



Polymer Communication

Spherulitic morphology and growth of poly(vinylidene fluoride)/poly(3-hydroxybutyrate-*co*-hydroxyvalerate) blends by optical microscopy

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Abstract

Poly(vinylidene fluoride) (PVDF) and poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), both semicrystalline polymers, are miscible as shown by the single glass transition temperature over the entire composition range. Morphology of PVDF/PHBV blends was investigated by optical microscopy under two different crystallization conditions. PVDF showed the spherulitic morphology at 150 °C in the PVDF/PHBV blends, where PHBV acted as the noncrystallizing component. PHBV also showed the spherulitic morphology within the matrix of the pre-existing PVDF crystals when PVDF/PHBV blends were quenched from the melt to the crystallization temperature below the melting point of PHBV. The spherulitic growth of PHBV was investigated as the function of both blend composition and crystallization temperature.

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1. Introduction

Polymer properties can be modified extensively by blending. Miscibility of polymer blends has been studied extensively in mixtures of two amorphous polymers, or mixtures in which one of the components is crystalline. However, miscible blends of two crystalline polymers have received much less attention than fully amorphous or amorphous/crystalline systems. This special kind of blends of two crystalline polymers can provide various conditions to study the crystallization behavior and morphology in polymer blends since both components are able to crystallize. The crystallization and morphology of miscible crystalline/crystalline blends are far away from being really understood though some related works have been published in the literature [1–25]. Particularly much less attention has been paid to the crystallization and morphology of the

second component, usually the low melting point (T_m) component with slow crystallization rate, because it was not only affected apparently by the blend composition and the thermal conditions but also affected strongly by the pre-existing crystals of the first component, usually the high- T_m component with fast crystallization rate.

Poly(vinylidene fluoride) (PVDF) and poly(hydroxybutyrate) (PHB) are miscible, and the crystallization and morphology of PVDF/PHB blends have been investigated by differential scanning calorimetry, optical microscopy and small angle X-ray scattering [4,6]. Thus PVDF/poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) may be a new ideal system of miscible blends of two crystalline polymers because PHBV is a random copolymer of PHB and poly(hydroxyvalerate) (PHV). However, such kind of work has not been reported so far in the literature. Our research group has been doing some work on the miscibility and crystallization behavior in crystalline/crystalline polymer blends [19–25]. The purpose of the present study is to continue to investigate the miscibility and crystallization behavior of crystalline/crystalline blends to get a better understanding of the nature of this special kind of polymer

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blends. In this communication, we choose PVDF and PHBV as the blend system. The two polymers are both crystalline in their neat state, which undergo crystallization over a wide range of temperature. Although the difference in the melting points between PVDF (ca. 170 °C) and PHBV (ca. 150 °C) is only 20 °C, the simultaneous crystallization of the two components is impossible because the disparity in crystallization rate between PVDF and PHBV is very large. PHBV is basically an amorphous diluent throughout the crystallization of PVDF, which is similar to the crystallization process of PVDF/PHB blends [6]. Therefore, two crystallization conditions were adopted in this work to study the crystallization and morphology of PVDF/PHBV blends. One was to crystallize PVDF at 150 °C. In this case PHBV was still in the melt, and the crystallization of PVDF corresponded to the transition from the fully amorphous to the amorphous/semicrystalline state. The other was to quench the PVDF/PHBV blends from the homogeneous melt directly to the crystallization temperatures T_c below the T_m of PHBV. In this case, PVDF always crystallized during the quenching process before T_c was reached, and PHBV crystallized in the matrix of the pre-existing PVDF crystals. The crystallization of PHBV corresponded to the transition from the amorphous/semicrystalline to semicrystalline/semicrystalline state.

