

Crystallization Behavior of Partially Crosslinked Poly(β -hydroxyalkonates)/Poly(butylene succinate) Blends

Piming Ma,^{1,2} Xiaoxia Cai,^{2,3} Wei Wang,¹ Fang Duan,¹ Dongjian Shi,¹ Piet J. Lemstra²

¹The Key Laboratory of Food Colloids and Biotechnology of Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

²Department of Chemical Engineering and Chemistry, Laboratory of Polymer Technology, Eindhoven University of Technology, Eindhoven 5612 AZ, the Netherlands

³School of Food Science and Technology, Jiangnan University, Wuxi 214122, China

Correspondence to: P. Ma (E-mail: p.ma@jiangnan.edu.cn)

ABSTRACT: Partially crosslinked poly(β -hydroxybutyrate-co- β -hydroxyvalerate)/poly(butylene succinate) (PHBV/PBS) and poly(β -hydroxybutyrate)/poly(butylene succinate) (PHB/PBS) blends were prepared by melt compounding with dicumyl peroxide. The effect of partial crosslinking on crystallization of the PHBV/PBS and PHB/PBS blends was investigated systematically. Differential scanning calorimetry results showed that the overall crystallization rates of both PHBV and PBS in their blends were enhanced considerably by the partial crosslinking. Similar results were also detected in the PHB/PBS blends. The polarized optical microscope observation displayed that the nuclei density of PHBV was increased while the spherulitic morphology did not change much. Conversely, the PBS spherulites turned into cloud-like morphology after the partial crosslinking which is a result of the decrease in spherulite size, the reduction in interspherulite distance and the interconnection of fine PBS domains. Wide angle X-ray diffraction patterns confirmed the enhancement in crystallization of the PHBV/PBS blends after the partial crosslinking without modification on crystalline forms of the PHBV and PBS components. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41020.

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INTRODUCTION

Poly(β -hydroxyalkonates) (PHA), such as poly(β -hydroxybutyrate-co- β -hydroxyvalerate) (PHBV) and poly(β -hydroxybutyrate) (PHB) are bacterially synthesized semicrystalline thermoplastics, which have drawn considerable attention due to their biocompostable and renewable features. However, their application is often limited by the high price, brittleness, and poor processability. The poor processability is associated with narrow processing window and low crystallization rate.¹

The toughness and processing window of PHBV can be improved by increasing the β -hydroxyvalerate (HV) content to high values (e.g., >20 mol %). However, commercial grade PHBV (e.g., Enmart® from Tianan Biologic Materials Co., Ningbo, China) usually has very low HV content due to a cost issue. Moreover, high HV content compromises the strength, modulus, and crystallization rate of PHB(V) as well.

Blending is an effective and economical route to tune properties of polymers. Biodegradable polymers such as poly (vinyl alco-

hol),² poly (lactic acid),^{3,4} cellulose fiber,⁵ poly(caprolactone),⁶ poly(propylene carbonate),^{7,8} poly(butylene succinate) (PBS),⁹ and poly(ethylene succinate)¹⁰ were physically blended with PHBV or PHB to fabricate new biodegradable materials. Whereas, the toughness of PHB(V) was not significantly improved due to a poor affinity between PHB(V) and the other polymers. In our previous work, *in situ* compatibilization was introduced to PHBV/PBS, PHB/PBS, and PHBV/P(DL-lactic acid) (PDLA) blends using dicumyl peroxide (DCP) as a free-radical initiator.^{11,12} Interestingly, the size of the PBS and the PDLA domains was reduced with an increase in interfacial adhesion, leading to toughness and ductility of the blends. The elongation at break of the PHBV/PBS (80/20, wt/wt) blend was increased by a factor of 50 while the un-notched Izod impact toughness of the PHB/PBS (70/30) blends was improved by a factor of 5 after addition of 0.5 wt % of the DCP.¹¹ Although considerable work has been devoted to the mechanical and morphological behavior of the *in situ* compatibilized PHB(V)/PBS blends, no studies on the crystallization of these blends have been reported yet.

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Crystallization behavior of a polymer (or a polymer blend) has close relation with its performances. PHBV, PHB, and PBS are all semicrystalline polyesters. The overall crystallization rates of PHBV and PHB are low. Consequently large spherulites with cracks inside are usually obtained which are responsible for the brittleness.¹³ Furthermore, the low crystallization rate presents a major drawback on injection molding, as the injected art cannot be ejected immediately due to the lack of stiffness. In addition, physical ageing of PHB(V) occurs because of the incomplete crystallization on cooling.¹⁴ Conversely, PBS exhibits moderate crystallization rate and mechanical properties. The crystallization of PBS could be pronouncedly enhanced by partial crosslinking, resulting in higher strength, elongation at break, and impact toughness.¹⁵

The low crystallization rates of PHBV and PHB are due to lacking of nuclei associated with the bacterial synthesis route.¹⁶ Both inorganic and organic nucleating agents such as boron nitride, talc, multiwalled carbon nanotube, saccharin, phthalimide, cyclodextrins, uracil, and cyanuric acid were used to increase the nuclei density of PHB and its copolymers.^{17–22} Boron nitride, uracil, and cyanuric acid were proven to be efficient in accelerating the crystallization of PHB. The crystallization of PHB can also be promoted by physical compounding with PBS due to a multinucleation mechanism.²³ The partially crosslinked crystallization of PHBV/PBS and PHB/PBS blends shows novel and interesting phenomena which may be correlated to the significantly improved mechanical properties of the PHBV/PBS and PHB/PBS blends.

