example, P3/4HB/BN (99.5/0.5) blend enhanced about 15°C increase in crystallization temperature (74.7°C) than that of neat P3/4HB (53.0°C). When the BN content was up to as high as 5 wt %, only a little further increase of crystallization temperature (79.7°C) attained. Thus, we concluded that lower content of nucleation agent BN promotes P3/4HB crystallization greatly, whereas excessive amount of BN has little further nucleating effect on P3/4HB crystallization.

Isothermal crystallization

Crystallization kinetics in copolymers is a complex phenomenon that includes several processes such as occurrence of primary nuclei, formation and spreading of bidimensional surface nuclei, interdiffusion of crystallizable and noncrystallizable chains at the advancing front of the growing crystallites.²⁰ These

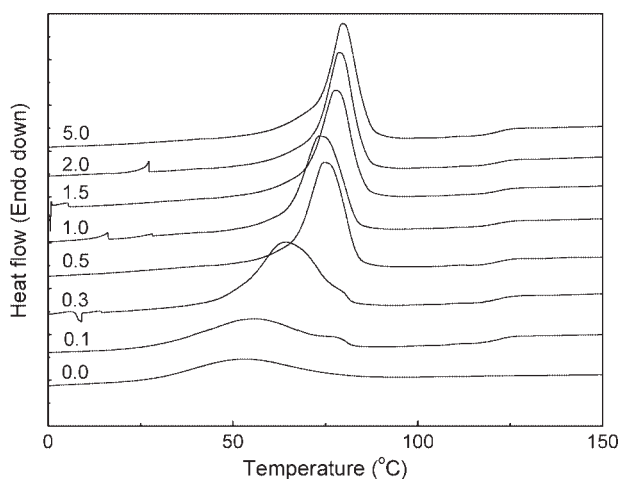


Figure 5 The DSC thermograms of neat P3/4HB and P3/4HB/BN blends with different amount of BN (cool scan at 10°C/min).

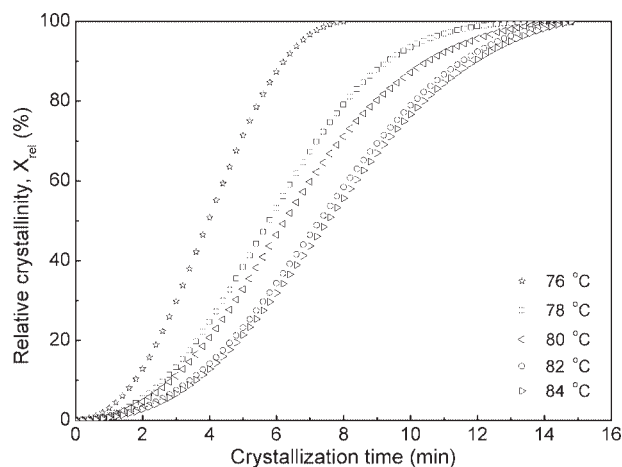


Figure 6 The plots of relative crystallinity X_{rel} versus crystallization time t of neat P3/4HB at different crystallization temperatures.

processes are affected to some extent by the thermodynamic conditions in which crystallization takes place, by the molecular characteristics of the components and the strength of their mutual interaction. The isothermal crystallization of polymers can be described by an Avrami equation,²⁵ and the crystallization kinetics data obtained by DSC was fitted following the guidelines described by Müller and co-workers.²⁶ The relative degree of crystallinity X_{rel} at time t is given by the following equation:

$$X_{rel} = \frac{X_c(t)}{X_c(\infty)} = \int_0^t \frac{dH(t)}{dt} dt / \int_0^\infty \frac{dH(t)}{dt} dt \quad (1)$$

where $X_c(t)$ and $X_c(\infty)$ are the degree of crystallinity at time t and that at the end of crystallization, respectively; $dH(t)/dt$ is the rate of heat flow in the process of isothermal crystallization at time t . The time t was measured from the moment when the sample was cooled to the appropriate crystallization temperature. The relative crystallinity X_{rel} versus the crystallization time t for isothermal crystallization of neat P3/4HB and that of P3/4HB/BN (99.5/0.5) blend at appropriate crystallization temperatures are given in Figures 6 and 7, respectively. It can be seen that the crystallization time increased with the increase of crystallization temperature for both neat P3/4HB and P3/4HB/BN (99.5/0.5) blend, indicating that the crystallization was retarded with the increasing crystallization temperature. Compared with neat P3/4HB, at a given temperature, however, the crystallization time of P3/4HB/BN blend reduced deeply, indicating that the addition of nucleation agent BN increased the crystallization rate of P3/4HB.