2. Experimental

PVDF ($M_w = 140,000$) and PHBV ($M_w = 454,000$, $M_n = 153,000$ and HV% = 14) were purchased from Polysciences, Inc and Aldrich Chemical Company Inc., respectively. PVDF/PHBV blends were prepared with mutual solvent *N,N*-dimethylformamide at an elevated temperature. The solution of both polymers (0.02 g/ml) was cast on glass plate at room temperature. The solvent was allowed to evaporate in a controlled air stream for 1 day and the resulting films were further dried in vacuum at 50 °C for 3 days. In this way, blends were prepared with various compositions ranging from 80/20 to 20/80 in weight ratio, the first number referring to PVDF.

The glass transition temperature (T_g) of the melt-quenched PVDF/PHBV blends was measured by a TA Instruments differential scanning calorimetry (DSC) 2910 with a Thermal Analyst 2000 at 20 °C/min. The samples were first annealed at 200 °C for 3 min to destroy any thermal history and subsequently quenched into liquid nitrogen. The spherulitic growth was observed with a polarizing microscope (Olympus BHA-P) equipped with a first order retardation plate and a temperature controller (Linkam LK-600PM). The sample was first held at 200 °C for 3 min to destroy any thermal history and then quenched to crystallization temperature T_c at a cooling rate of 100 °C/min. The spherulitic growth rate G was calculated from the change of radius R with time t , i.e. $G = dR/dt$.

3. Results and discussion

3.1. Miscibility study of PVDF/PHBV blends by DSC

The miscibility of PVDF/PHBV blends was studied by measuring the T_g with DSC. As introduced in the experimental part, the samples were first annealed at 200 °C for 3 min to destroy any thermal history and then quenched into liquid nitrogen as quickly as possible. The melt-quenched samples were transferred quickly into the DSC cell, which had been set below –100 °C in advance. The samples were heated to 200 °C at a heating rate of 20 °C/min. Neat PVDF has a T_g of ca. –35 °C and a T_m of 171.2 °C. Neat PHBV has a T_g of ca. –1 °C, a cold crystallization temperature of 69 °C and a T_m of 150.2 °C with a shoulder at 132.3 °C. In the PVDF/PHBV blends, only a single composition dependent T_g can be detected. The T_m of PHBV was masked with that of PVDF and was not able to exhibit as a separate melting peak. Fig. 1 summarizes the variation of T_g of PVDF/PHBV blends and the T_m of PVDF as a function of the weight fraction of PHBV. PVDF/PHBV blends exhibited a single composition dependent T_g intermediate between the T_g s of the respective components, indicative of miscibility. On the other hand, the T_m of PVDF shifted to low temperature range with the increase of PHBV, indicating again the miscibility between PVDF and PHBV. The investigation of the depression of the equilibrium melting point of PVDF is currently underway, which can give a more reliable proof of the miscibility of PVDF/PHBV blends [26]. Based on the above results of the single composition dependent T_g and the decrease of the T_m of PVDF with the increase of PHBV, it can be concluded that PVDF is miscible with PHBV in the PVDF/PHBV blends.

3.2. Morphology study of PVDF/PHBV blends by OM

The morphology of PVDF/PHBV blends was investi-

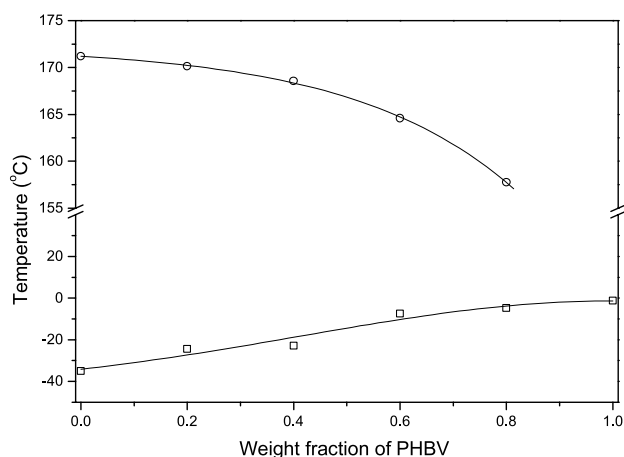


Fig. 1. Variation of the T_g of PVDF/PHBV blends (□) and the T_m of PVDF (○) as a function of the PHBV composition.