The prime objective of this work is to provide a systematic investigation on the crystallization behavior of the partially crosslinked PHBV/PBS blends which is free of any prior art reported in literature and offers a deeper understanding about these systems. The overall crystallization, spherulitic morphology, and crystalline form of the PHBV/PBS blends were studied using differential scanning calorimetry (DSC), polarized optical microscope (POM), and wide angle X-ray diffraction (WAXD). As a complement to the PHA/PBS systems, the overall crystallization behavior of partially crosslinked PHB/PBS blends with varying PBS contents and different preparation methods were studied as well.

EXPERIMENTAL

Materials

PHBV copolymer with a HV content of 12.7 mol %, measured by ¹H-NMR spectroscopy, was provided by Tianan Biologic Material Co., Ningbo, China. Its molar mass was measured based on viscosity in chloroform at 30°C and yielded $M_{\eta} = 250$ KDa according to the equation²⁴ $[\eta] = 1.18 \times 10^{-4} \cdot M_{\eta}^{0.78}$, where $[\eta]$ is the intrinsic viscosity. PHB (containing ~ 1 mol % HV) was provided by the same company with $M_{\eta} = 200$ KDa. Due to the very low HV content this sample is considered to be a homopolymer and is referred to as PHB in the text. PBS was supplied by Zhejiang Hangzhou Xinfu Pharmaceutical Co., China with a melt-flow index of 7.8 g/10 min (150°C × 2.16 kg). DCP (purity ≥ 99.5%) with typical half-life time about 1 min at 171°C was purchased from Sinopharm Chemical Reagent Co., China.

Blend Preparation

PHBV, PHB, and PBS were dried in a vacuum oven at 50°C for 12 h before use. PHBV/PBS (80/20, wt/wt) blends with DCP contents of 0, 0.2, 0.5, and 1.0 wt % were melt-blended in a mixing chamber of a Rheocord 90 Haake Rheometer (Mess-Technic GmbH, Germany) at 170°C and 40 rpm (rotation speed) for 4 min. After preheating, the samples were compression molded at 170°C for 3 min into sheets using a compression-molding machine. The compression-molded samples were used for further testing and characterization. Compared with PHBV, homopolymer PHB is more commercially available and widely processed by extrusion and injection molding. Thus, PHB/PBS blends with and without DCP were prepared using a twin-screw extruder ($L/D = 41$, $D = 25$ mm) with a water-bath cooling system. The setting temperatures along the extruder (from feeder to die) were 40, 160, 160, 160, 160, 165, and 160°C, respectively. The screw rotation speed was fixed at 160 rpm. The extrudes were palletized, dried and injection molded ($L/D = 28$, $D = 25$ mm) for characterization. The barrel temperatures of the injection molding machine were 160, 170, 170, and 165°C, respectively, from hopper to nozzle. A holding time of 5 s and a cooling time of 15 s were used. The injection pressure was controlled approximately at 30 MPa.

Differential Scanning Calorimetry

The DSC measurements were performed on a Perkin–Elmer DSC (Pyris 1) in nitrogen atmosphere. All samples were first heated to 190°C at a heating rate of 20°C/min and maintained at this temperature for 3 min to erase previous thermal history, then cooled to –20°C and reheated to 190°C. The cooling and reheating rates were 10°C/min. The crystallinity of PHB(V) in the blends was calculated via eq. (1)

$$X_c = (\Delta H_m - \Delta H_{cc}) / (\Delta H_0 \times w) \times 100\%, \quad (1)$$

where ΔH_0 is the thermodynamic enthalpy of fusion per gram of PHB ($\Delta H_0 = 146.6 \text{ Jg}^{-1}$),²⁵ ΔH_m and ΔH_{cc} are the apparent melt enthalpy and the apparent cold crystallization enthalpy of PHBV (or PHB) in per gram blends and w is the mass concentration of the PHBV (or PHB) in the blends. The crystallinity of PBS was calculated via the same method using a thermodynamic enthalpy of fusion per gram of PBS ($\Delta H_0 = 200 \text{ Jg}^{-1}$).²⁶

Polarized Optical Microscope

The spherulitic morphology of PHBV/PBS blends were monitored with a POM (Leica DMLP, Germany) equipped with a Linkam hot stage. Thin samples were cryo-microtomed from compression molded sheets. Then the thin samples were placed inside Linkam hot stage (between two glass slides) and inserted under the microscope. The crystallization behavior of PHBV and PBS was investigated using the following procedures: heating the samples from room temperature to 200°C at 60°C/min, holding for 3 min at 200°C, then quenching to isothermal crystallization temperatures (i.e., 120 or 100°C, respectively) at a cooling rate of 60°C/min where spherulitic growth was recorded.