The relative degree of crystallinity X_{rel} can be developed as a function of crystallization time t as

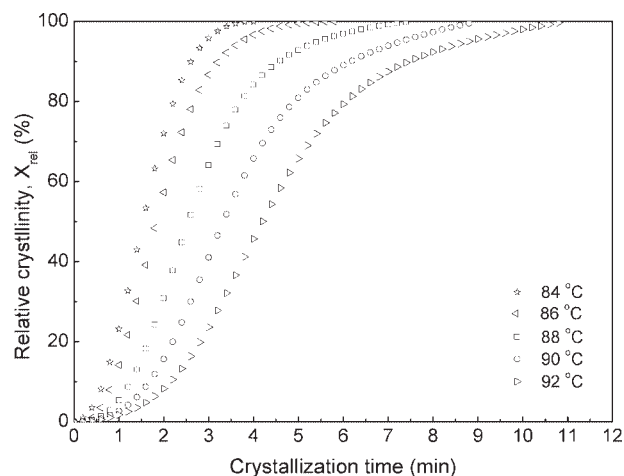


Figure 7 The plots of relative crystallinity X_{rel} versus crystallization time t of P3/4HB/BN (99.5/0.5) blend at different crystallization temperatures.

follow:^{25,27}

$$1 - X_{rel} = \exp(kt^n) \quad (2)$$

Here n is the Avrami exponent, which is determined by the mode of crystal nucleation and the crystal growth geometry in the actual circumstance, and k is the parameter of isothermal crystallization rate. Taking a double logarithm of eq. (2) gives:

$$\log[-\ln(1 - X_{rel})] = n \log t + \log k \quad (3)$$

The plot of $\log[-\ln(1 - X_{rel})]$ against $\log t$ gives a straight line, whose slope is n and intercept on the ordinate is $\log k$. In the experiment of isothermal crystallization at time t , $dH(t)/dt$ was recorded, and then integrated against time t , and the crystallization finished time gives the values of $X_c(t)$ and $X_c(\infty)$, respectively.

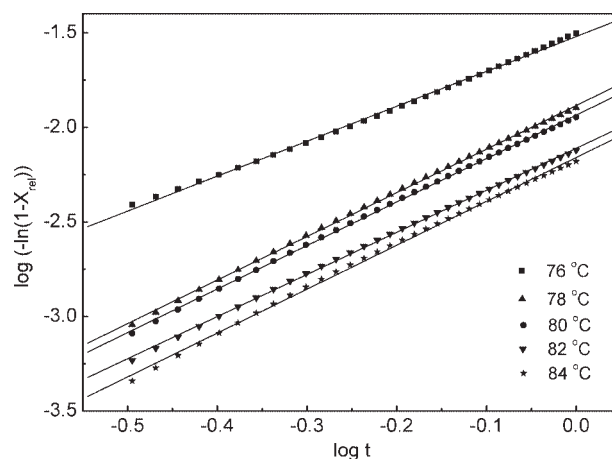


Figure 8 Avrami plots for isothermal crystallization of neat P3/4HB.

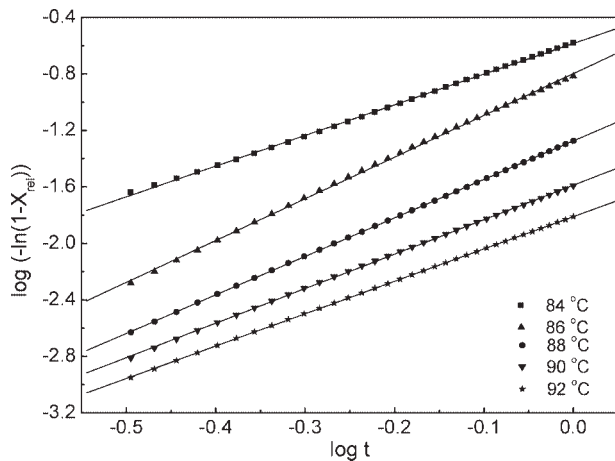


Figure 9 Avrami plots for isothermal crystallization of P3/4HB/BN (99.5/0.5) blend.