gated extensively by OM in this work. First, we studied the morphology of the high- T_m component PVDF. Fig. 2 shows the spherulitic morphology of the neat and blended PVDF with various weight fractions of PHBV (80/20–40/60) crystallized at 150 °C. PHBV was still in the melt in this case, and the crystallization of PVDF corresponded to the transition from the fully amorphous to the amorphous/semicrystalline state. The PVDF spherulites showed the familiar Maltese cross birefringence pattern with concentric extinction bands, and the band spacing became progressively larger with the PHBV content. Similar results were also found in PVDF/poly(butylene adipate) blends, and the band spacing was found to increase with decreasing crystal growth rate, i.e. with crystallization temperature and with increasing the noncrystallizing component [8]. The spherulites of PVDF became larger after blending with PHBV, indicative of a decrease in nucleation density. And the coarseness of PVDF spherulites increased with increasing PHBV in the blends, too. Up to high PHBV contents, the PVDF spherulites remained more or less volume filling, though nonbirefringent space could be found at the

spherulitic boundaries for PHBV-rich blends. The result that the PVDF spherulites were more or less volume filling indicated that PHBV was first rejected into the interlamellar and interfibrillar regions of PVDF spherulites during the crystallization process of PVDF [27,28].

The crystallization and morphology of PHBV, the low- T_m component with slow crystallization rate in PVDF/PHBV blends, were also studied in this communication in order to get a better understanding of the nature of the miscible blends of two crystalline polymers. The crystallization of PHBV corresponded to the transition from the amorphous/semicrystalline to semicrystalline/semicrystalline state. It should be pointed out that PVDF always crystallized during the quenching process before the crystallization temperature of PHBV was reached even at a maximum cooling rate of 100 °C/min. Similar to the crystallization of PVDF at 150 °C, the spherulites (or dendrites) of PVDF formed during the quenching process were more or less space filling, and the melt of PHBV is supposed to reside in the interlamellar and interfibrillar regions of PVDF spherulites (or dendrites).