Wide Angle X-ray Diffraction

The WAXD experiments were performed using an X-ray diffractometer (SA-HF3, Rigaku, Japan) equipped with a Ni-filtered

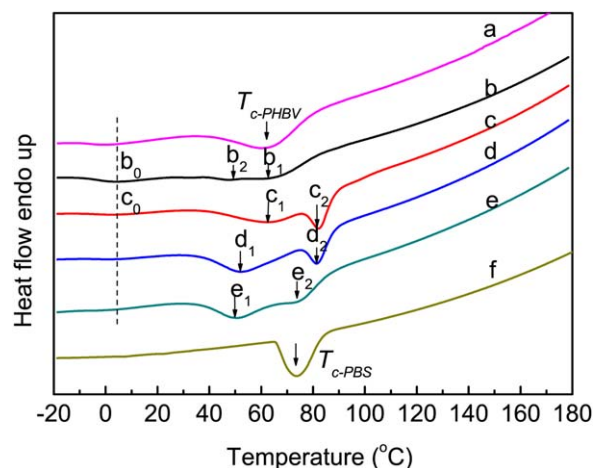


Figure 1. DSC cooling curves of (a) neat PHBV, (b–e) PHBV/PBS (80/20, wt/wt) blends with DCP content of (b) 0.0 wt %, (c) 0.2 wt %, (d) 0.5 wt %, (e) 1.0 wt %, and (f) neat PBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Cu K α radiation source with a wavelength of 1.54 Å. The measurements were operated at 40 kV and 40 mA at a scan rate of 4°/min. The scan angles were from around 10 to 30°.

RESULTS AND DISCUSSION

Crystallization and Melting Behavior of PHBV/PBS/DCP Blends

PHBV and PBS are not miscible showing phase separation and clear boundaries in PHBV/PBS blends which was reported in our previous study.¹¹ Partial crosslinking was initiated in the PHBV/PBS (80/20, wt/wt) blends after addition of DCP, leading to a considerable reduction in the PBS domain size and an improvement in the mechanical properties.¹¹ The presence of partial crosslink network and the changes in morphology influenced the crystallization of PHBV and PBS.

Both PHBV and PBS are crystallizable. The crystallization and melting behavior of the PHBV and PBS were first studied using DSC, as shown in Figures 1 and 2. PHBV crystallized incompletely ($T_{c\text{-PHBV}} = 63^\circ\text{C}$) [Figure 1(a)] on cooling as evidenced by a pronounced cold crystallization peak ($T_{cc\text{-PHBV}} = 53^\circ\text{C}$) and a notable glass transition process ($T_{g\text{-PHBV}} = -3^\circ\text{C}$) in the subsequent heating DSC curve [Figure 2(a)]. A melting peak of PHBV was observed at 160°C [$T_{m\text{-PHBV}}$, Figure 2(a)]. Conversely, the PBS crystallized completely ($T_{c\text{-PBS}} = 74^\circ\text{C}$) during

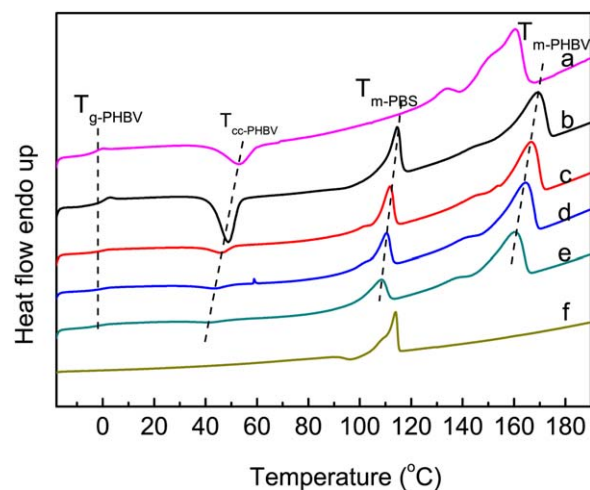


Figure 2. The second DSC heating curves of (a) neat PHBV, (b–e) PHBV/PBS (80/20, wt/wt) blends with DCP content of (b) 0.0 wt %, (c) 0.2 wt %, (d) 0.5 wt %, (e) 1.0 wt %, and (f) neat PBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cooling and melted at 114°C ($T_{m\text{-PBS}}$) in the subsequent heating process [Figures 1(f) and 2(f)].

The crystallization and melting behavior of the PHBV and PBS in their blends are also shown in Figures 1 and 2, respectively. The corresponding thermal parameters are summarized in Table I. Compared with neat PBS [Figure 1(f)], its crystallization temperature in the PHBV/PBS (80/20, wt/wt) blend was reduced to around 47°C [peaks b_2 in Figure 1(b)] due to a confined crystallization mechanism.²³ Meanwhile, an indistinctive crystallization peak of PHBV in the blend was observed [peak b_1 , Figure 1(b)], accompanied by a pronounced cold crystallization in the subsequent heating process [$T_{cc\text{-PHBV}}$, Figure 2(b)]. Moreover, a small peak (b_0) was detected at around 3°C for this blend. The small peak is regarded as an overall result of the glass transition of PHBV and the secondary crystallization of the PHBV and/or PBS.

