# Miscibility and Crystallization Behavior of Biodegradable Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/Phenolic Blends

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**ABSTRACT:** Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV)/phenolic blends are new miscible crystalline/amorphous polymer blends prepared via solution casting method in this work, as evidenced by the single composition dependent glass transition temperature. The measured $T_g$s can be well fitted by the Kwei equation with a $q$ value of 13.6 for the PHBV/phenolic blends, indicating that the interaction between the two components is strong. The negative polymer–polymer interaction parameter, obtained from the melting depression of PHBV using the Nishi-Wang equation, indicating the thermal miscibility of PHBV and phenolic. The spherulitic morphology and crystal structure of PHBV/phenolic blends were studied with polar optical microscopy and wide angle X-ray diffraction compared with those of neat PHBV. It is found that the growth rates of PHBV in the blends are lower than that in neat PHBV at a given crystallization temperature, and the crystal structure of PHBV is not modified by the presence of phenolic in the PHBV/phenolic blends, but the crystallinity decrease with the increasing of phenolic. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2781–2786, 2012

**Key words:** miscibility; morphology; PHBV; phenolic; blends

## INTRODUCTION

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is the most well known member of the bacterial polyester family and has been commercially available under the trade name Biopol since the early 1980s.[1] The crystal structure and crystallinity of PHBV have been investigated by X-ray diffraction. It is found that the PHBV samples with compositions from 0 to 37 mol % HV crystallized in the poly(3-hydroxybutyrate) (PHB) lattice.[2–7] And PHBV samples show a high crystallinity (>50%) throughout a wide range of compositions from 0 to 95 mol % 3HV.[2,4]

Compared to the conventional thermoplastics, PHBV suffers from some disadvantages such as its brittleness, narrow processing window, and high cost that prevent wider application. Blending with second polymer can offer opportunities for lower costs and enlarge the range of applicability of these biopolymers, without impairing their desirable properties. PHBV is miscible with many polymers such as poly (*p*-vinylphenol) (PVPh), poly (epichlorohydrin-*co*-ethylene oxide) (PECH-EO), poly(vinyl acetate) (PVAc) as evidenced by a single composition dependent glass transition temperature.[8–10] On the other hand, PHBV is immiscible with ethylene-vinyl acetate copolymer (EVA) (containing 28 mol % vinyl acetate), poly(ethylene succinate) (PES), poly(propylene carbonate)(PPC), poly(butylene succinate) (PBSU), and poly(vinylidene fluoride) (PVDF).[11–15]

Phenolic resin contains a high density of hydroxyl groups that are able to interact with numerous other polymers through hydrogen bonding. Phenolic is miscible with many polymers such as poly(ε-caprolactone) (PCL), poly(acetoxystyrene) (PAS), poly(vinylpyridines) (PVP), poly(vinyl acetate) (PVAc), and poly(methyl methacrylate) (PMMA).[16–20] The miscibility of polymer blends containing phenolic usually arises from the hydrogen bonding interaction between the hydroxyl group of phenolic and other groups of the partners, such as the carbonyl group. To our knowledge, PHBV/phenolic blends have not been reported so far. In this work, miscibility and crystallization of PHBV/phenolic blends were studied in detail.
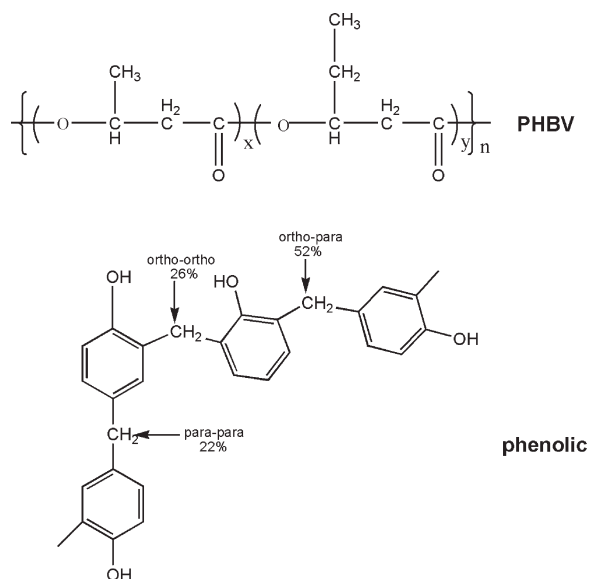
## EXPERIMENTAL

### Materials and preparation of PHBV/phenolic blends

PHBV ($M_w = 6.24 \times 10^5$), a copolymer with 5 wt % HV content, was purchased from Aldrich Chemical.