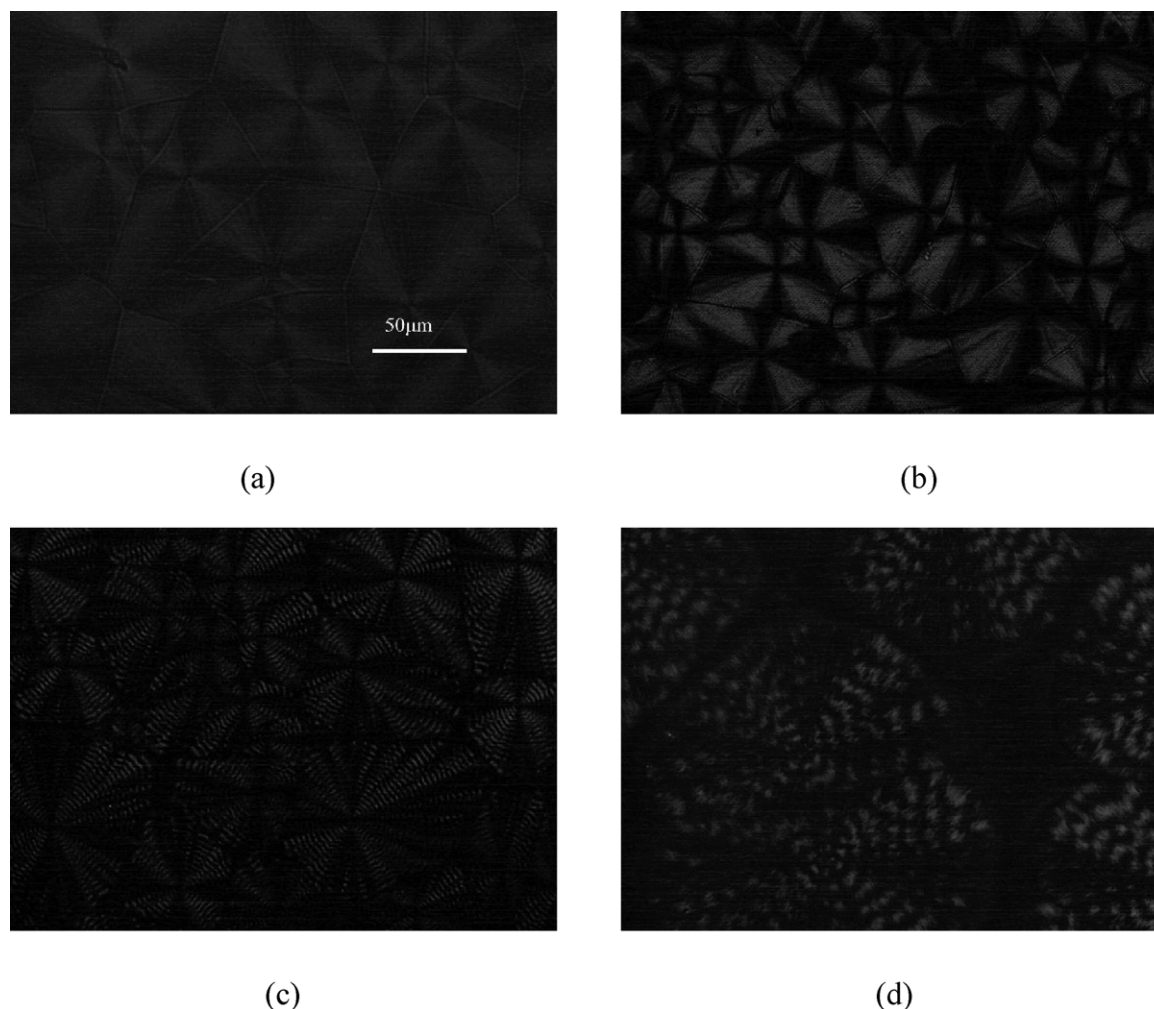


Fig. 2. Optical micrographs (same magnification, bar = 50 μm) of the spherulitic morphology of PVDF in PVDF/PHBV blends after complete crystallization at 150 °C; (a) 100/0, (b) 80/20, (c) 60/40, and (d) 40/60.

However, the size of PVDF crystals was suppressed significantly by the quenching process at 100 °C/min. The PVDF spherulites (dendrites) were too small to be observed clearly by OM due to the limited resolution. Fig. 3 shows the optical micrographs of the spherulitic morphology of PHBV for 0/100 and 40/60 crystallized at 60 and 65 °C, respectively. Neat PHBV showed positive spherulites with concentric extinction bands when it was observed with the first order retardation plate (Fig. 3(a)). On the other hand, neat PHBV exhibited Maltese cross birefringence pattern with concentric extinction bands when it was observed without the first order retardation plate (Fig. 3(b)). In general, the observation of the spherulitic growth of the second component, usually the low- T_m component with slow crystallization rate, is very difficult in crystalline/crystalline blend because it must crystallize in the matrix of the pre-existing crystals of the first component, usually the high- T_m component with fast crystallization rate. Therefore, only tiny crystals of the second component can grow within the spherulites or at the boundaries of the spherulites of the first component

[8]. However, it is interesting in this work that PHBV spherulitic morphology was also observed in the matrix of the pre-existing PVDF crystals for the blends containing PHBV more than 60%. Fig. 3(c) and (d) show the PHBV spherulites growing in the matrix of PVDF crystals for 40/60 sample. In this case, PHBV did not show positive spherulites with concentric extinction bands any more (Fig. 3(c)). Meanwhile, no Maltese cross can be observed for the PHBV spherulites in the blends (Fig. 3(d)). The above results indicate that the morphology of PHBV has been influenced significantly by the presence of PVDF crystals. We suppose that the existence of the PVDF crystals interrupted the lamellar twisting and the observation of Maltese of the PHBV spherulites. The observation of the spherulitic growth of the second component in the matrix of the pre-existing crystals of the first component was also found in our previous works for PVDF/poly(butylene succinate) (PBSU) and PBSU/poly(ethylene oxide) blends [19,25]. From the previous studies we propose that the possibility of the observation of the spherulitic growth of the second