Both PHBV and PBS in their partially crosslinked blends showed crystallization as the gel fraction is low (see Supporting Information Figure S1). Two notable crystallization peaks in the range of 30–90°C were detected corresponding to the PHBV and PBS components, respectively. The sharper crystallization peaks at higher temperatures (i.e., c_2 , d_2 , and e_2 , Figure 1) are more related to the PBS phase because the crystallization rate of PBS could be significantly enhanced by partial crosslinking.¹⁵ A

Table I. Thermal Parameters of PHBV/PBS/ (80/20, wt/wt) Blends with Different DCP Content

DCP (wt %)	$T_{c\text{-PHBV}}$ (°C)	$T_{c\text{-PBS}}$ (°C)	$T_{cc\text{-PHBV}}$ (°C)	$T_{g\text{-PHBV}}$ (°C)	$T_{m\text{-PHBV}}$ (°C)	$T_{m\text{-PBS}}$ (°C)	$X_{c\text{-PBS}}$ (%)	$X_{c\text{-PHBV}}$ (%)
0.0	65	47	49	-1	169	114	36	13
0.2	63	82	46	-1	167	112	27	24
0.5	52	82	44	-1	164	110	27	26
1.0	50	75	41	-1	161	108	23	25

$T_{c\text{-PHBV}}$: crystallization peak temperature of PHBV; $T_{c\text{-PBS}}$: crystallization peak temperature of PBS; $T_{cc\text{-PHBV}}$: cold crystallization peak temperature of PHBV; $T_{g\text{-PHBV}}$: glass transition temperature of PHBV; $T_{m\text{-PHBV}}$: melting peak temperature of PHBV; $T_{m\text{-PBS}}$: melting peak temperature of PBS; $X_{c\text{-PHBV}}$ and $X_{c\text{-PBS}}$: crystallinity of PHBV and PBS, respectively, calculated via eq. (1).

direct evidence is given by the POM observation (to be discussed below) that PBS showed faster crystallization prior to the PHBV. Although the content of PBS in the blends is only 20 wt %, it was the PBS component that dominantly crosslinked leading to the faster crystallization.^{11,15} Consequently, the peaks b_0 and c_0 (Figure 1) become weak and even disappear with increasing the DCP content. The peaks b_1 , c_1 , d_1 , and e_1 in Figure 1 are mainly associated with the PHBV matrix. The crystallization peak of PHBV in the blend (peak b_1 , Figure 1) becomes pronounced after addition of a small amount of DCP, meanwhile the cold crystallization peak ($T_{cc-PHBV}$, Figure 2) gets weak and shifts to lower temperatures. As a consequence, the crystallinity of PHBV (X_{c-PHBV} , Table I) is increased after the partial crosslinking. Such crosslink enhanced crystallization was reported in other polymers as well.^{27–29} Conversely, overloading of DCP compromised the crystallization of PHBV and PBS in the blends. Hence, the crystallization peaks d_1 and d_2 decreased to e_1 and e_2 , respectively, when the DCP content was increased from 0.5 to 1.0 wt %. It has to be remarked that the crystallization processes of the two components are not completely separated.

The melting temperatures of PHBV and PBS in the blends decrease with DCP content (Figure 2) due to the imperfection of crystals which relate to branched/crosslinked polymer chains.^{15,30–32} The glass transition process of PHBV became less pronounced without changing the glass transition temperature (T_{g-PHBV} , Figure 2). These results indicate that local mobility of the PHBV segments is not obviously affected because of low gel fraction and low PHBV fraction in the gel (Supporting Information Figure S1).¹¹

Crystallization and Melting Behavior of PHB/PBS/DCP Blends

PHB is a homopolymer in poly(hydroxyalkanoate)s (PHA) family. As a complement to the PHA/PBS systems, the overall crystallization behavior of partially crosslinked PHB/PBS blends with varying PBS contents were studied, as shown in Figure 3. The corresponding thermal parameters from DSC measurements are summarized in Table II. The gel fraction of these samples with 0.5 wt % DCP is provided as Supporting Information (Figure S2).