**Scheme 1** Chemical structures of PHBV and phenolic.

The novolac type phenolic resin used in this work was synthesized with sulfuric acid via a condensation reaction ($M_w$ = 2400), and consists of phenol ring bridge-linked randomly by methylene groups with 26% *ortho*-ortho, 52% *ortho*-para, 22% *para*-para determined by solution ^{1}H nuclear magnetic resonance (NMR).[21] The chemical structures of PHBV and phenolic are shown in Scheme 1.

PHBV/phenolic blends were prepared with mutual solvent *N,N*-dimethylformamide (DMF). The solution of both polymers was cast on a petri dish at room temperature and was allowed to evaporate in a controlled air stream for 1 day. The resulting films were further dried in vacuum at 80°C for 3 days. In this way, PHBV/phenolic blends were prepared with various compositions ranging from 90/10 to 15/85 in weight ratio, the first number referring to PHBV.

## Characterizations

The glass transition temperature ($T_g$) and melting point ($T_m$) of the melt-quenched PHBV/phenolic blends were measured by a TA instruments differential scanning calorimetry (DSC) Q100 with a Thermal Analyst 2000 at a heating rate of 20°C min$^{-1}$. The samples were first annealed at 190°C for 3 min to erase any thermal history and subsequently quenched at a cooling rate of 100°C min$^{-1}$ to −50°C. For the isothermal melt crystallization, the samples were first annealed at 190°C for 3 min to erase any thermal history, cooled quickly to the crystallization temperature ($T_c$), and then maintained at $T_c$ for a period of time until the crystallization was complete. And the subsequent melting curves were also recorded to get the information of $T_m$ of PHBV at 20°C min$^{-1}$.

Spherulitic morphology and growth rate of PHBV were observed with a polarizing optical microscopy (POM) (Olympus BX51) equipped with a Linkam THMS600 hot stage. The samples were heated to 190°C at 40°C min$^{-1}$, held for 3 min to erase any thermal history, and then cooled to the designated crystallization temperature for the isothermal crystallization at 60°C min$^{-1}$.

Wide angle X-ray diffraction (WAXD) was performed on an X-ray Diffractometer (Rigaku D/Max 2500 VB2t/PC) at 40 kV and 200 mA from 5° to 50° at a scanning rate of 2° min$^{-1}$. The samples for the WAXD experiments were prepared as follows. The samples were first pressed into films with thickness around 1 mm on a hot stage at 190°C and then transferred into an oven at 115°C for 3 days.