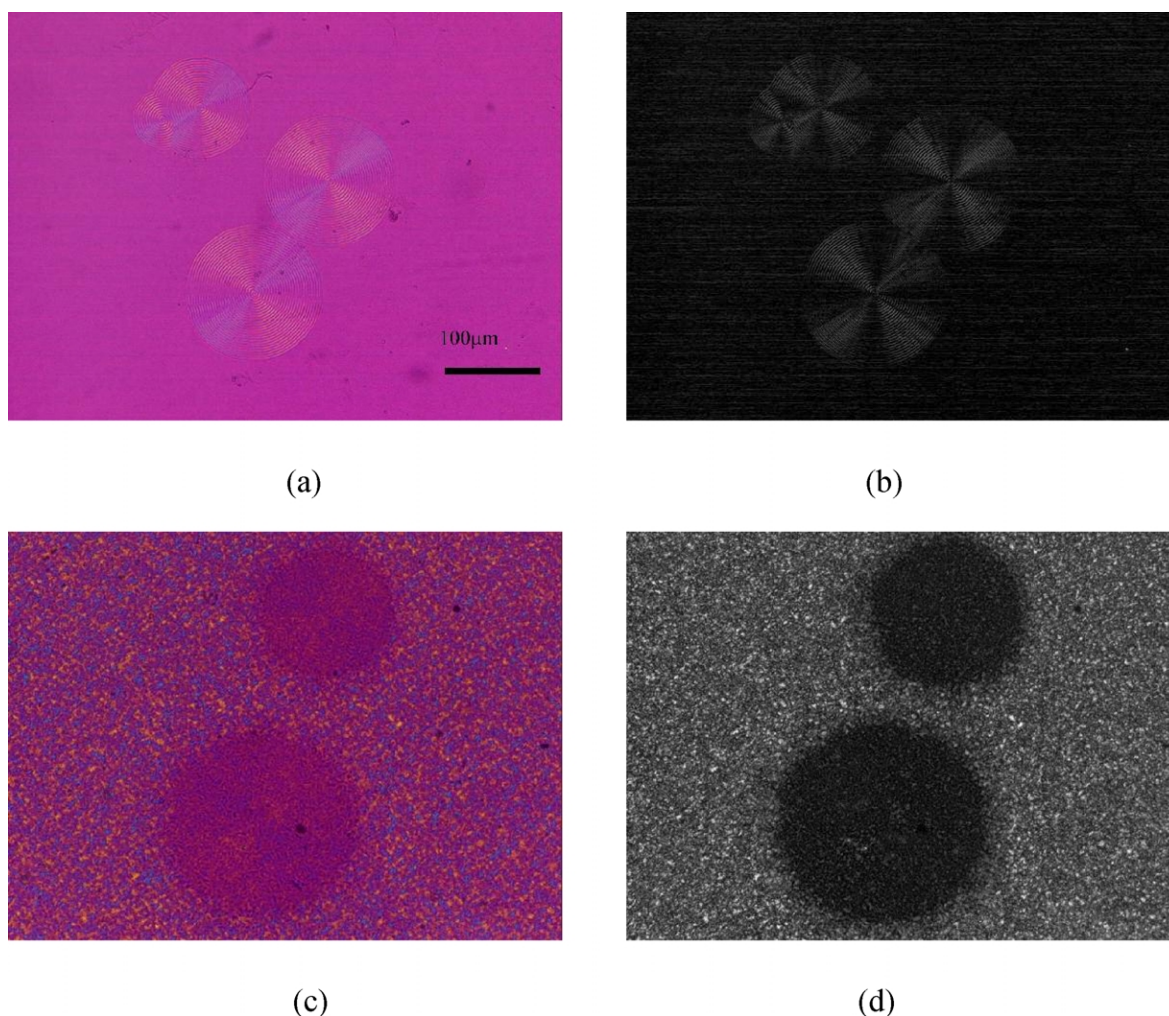


Fig. 3. Optical micrographs (same magnification, bar = 100 μ m) of the spherulitic morphology of PHBV; (a), (b) 0/100 at 60 °C; (c), (d) 40/60 at 65 °C. (a) and (c) were observed with the first order retardation plate; (b) and (d) were observed without the first order retardation plate.