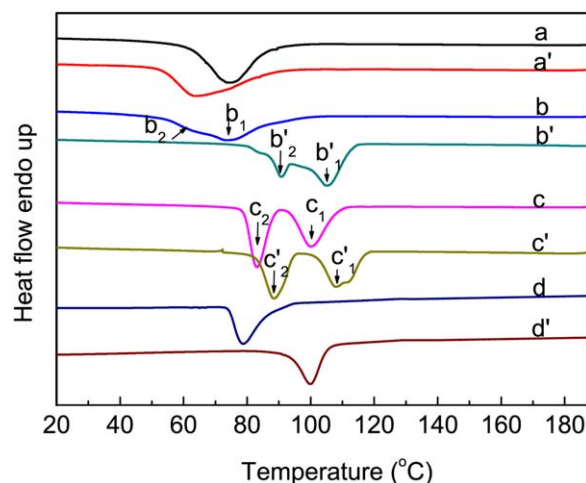


Figure 3. DSC cooling curves of (a) PHB, (a') PHB with 0.5 wt % DCP, (b) PHB/PBS (70/30, wt/wt), (b') PHB/PBS (70/30, wt/wt) with 0.5 wt % DCP, (c) PHB/PBS (50/50, wt/wt), (c') PHB/PBS (50/50, wt/wt) with 0.5 wt % DCP and (d) PBS and (d') PBS with 0.5 wt % DCP. Peaks b_1 , b'_1 , c_1 , and c'_1 mainly correspond to the crystallization of PHB phase while peaks b_2 , b'_2 , c_2 , and c'_2 mainly represent the crystallization of PBS component in the blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The crystallization temperature (T_c) of neat PHB was decreased, as shown in Figure 3(a,a'). This is probably due to degradation and very low gel fraction of neat PHB (0.5%) after addition of 0.5 wt % DCP. In contrast, the T_c of neat PBS was considerably increased after addition of DCP [Figure 3(d,d')]. Interestingly, the crystallization of both PHB and PBS in their blends was enhanced by the partial crosslinking. As shown in Figure 3(b,b' and c,c'), the T_c of PHB was increased by 10–30°C while the T_c of PBS was increased by 5–25°C after addition of 0.5 wt % DCP in the PHB/PBS blends. These results are similar as crystallization of the partially crosslinked PHBV/PBS blends. A notable difference is that PBS crystallized prior to PHBV in the partially crosslinked PHBV/PBS (80/20, wt/wt) blends whereas PHB crystallized prior to PBS in the studied PHB/PBS blends

Table II. Thermal Parameters of PHB, PBS, and PHB/PBS Blends with Different DCP Content

Samples	PHB					PBS				
	T_c , °C	T_{onset} , °C	t_c , min	T_m , °C	X_c , %	T_c , °C	T_{onset} , °C	t_c , min	T_m , °C	X_c , %
PHB	74	86	2.3	162	58					
PHB + DCP 0.5 wt %	64	87	3.4	163	51					
PHB/PBS (70/30)	74	90		170	54	64			113	36
PHB/PBS (70/30) + DCP 0.5 wt %	105	113		169	52	90			111	29
PHB/PBS (50/50)	100	108	1.4	172	55	83	88	0.9	113	30
PHB/PBS (50/50) + DCP 0.5 wt %	108	117	1.5	168	51	88	94	1.1	111	30
PBS						79	88	1.4	113	30
PBS + DCP 0.5 wt %						100	105	1.1	112	28

T_c is the crystallization peak temperature; T_{onset} is the onset crystallization temperature; T_m is melting peak temperature; X_c is the crystallinity calculated via eq. (1); t_c is the overall crystallization time calculated via $t_c = (T_{onset} - T_{offset})/\beta_0$, where β_0 is the cooling rate and T_{offset} are the offset temperature of crystallization. The higher melting peak temperature was taken as the T_m in the case of double melting behavior. The X_c obtained from double melting peaks is not so accurate because of the melt/recrystallization/remelt mechanism.

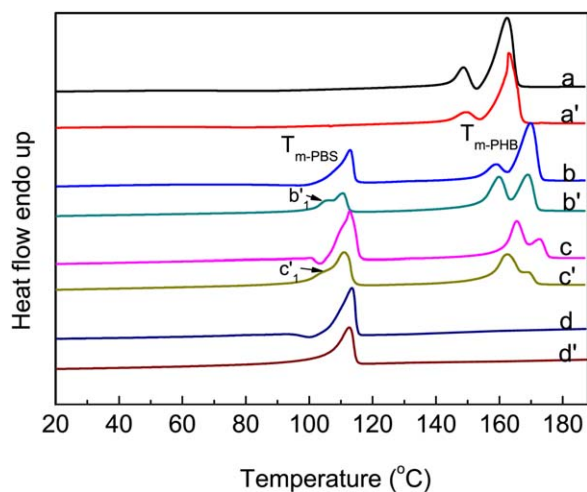


Figure 4. The second DSC heating curves of (a) PHB, (a') PHB with 0.5 wt % DCP, (b) PHB/PBS (70/30, wt/wt), (b') PHB/PBS (70/30, wt/wt) with 0.5 wt % DCP, (c) PHB/PBS (50/50, wt/wt), (c') PHB/PBS (50/50, wt/wt) with 0.5 wt % DCP, and (d) PBS, (d') PBS with 0.5 wt % DCP. The endothermic peaks around 110°C correspond to the PBS phase (T_{m-PBS}) while the endothermic peaks around 170°C represent the PHB component in the blends (T_{m-PHB}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which is in agreement with a previous study.²³ This difference is ascribed to the fact that PHB homopolymer crystallizes faster than PHBV copolymer. The crystallization rate can also be evaluated by the overall crystallization time (t_c) which was obtained via $t_c = (T_{onset} - T_{offset}) / \beta_0$, where β_0 is the cooling rate, T_{onset} and T_{offset} are the onset and offset crystallization temperature, respectively. Although T_c of the PHB and PBS in their blends increased after addition of 0.5 wt % DCP, the t_c (Table II) did not change so much. Thus, the partial crosslinking affected the nucleation process rather than the crystal growth.