## RESULTS AND DISCUSSION

### Miscibility study based on the glass transition temperature analysis

Miscibility of PHBV/phenolic blends in the amorphous state was studied in detail by DSC in this work. Figure 1 shows the DSC traces of the melt-quenched samples of neat PHBV, neat phenolic, and their blends at a heating rate of 20°C min$^{-1}$. Neat PHBV is a semicrystalline polymer with a $T_g$ of about −2.0°C, a cold crystallization temperature ($T_{cc}$) of ~ 58.0°C and a $T_m$ of ~ 153.2°C, while neat phenolic is an amorphous polymer with a $T_g$ of ~ 51.9°C. All the PHBV/phenolic blends exhibit a single composition dependent $T_g$ between those of the two individual polymers; and the values of $T_g$ increase with increasing the phenolic content in the blends, suggesting that PHBV is miscible with phenolic over the whole composition range in the amorphous region. The miscibility of PHBV/phenolic
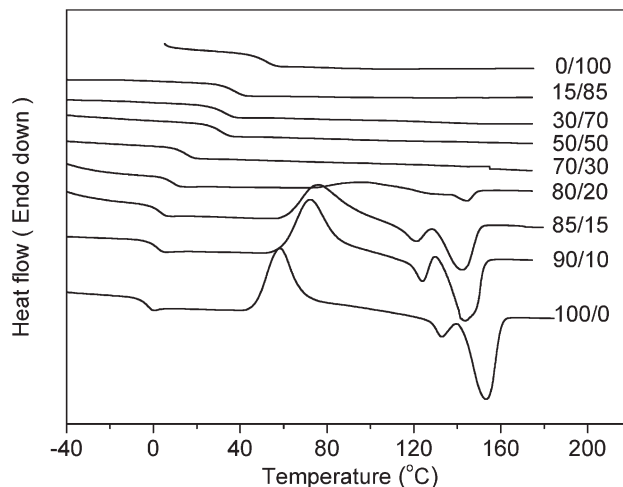


**Figure 1** DSC traces of PHBV/phenolic blends for the melt-quenched samples at a heating rate of 20°C min$^{-1}$.
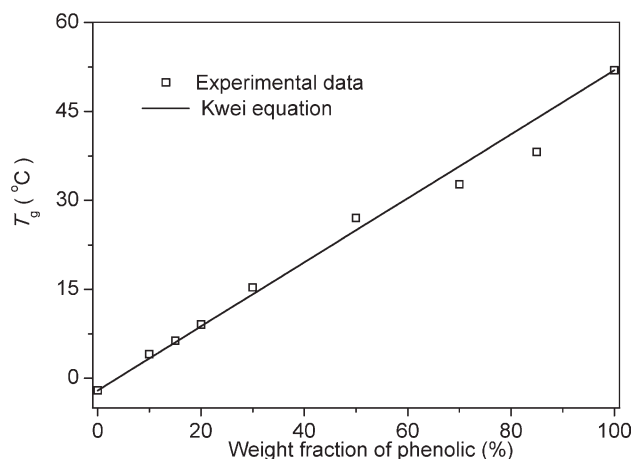
**Figure 2** Variation of $T_g$ of PHBV/phenolic blends as a function of the weight fraction of phenolic. (The solid line is based on the Kwei equation).

blends may arise from the formation of hydrogen bonding between the carbonyl group of PHBV and the hydroxyl group of phenolic. It is found that $T_{cc}$ of PHBV shifts from $\sim 58.0°C$ for neat PHBV to $\sim 95.6°C$ for the 80/20 blend; moreover, $T_{cc}$ can not be detected in the blends containing phenolic higher than 30 wt %, indicating that the cold crystallization of PHBV is retarded due to the presence of phenolic. $T_m$ of PHBV also shifts from $\sim 153.2°C$ for neat PHBV to $\sim 147.3°C$ for the 80/20 blend. When the amorphous phenolic content is higher than 30 wt %, $T_m$ of PHBV can not be detected in the blends. It is clear that blending with amorphous phenolic increases $T_g$ and $T_{cc}$ but reduces $T_m$ of PHBV in the PHBV/phenolic blends.

To show the variation of $T_g$ with weight fraction of phenolic clearly, Figure 2 summarizes the composition dependence of $T_g$ for the PHBV/phenolic blends. It is clear that PHBV/phenolic blends display a single composition dependent $T_g$, which increases with increasing the phenolic content.

Furthermore, the Kwei equation[22] is applied in this work to fit the variation of $T_g$ as a function of composition. The Kwei equation is as follows.