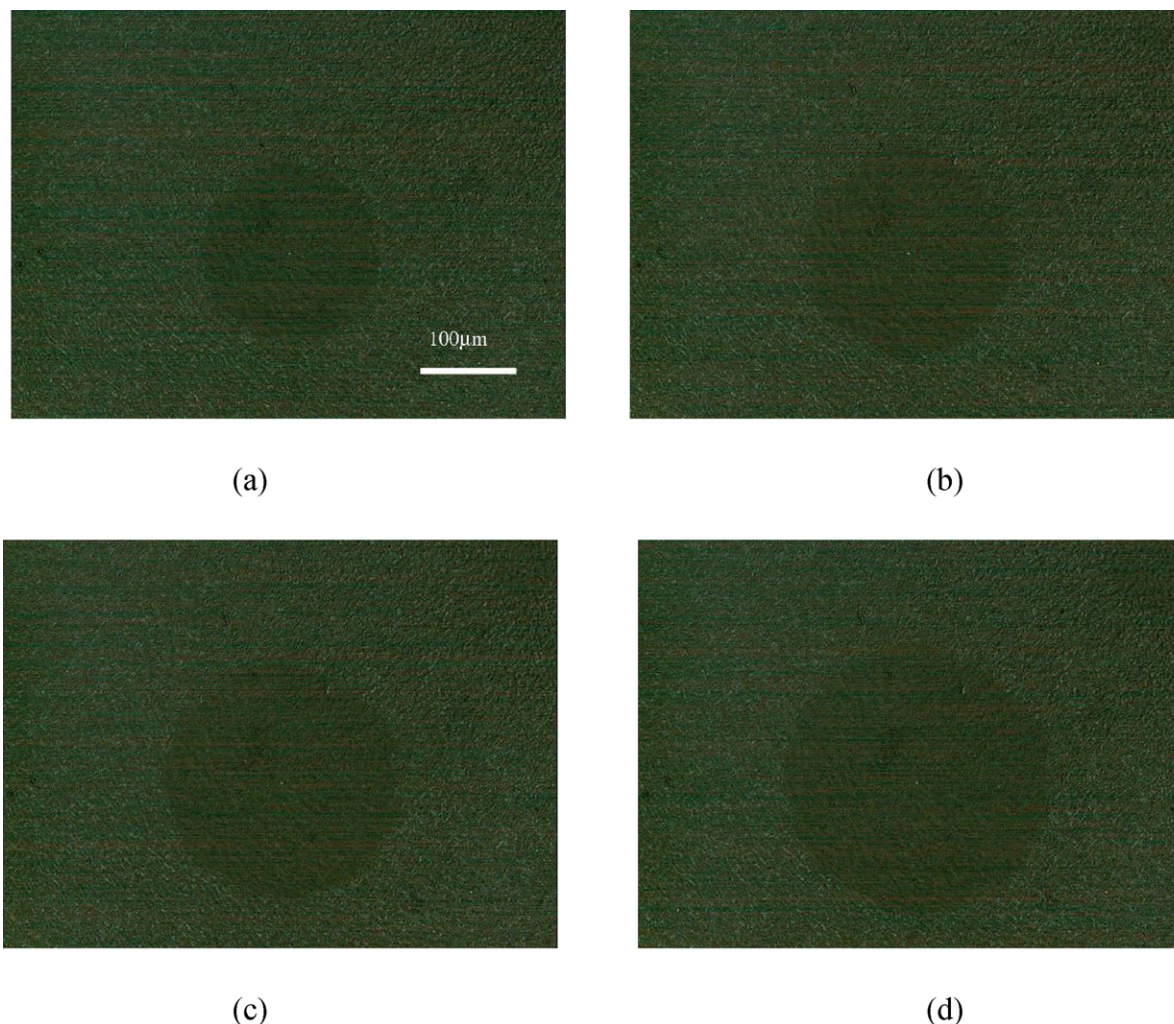


Fig. 4. Spherulitic growth of PHBV in the matrix of PVDF crystals at 65 °C for 40/60 (same magnification, bar = 100 μm). The time interval is 2 min.