The subsequent DSC heating curves of PHB, PBS, and PHB/PBS blends after the nonisothermal crystallization are shown in Figure 4. The corresponding thermal parameters are listed in Table II. Small changes in melting temperatures of PHB and PBS in the blends are detected after addition of 0.5 wt % of DCP. Meanwhile, double melting peaks (or one main peak with a weak shoulder) of PHB are observed in the PHB/PBS blends. Double melting peaks are generally associated with a melt/recrystallization/remelt mechanism.^{33,34} The lower melting temperature peak of PHB in the blends became more pronounced after addition of DCP [Figure 4(b,b' and c/c')]. Meanwhile, weak shoulders (b'₁ and c'₁) on the lower temperature side of PBS melting peaks [Figure 4(b' and c')] were detected. These results indicated that percentage of imperfect crystals in the PHB/PBS blends was increased after the partial crosslinking.

Mechanism Discussion of the Enhanced Crystallization in the Partially Crosslinked PHB(V)/PBS/DCP Blends

In general, the mobility of polymer chains/segments increases with temperature. The partially crosslinked chains/segments remain certain mobility, however, the mobility is lower than

that of linear chains/segments at the same temperature. To obtain the same mobility, partially crosslinked polymer chains/segments need a higher temperature in comparison with linear ones.

Polymer crystallization includes nucleation and crystal growth. The nucleation can be promoted by addition of heterogeneous nuclei, more pronounced at high temperatures. To be effective, the nuclei need to exceed a critical size (r^*) characterized by $r^* = 2\sigma / \Delta G_v$, where σ is the Gibbs free surface/interface energy (enthalpy) per unit area and ΔG_v (expressed per unit volume) stands for the free enthalpy of crystallization of a nucleus of crystal size which is the driving force of nucleation.³⁵ The overall crystallization rate is dominated by the thermodynamic and kinetic reasons at high and low temperatures, respectively.

At high temperature, free linear chains are too mobile to easily form stable nuclei with a sufficient size (r^*). As discussed, the chains/segments bonded to the crosslink points have less mobility than free linear chains/segments at the same temperature. So the bonded chains/segments may pack first at high temperatures. The packed chain units could act as nucleating agents and initiate the subsequent crystallization of (linear) chains. Conversely, the diffusion and packaging of polymer chains would be an issue if the mobility is too low. Consequently, the crystallinity of PBS is reduced after the partial crosslinking even the nucleation is promoted (Table I). The crystallization of PHBV in this system is more complicated as the PBS crystallized prior to the PHBV. The crystallization of PHBV could be affected by the precrystallized PBS phase and the partially crosslinked structure.

Spherulitic Morphology of the PHBV/PBS/DCP Blend

The spherulitic morphology of the partially crosslinked PHBV/PBS blends was studied using POM at 120°C (Figure 5) and 100°C (Figure 6), respectively. The temperature of 120°C was chosen to allow crystallization of PHBV only while PBS was still in the molten state. It is clearly seen from Figure 5 that typical spherulites of PHBV were formed in all the blends. However, the spherulitic density was increased after the partial crosslinking, indicating an enhanced nucleation effect. These results are in consistent with above DSC results and proposed mechanism.

The temperature of 100°C allows the crystallization of both PHBV and PBS. The big spherulites are associated with PHBV while the bright tiny spots represent PBS crystals [Figure 6(a)]. The spherulitic morphology of PBS in the blends was changed significantly after addition of DCP. Cloud-like and fibril-like crystals were observed in the compatibilized blends, corresponding to the partially crosslinked PBS phase [Figure 6(b-d)]. Similar morphology was also observed in partially crosslinked neat PBS.¹⁵ Both bright tiny spots and cloud-like crystals are detected at low DCP content [0.2 wt %. Figure 6(b)], indicating a transition of the morphology. In this study, few PHBV spherulites were observed in the early stage, accompanied by a quick formation of cloud-like crystals in partially crosslinked samples. Conversely, few PHBV spherulites were accompanied by a slow growth of PBS spherulites in the physically blended sample.