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2, \qquad (1)$$

where $W_1$ and $W_2$ are the weight fraction of two pure components, $T_{g1}$ and $T_{g2}$ are the respective $T_g$ of the neat component, $q$ is a parameter corresponding to the strength of hydrogen bonding in the blends, reflecting a balance between the breaking of the self-association and the forming of the interassociation hydrogen bonding, and $k$ is a fitting constant. As showed in Figure 2, the Kwei equation fits $T_g$ of PHBV/phenolic blends very well. In this work, a positive $q$ of 13.6 ($k = 1$) is obtained, which is greatly higher than that of $-10$ for PCL/phenolic blends and $-15.1$ for

PHBV/PECH-EO blends,[9,16,23] indicating that the interaction between PHBV and phenolic is stronger than that in the PCL/phenolic and PHBV/PECH-EO blends.

## The depression of equilibrium melting point of PHBV in the PHBV/phenolic blends

The melting point of a polymer is affected not only by the thermodynamic factors but also by the morphological factors such as crystalline lamellar thickness and the perfection of spherulites. Therefore, the equilibrium melting point ($T_m^o$) is introduced to separate the morphological effect from the thermodynamic effect in discussing the melting point depression as described by the Flory-Huggins theory.[24] $T_m^o$ can be derived from the Hoffmann-Weeks equation.[25]

$$T_m = \eta T_c + (1 - \eta) T_m^0, \qquad (2)$$

where $T_m$ is the apparent melting point, $T_c$ is the crystallization temperature, and $\eta$ may be regarded as a measure of the stability. The melting behavior of PHBV/phenolic blends after isothermal crystallization was studied with DSC. As an example, Figure 3 shows the melting behavior of a 90/10 blend crystallized isothermally at various $T_c$s. Two endothermic melting peaks are observed. The lower endothermic peak ($T_{m1}$) shifts to higher temperature range with increasing $T_c$ apparently. Moreover, the magnitude of the area of $T_{m1}$ increases and that of $T_{m2}$ decreases with the increase of $T_c$. This is also observed in the 85/15 and 80/20 blends. Such melting behavior can be explained by the melt-recrystallization model.[26,27] $T_{m1}$ is the melting of crystals formed during the isothermal crystallization process which are present prior to the heating scan, and dependent greatly on $T_c$; $T_{m2}$ is the melting of the crystals formed through the recrystallization during the
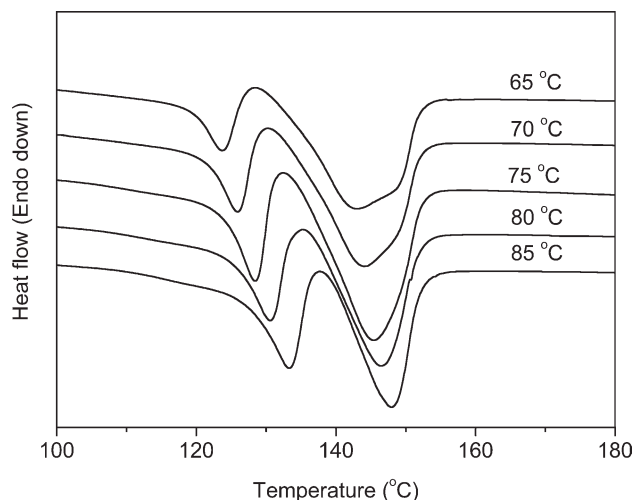


**Figure 3** Melting behavior of 90/10 isothermally crystallized at various $T_c$s from the melt.
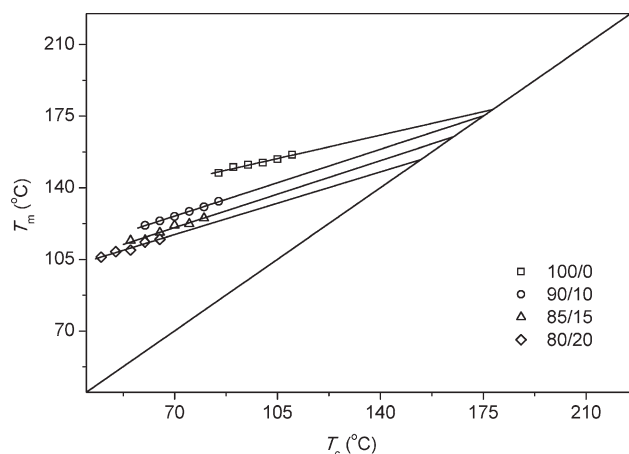
**Figure 4** Hoffman-Weeks plots of PHBV/phenolic blends for the estimation of the $T_m^o$s.