When $X_{rel} = 0.5$ in eq. (3), the half crystallization time $t_{1/2}$, which is the time taken for 50% of total volume crystallization, is given by the following formula:

$$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{1/n} \quad (4)$$

The plots of $\log(\ln(1 - X_{rel}))$ versus $\log t$ for neat P3/4HB and the P3/4HB/BN (99.5/0.5) blend are shown in Figures 8 and 9, respectively. Each curve shows an initial linear portion during the early stage of crystallization and a tendency to level off due to the existence of secondary crystallization at the later stage.²⁸ This secondary crystallization is generally considered to be the result of slower crystallization, crystal perfection, and/or spherulite impingement in the later stage of the crystallization process. In P3/4HB samples, the secondary crystallization might also occur from spherulite impingement, which indicates that the form of crystal growth transformed from primary crystallization into the secondary one. This was similar to that of PHB.^{21,29} As we know, the product will continue to crystallize over the

course of usage if the secondary crystallization is not completed. To keep the shape and size of the P3/4HB plastics articles stable during usage, it is very important to anneal the material for enough time under the temperature at which the crystallization rate is the maximum. For P3/4HB/BN (99.5/0.5) blend, the upper part of each $\log(-\ln(1-X_{rel}))$ versus $\log t$ curve shows almost a straight line. These results demonstrated that the introduction of nucleation agents greatly reduces the secondary crystallization of P3/4HB. The addition of nucleation agent BN would help keep the shape and size stability of the P3/4HB plastics products.

The calculation of n and k is performed by fitting the data in the double-logarithmic plot. According to Müller's research,²⁶ the linear regression coefficient R^2 value must be 0.9990 or larger to represent a very good fit of the data in a specific conversion range. In this study, we chosen the conversion range of 5–30%, and the corresponding R^2 value (all of the result is larger than 0.9990) was listed in Table III, respectively. Also the values of n and k were determined from the fit line in Figures 8 and 9, and the results are summarized in Table III. According to the Avrami equation, in the ideal state of nucleated crystallization for three-dimensional crystallization growth, the n value should be exactly 3.²² The Avrami exponent n for neat P3/4HB and the P3/4HB/BN is very close and about two to three. The little change of n value hints that the addition of nucleation agent BN does not alter the crystallization mode of P3/4HB obviously. This n value changes very little with the temperature and the nucleation agent at the range of 2–3, which might indicate that the P3/4HB crystal would be a mixture of laminar and spherulite or much defected spherulite.

As shown in Table III, the value of k , parameter of isothermal crystallization rate, decreased with the increase of crystallization temperature, while the crystallization half time ($t_{1/2}$) value was in an upward trend with crystallization temperature increase. In other words, the crystallization rate of

TABLE III
The Isothermal Crystallization Kinetic Parameters for Neat P3/4HB and P3/4HB/BN (99.5/0.5) Blend at Different Crystallization Temperatures

Samples	T_c (°C)	n	k (min ⁻ⁿ)	$t_{0.5}$ (min)	$1/t_{0.5}$ (min ⁻¹)	R^2
Neat P3/4HB	76	2.10	0.0221	5.16	0.19	0.9995
	78	2.30	0.0116	5.92	0.18	0.9996
	80	2.22	0.0078	7.55	0.13	0.9994
	82	2.32	0.0069	7.29	0.14	0.9993
	84	2.33	0.0066	7.37	0.14	0.9995
P3/4HB/BN 99.5/0.5	84	2.17	0.2606	1.57	0.64	0.9996
	86	2.96	0.1594	1.64	0.61	0.9994
	88	2.73	0.0532	2.56	0.39	0.9999
	90	2.44	0.0258	3.85	0.26	0.9998
	92	2.22	0.0155	5.53	0.18	0.9999

P3/4HB was decreased with the increase of crystallization temperature. In addition, the k value of P3/4HB/BN blend is much higher than that of neat P3/4HB at the same crystallization temperature, while the $t_{1/2}$ value showed a reverse trend. These results further illuminated that the crystallization rate of P3/4HB/BN blend was much faster than that of neat P3/4HB at the same crystallization temperature, suggesting that BN is a very efficient nucleation agent to enhance crystallization rate of P3/4HB plastics.