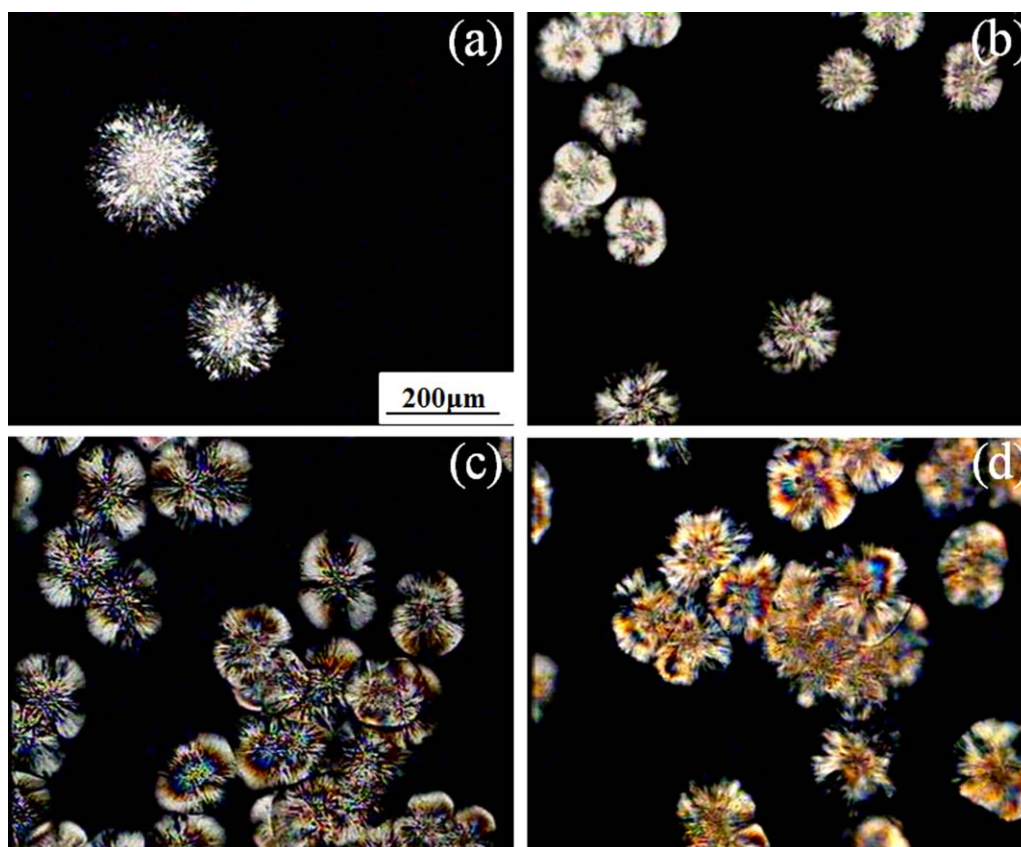


Figure 5. POM images (same magnification, scale bar = 100 μm) of PHBV spherulites in the PHBV/PBS (80/20, wt/wt) blends with DCP content of: (a) 0.0, (b) 0.2, (c) 0.5, and (d) 1.0 wt %. The samples were cooled from 200° to 120°C at a cooling rate of 60°C/min. The images were taken at around 15 min after isothermal crystallization at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Assume that the crosslink points are capable of fabrication of nuclei, then countless nuclei/spherulites would be formed, leading to a significant reduction in interspherulite distance (i.e., surface-to-surface distance between neighboring spherulites). In addition, the partial crosslinking leads to decreases in PBS particle size (up to 200 nm) and interparticle distance.¹¹ This may also result in a larger number of PBS spherulites and smaller interspherulite distance. Moreover, the PBS domains interconnected to each other after the partial crosslinking. Therefore, the increased number of spherulites, decreased interspherulite distance and interconnection of the PBS domains could be responsible for the cloudlet-like morphology of PBS crystals.

Crystalline Form Analysis of the PHBV/PBS/DCP Blend

The effect of partial crosslinking on the crystal structure of the PHBV, PBS, and PHBV/PBS blends was studied using WAXD to get a deeper insight into the crystallization behavior of these samples. The WAXD patterns of PHBV and PBS before and after addition of DCP were shown in Figure 7. Two specific peaks ($2\theta = 13.4$ and 16.8°) of PHBV corresponding to the [020] and [110] lattices,^{36,37} and three specific peaks ($2\theta = 19.7$, 22 , and 22.8°) of PBS corresponding to the [020], [021], and [110] lattices, respectively, are detected.^{38,39} The WAXD patterns of partially crosslinked PHBV and PBS with 0.5 wt % DCP are very close to those of the neat PHBV and PBS, respectively.

These results indicate that the crystalline forms of neat PHBV and PBS were not modified by the partial crosslinking.

The WAXD patterns of PHBV/PBS (80/20, wt/wt) blends with different DCP contents are shown in Figure 8. The peak positions (2θ) of PHBV and PBS WAXD patterns did not change after blending and addition of the DCP, meanwhile no new peaks were detected. These results confirm that the crystalline forms of PHBV and PBS were not modified by the partial crosslinking in their blend. However, the intensity of the two diffraction peaks of PHBV (i.e., $2\theta = 13.4^\circ$ and 16.8°) increased and became sharper after addition of the DCP. These results demonstrate that the crystallization of PHBV was promoted in the [020] and [110] lattices. Similar phenomena are observed for the PBS component in the blends as well. The WAXD results are in accordance with the DSC and POM analysis, that is, the partial crosslinking accelerated the crystallization of PHBV and PBS in their blends.

CONCLUSIONS

Partially crosslinked PHBV/PBS and PHB/PBS blends were prepared via melt compounding with DCP. The partial crosslinking increased the nuclei density of both PHBV and PBS in their blends. Consequently, the crystallization of PHBV and PBS in their blends was enhanced by the partial crosslinking. As a result, a higher crystallinity of PHBV and a higher crystallization