heating process. Therefore, $T_{m1}$ is used for the analysis of the Hoffman-Weeks equation. Figure 4 shows the Hoffman-Weeks plots for neat PHBV and the blends. From Figure 4, the values of $T_m^o$s are determined to be around 178.3, 175.3, 165.0, and 153.9°C for neat PHBV, 90/10, 85/15, and 80/20 blends, respectively. It is clear that $T_m^o$ of PHBV decreases with increasing the phenolic content. The depression of $T_m^o$ indicates again that PHBV and phenolic are miscible polymer blends. $T_m^o$s obtained on this study are further analyzed by the Nishi-Wang equation[28] based on the Flory-Huggins theory.[24]

$$\frac{1}{T_m^0(b)} - \frac{1}{T_m^0(p)} = -\frac{RV_2}{\Delta H^0 V_1}\left[\frac{\ln \phi_1}{m_2}\right.$$
$$\left. + (\frac{1}{m_2} - \frac{1}{m_1})\phi_1 + \chi_{12}\phi_1^2\right], \quad (3)$$

where $T_m^o$ (p) and $T_m^o$ (b) are the equilibrium melting points of the pure crystallizable polymer and of the blend, respectively. $\Delta H^0$ is the fusion heat of the perfectly crystallizable polymer per mole of the repeat unit, $V$ is the molar volume of the repeating units of the polymers, $m$ and $\phi$ are degree of polymerization and the volume fraction of the component in the blends, respectively. Subscripts 1 and 2 refer to the amorphous and crystalline polymer, respectively. $R$ is the universal gas constant, and $\chi_{12}$ is the polymer–polymer interaction parameter. When both $m_1$ and $m_2$ are large, for high molecular weight polymers, these related terms in eq. (3) can be neglected. The interaction parameter $\chi_{12}$ can thus be written as,

$$\frac{\Delta H^0 V_1}{RV_2}(\frac{1}{T_m^0(b)} - \frac{1}{T_m^0(p)}) = -\beta = \chi_{12}\phi_1^2. \quad (4)$$

To calculate the left-hand side term of eq. (4), the following parameters are used: $V_1 = 78.5$ cm$^3$ mol$^{-1}$,

$V_2 = 75.5$ cm$^3$ mol$^{-1}$ (calculated using $V_{PHB} = 75$ cm$^3$ mol$^{-1}$[29] and $V_{PHV} = 86.3$ cm$^3$ mol$^{-1}$[30]), and $\Delta H^0 = 9439.4$ J mol$^{-1}$.[31] The weight fraction of amorphous polymer is transformed to volume fraction. The plot of the left-hand of eq. (4) versus $\phi_1^2$ is shown in Figure 5, from which the value of $\chi_{12}$ is obtained as −4.7. The value of $\chi_{12}$ is negative, indicating that PHBV and phenolic are thermodynamically miscible. In the PHBV/phenolic blends, $\chi_{12}$ is lower, i.e., −0.075 in the PHBV/PECH-EO blends.[9] It indicates that the interaction between PHBV and phenolic is much stronger than those in the PHBV/PECH-EO blends. It should be noted that the $\chi_{12}$ value of −4.7 is relatively large, indicating that the interaction between PHBV and phenolic is very strong. Such result may be attributed to the fact that phenolic has so many hydroxyl groups that they can form strong hydrogen bonding with the carbonyl group of PHBV.