component in the matrix of the pre-existing crystals of the first component may be related to the nucleation frequency of the second component and the amount of the melt of the second component in the matrix of the pre-existing crystals of the first component. Usually the lower the nucleation frequency and the higher amount of the melt of the second component, the more possible the observation of its spherulitic growth. In the case of PVDF/PHBV blends of this work, the nucleation frequency of PHBV remains still very low despite the presence of the PVDF crystals, and this kind of low nucleation frequency of PHBV is very typical for the biodegradable polymers because of the lack of the impurities required for the nucleation of the spherulites.

The spherulitic growth rate of PHBV was investigated by monitoring the variation of the radius with time. Linear growth rate of the PHBV spherulites was also found in PHBV-rich blends. As an example, Fig. 4 shows the growth process of the PHBV spherulites as a function of time for 40/60 at 65 °C with the time interval being 2 min. The growth rate could be obtained from the slope of the plot of

the radius of the PHBV spherulites as a function of crystallization time. Fig. 5 summarizes the variation of the growth rate of PHBV spherulites in PHBV-rich blends as a function of crystallization temperature. The growth rate of

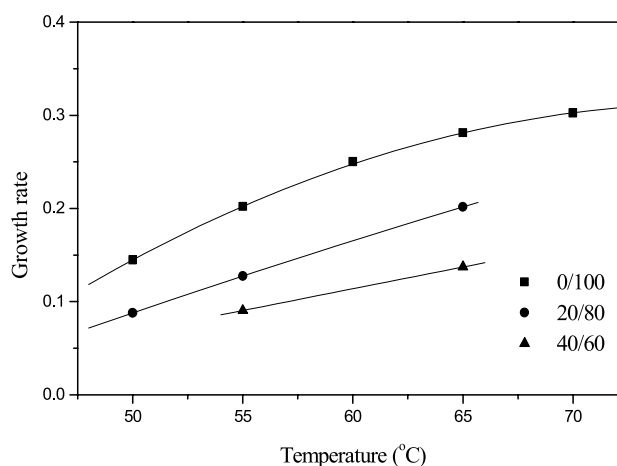


Fig. 5. Plots of spherulitic growth rate of PHBV as a function of crystallization temperature. The unit of growth rate is $\mu\text{m}/\text{sec}$.

the PHBV spherulites was found to decrease with increasing the PVDF content. On the other hand, the growth rate of the PHBV spherulites was found to increase with increasing the temperature, indicating that the crystallization temperature range 50–70 °C used in this study fell in the left part of the whole bell shape curve of the growth rate against the crystallization temperature range.

4. Conclusions

Miscibility and morphology of crystalline/crystalline blends of PVDF/PHBV were studied in this work by DSC and OM. PVDF was found to be miscible with PHBV based on the experimental results of the single composition dependent T_g over the entire composition range and the decrease of the T_m of PVDF with the increase of PHBV. Morphology of PVDF/PHBV blends was investigated by OM under two different crystallization conditions. PVDF showed the spherulitic morphology at 150 °C in the PVDF/PHBV blends, where PHBV acted as the noncrystallizing component. PHBV could show the spherulitic morphology within the matrix of the pre-existing PVDF crystals when PVDF/PHBV blends were quenched from the melt to the crystallization temperature below the T_m of PHBV. The spherulitic morphology of PHBV has been influenced significantly by the presence of the pre-existing PVDF crystals. The spherulitic growth rate of PHBV decreased with increasing PVDF and increased with the crystallization temperature.

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