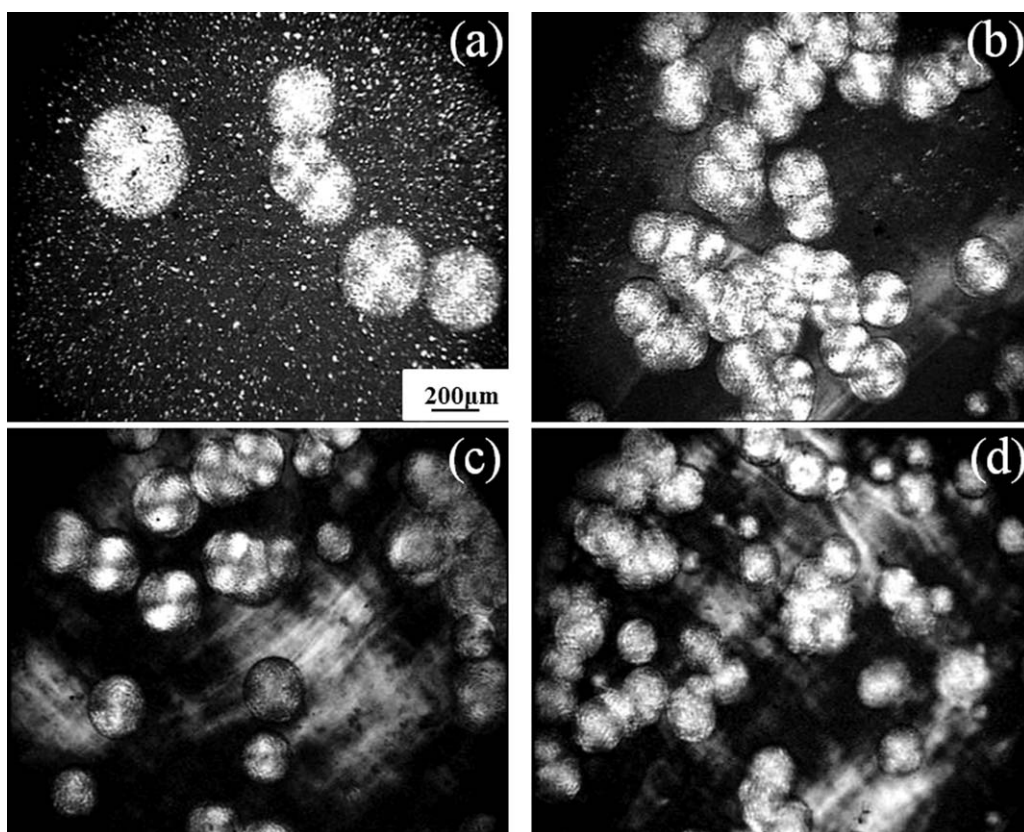


Figure 6. POM images (same magnification, scale bar = 200 μm) of PHBV spherulites in the PHBV/PBS (80/20, wt/wt) blends with DCP content of: (a) 0.0, (b) 0.2, (c) 0.5, and (d) 1.0 wt %. The samples were cooled from 200 to 100°C at a cooling rate of 60°C/min. The images were taken at around 10 min after isothermal crystallization at 100°C.

temperature (T_c) of PBS were obtained. The PBS spherulitic morphology was changed and turned to be cloud-like morphology after addition of the DCP. However, no modification on the crystalline form of the PHBV and PBS was observed after the partial crosslinking. In addition, the overall crystalli-

zation of PHB (homopolymer) and PBS in the PHB/PBS blends was also accelerated by the partially crosslinking. This investigation provides a deeper insight into the partially crosslinked PHBV/PBS and PHB/PBS blends which were reported previously.¹¹

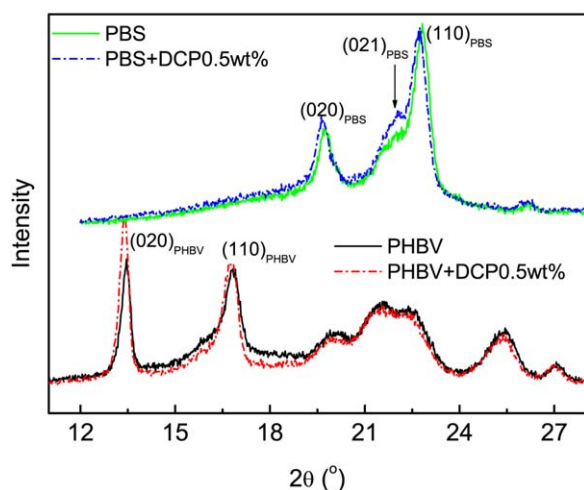


Figure 7. WAXD patterns of PHBV and PBS without and with 0.5 wt % of DCP. The patterns were shifted in y -axis for a better comparison. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

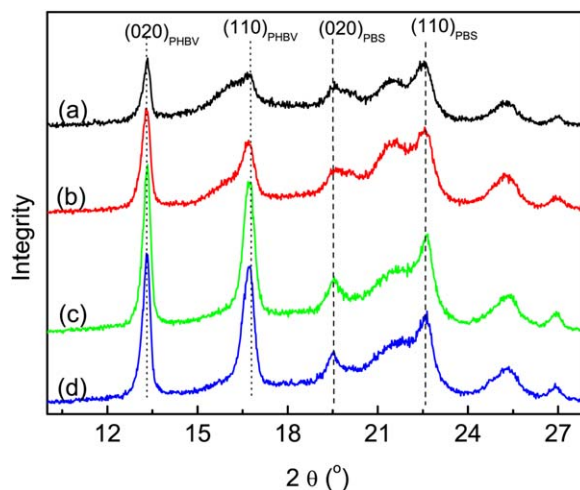


Figure 8. WAXD patterns of PHBV/PBS (80/20, wt/wt) blends with DCP content of (a) 0.0, (b) 0.2, (c) 0.5, and (d) 1.0 wt %. The patterns were shifted in y -axis for a better comparison. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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