## Isothermal melt crystallization of neat and blended PHBV

Figure 6 shows POM images of neat and blended PHBV crystallized at 60°C. The spherulites of neat PHBV and the PHBV rich blends exhibit Maltese crosses with different band spacings. The band spacing of neat PHBV at 60°C is about 13 μm, while that for the 85/15 blend is nearly 4 μm. Banded spherulites are believed to arise from the twisting of lamellae. However, it is still an open question about the origin of lamellae twisting.[32–35] The fact that PHBV spherulites are space-filling indicates that phenolic is rejected in the crystallization process as a noncrystallizable component and resides primarily in the interlamellar and interfibrillar domains of the PHBV spherulites.

The spherulitic growth rates of neat and blended PHBV at 60°C were also observed. The spherulitic
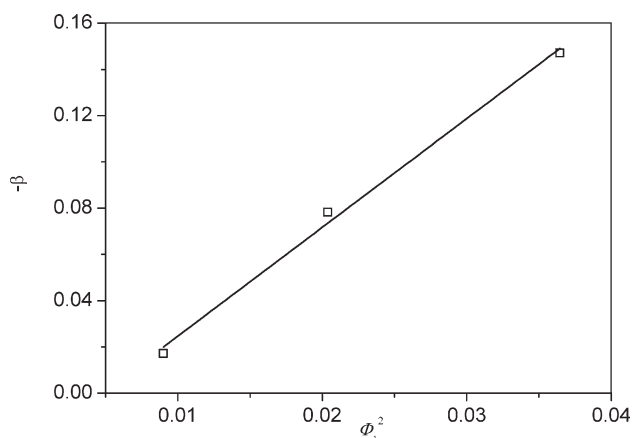


**Figure 5** Nishi-Wang plots for the calculation of the polymer-polymer interaction parameter of PHBV/phenolic blends.
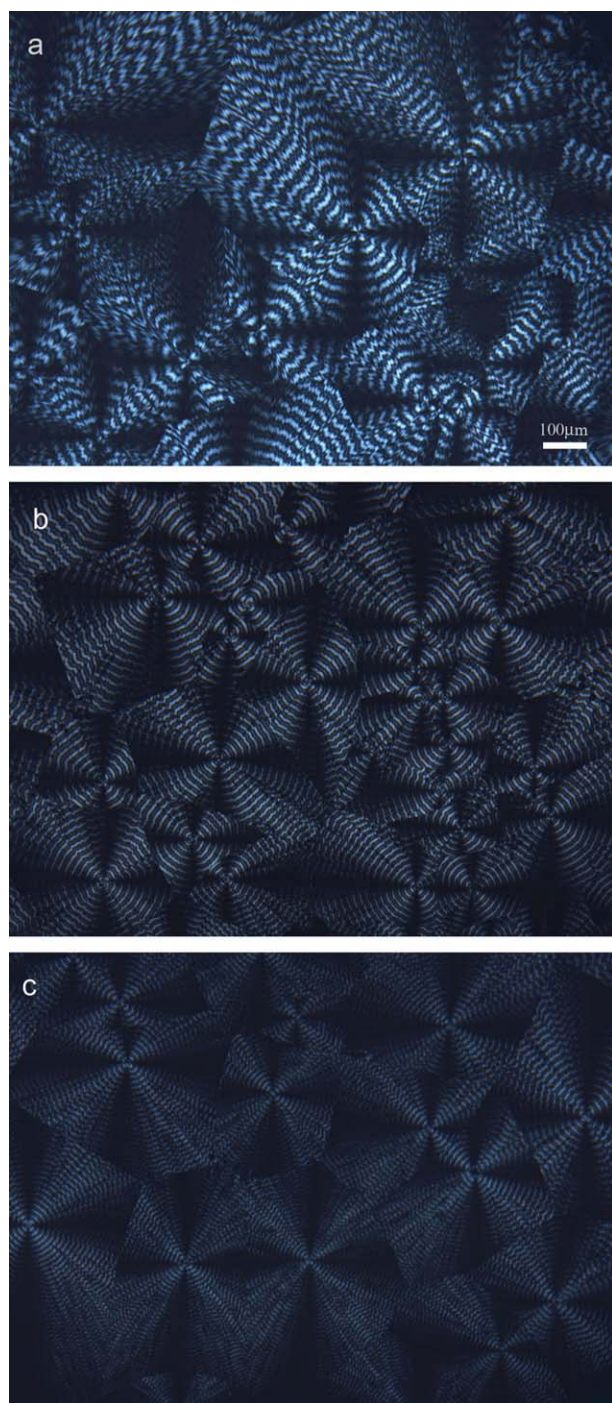
**Figure 6** POM graphs (same magnification with bar = 100 μm) of the spherulitic morphology of PHBV crystallized at 60°C in the PHBV/phenolic blends; (a) 100/0, (b) 90/10, (c) 85/15. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