CONCLUSIONS

Among the four kinds of chemical agents BN, talc, hydroxyapatite, and zinc stearate, BN showed the most efficient nucleating effect on P3/4HB. Lower content (0.1–1 wt %) of nucleation agent BN promotes P3/4HB crystallization rate greatly, while excessive BN imposes little further effect on P3/4HB crystallization. Therefore, 0.5 wt % BN would be the appropriate amount for P3/4HB plastics nucleation. It is seemed that BN does not increase the crystallization degree of P3/4HB. Isothermal crystallization analysis verified that the addition of BN did not change the crystallization mode of P3/4HB. Avrami parameter n value maintains around 2.30. Furthermore, the addition of BN suppressed the lasting crystallization of P3/4HB plastics, which would improve the processing ability in practical applications.

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References

- Chen, G. Q.; Wu, Q.; Xi, J. Z.; Yu, H. P.; Chan, A. *Progress Nat Sci* 2000, 10, 843.
- Lenz, R. W.; Marchessault, R. H. *Biomacromolecules* 2005, 6, 1.
- Xu, K.T.; Zhao, S. J. *Chin J Appl Environ Biol* 1995, 1, 86.
- Kato, M.; Bao, H. J.; Kang, C. K.; Fukui, T.; Doi, Y. *Appl Microbiol Biotechnol* 1996, 45, 363.
- Khanna, S.; Srivastava, A. K. *Process Biochem* 2005, 40, 607.
- Wang, L.; Zhu, W. F.; Wang, X. J.; Chen, X. Y.; Chen, G. Q.; Xu, K. T. *J Appl Polym Sci* 2008, 107, 166.
- Kunioka, M.; Kawaguchi, Y.; Doi, Y. *Appl Microbiol Biotechnol* 1989, 30, 569.
- Ishida, K.; Wang, Y.; Inoue, Y. *Biomacromolecules* 2001, 2, 1285.
- Zhu, Z. Y.; Dakwa, P.; Tapadia, P.; Whitehouse, R. S.; Wang, S. Q. *Macromolecules* 2003, 36, 4891.
- Mitomo, H.; Hsieh, W. C.; Nishiwaki, K.; Kasuya, K.; Doi, Y. *Polymer* 2001, 42, 3455.
- Kunioka M; Tamaki, A.; Doi, Y. *Macromolecules* 1989, 22, 694.
- Abe, H.; Doi, Y. *Macromol Symp* 2001, 174, 43.
- Mitomo, H.; Doi, Y. *Int J Biol Macromol* 1999, 25, 201.
- Kunioka, M.; Doi, Y. *Macromolecules* 1990, 23, 1933.
- Yoon, J. S.; Chin, I. J.; Kim, M. N.; Kim, C. *Macromolecules* 1996, 29, 3303.
- Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *Macromolecules* 1988, 21, 2722.
- Doi, Y.; Segawa, A.; Kunioka, M. *Int J Biol Macromol* 1990, 12, 106.
- Nakamura, S.; Doi, Y.; Scandola, M. *Macromolecules* 1992, 25, 4237.
- Hu, C. X.; Zhang, W. J.; Xue, J. W.; Lv, Z. P.; Dou T. J. *Taiyuan Univ Technol* 2006, 37, 618.
- Liu, W. J.; Yang, H. L.; Wang, Z.; Dong, L. S.; Liu, J. J. *J Appl Polym Sci* 2002, 86, 2145.
- Kai, W.; He, Y.; Inoue, Y. *Polym Int* 2005, 54, 780.
- Qian, J.; Zhu, L.; Zhang, J.; Whitehouse, R. S. *J Polym Sci Part B: Polym Phys* 2007, 45, 1564.
- Wunderlich, B. *Macromolecular Physics*, Academic Press: New York, 1977; Vol 2.
- Zhang, J.; McCarthy, S.; Whitehouse, R. S. *J Appl Polym Sci* 2004, 94, 483.
- Avrami, M. *J Chem Phys* 1940, 8, 212.
- Lorenzo, A. T.; Arnal, M. L.; Albuerno, J.; Müller, A. J. *Polym Test* 2007, 26, 222.
- Binsbergen, F. L. *J Macromol Sci Phys* 1970, 4, 837.
- Liu, J. P.; Mo, Z. S. *Chin Polym Bull* 1991, 4, 199.
- An, Y.; Li, L.; Dong, L.; Mo, Z.; Feng, Z. *J Polym Sci Part B: Polym Phys* 1999, 37, 443.