growth rates are 51.5, 32.0, 27.7, and 6.0 μm min$^{-1}$ for 100/0, 90/10, 85/15, and 80/20 blend, respectively. The rates of nucleation and crystal growth of PHBV/phenolic blends are much slower than those of neat PHBV. It is found that the spherulitic growth rates decrease with the addition of phenolic at the same temperature. The reduction of the growth rate

of PHBV spherulites in the blend may be attributed to the following two factors. First, the addition of high $T_g$ component phenolic increases $T_g$s of the PHBV/phenolic blends, resulting in the decrease of the mobility of PHBV in blends compared with that of neat PHBV. Second, the presence of phenolic may play a role as a diluent to PHBV in the miscible blends, resulting in the dilution of PHBV chains at the spherulites growth front.[36,37]

Figure 7 shows the WAXD patterns of neat and blended PHBV crystallized at 115°C. It can be seen from Figure 7 that both neat and blended PHBV exhibit almost the same diffraction peaks at the same location. However, the intensity of the diffraction peaks decreases with the addition of phenolic. Computer peak splitting program was used to calculate the degree of absolute crystallinity ($X_t$). The results show that the values of $X_t$ are 62.3, 60.0, 50.2, and 36.2% for 100/0, 90/10, 85/15, and 80/20, respectively. The results indicate that blending with amorphous phenolic does not modify the crystal structure of PHBV but decreases the crystallinity of PHBV in the blend.

## CONCLUSIONS

PHBV/phenolic blends are new miscible crystalline/ amorphous polymer blends as evidenced by the single composition dependent glass transition temperature. The measured glass transition temperatures can be well fitted by the Kwei equation with a $q$ value of 13.6 for the PHBV/phenolic blends, indicating that the interaction between the two components is strong. The negative polymer–polymer interaction parameter, obtained from the melting depression of PHBV using the Nishi-Wang equation, indicates that the interaction between PHBV and phenolic are thermal dynamic miscible. The banded spherulites still exist in the PHBV/phenolic blends,
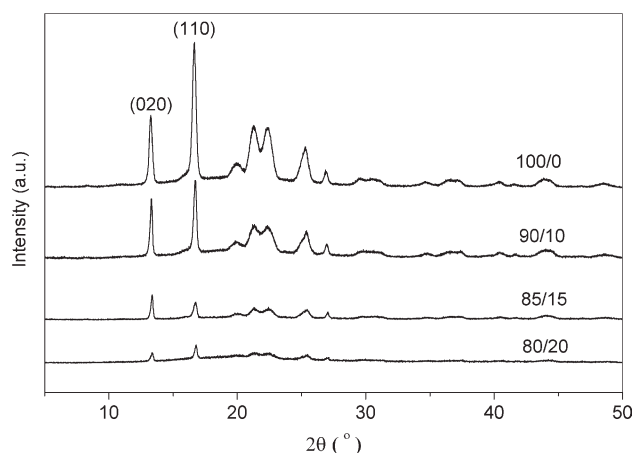


**Figure 7** WAXD patterns of neat PHBV and the blends crystallized at 115°C for 3 days.

but the band spacing decreases with the addition of phenolic. The growth rate of PHBV in the blends was slower than that in neat PHBV at a given crystallization temperature. The crystal structure of PHBV is not modified by the presence of phenolic in the PHBV/phenolic blends, but the crystallinity decrease with the increasing of phenolic.

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