

Conductive-Filler-Filled Poly(ϵ -caprolactone)/Poly(vinyl butyral) Blends. I. Crystallization Behavior and Morphology

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ABSTRACT: The crystallization behavior and morphology of poly(ϵ -caprolactone) (PCL)/poly(vinyl butyral) (PVB) blends containing carbon black (CB) were studied as functions of PVB and CB content. The presence of CB had no influence on the primary nucleation of PCL crystals or the spherulitic growth rate. They were only influenced by the blend ratio of PVB. The growth rates of spherulites were unchanged throughout the crystallization process, regardless of the CB content. The results indicate that the concentration of PCL at the front of growing spherulite remains constant during crystallization. The distribution of CB in the spherulites was observed using atomic force microscopy to explain these results. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 797–802, 1997

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INTRODUCTION

For crystalline/amorphous polymer blends, the morphology is dependent upon the miscibility, crystallizability, diffusion, and kinetic factors.¹ If the two polymers are immiscible in the melt, amorphous polymer does not affect the crystallization of crystallizable polymer. On the other hand, if the two polymers are miscible, the diffusion of the amorphous polymer acting as a diluent plays a very important role in the crystallization process. Owing to a broad variety of miscibility with other polymers, poly(ϵ -caprolactone) (PCL) has been widely used as a crystalline component in polymer blends.^{2–4} For example, miscible blends of PCL/poly(vinyl chloride) (PVC),^{5–7} a PCL/ ϵ -caprolactone–butadiene diblock copolymer (PCL–b-PB),⁸ and PCL/poly(vinyl butyral) (PVB)⁹ have been studied. Spherulites of these systems show periodical rings whereas those of pure PCL do not. Keith et al.⁹ reported marked morphological changes induced in PCL spherulite

by blending a small concentration ($\sim 1\%$) of PVB. They observed a striking reduction in the nucleation frequency and enhancement in the regularity of the twisted lamellar organization in banded spherulites. Although they explained that the adsorption of PVB on fold surfaces of lamellae caused these morphological changes, the reason is still unclear.

These morphological studies were only for the binary polymer blends containing no ingredients. For industrial purposes, however, polymers and polymer blends are used in the presence of non-polymeric ingredients, mainly fillers. No extensive investigation has been reported on the crystallization and morphology of crystalline polymers containing fillers. The main reason for the difficulty of the investigation in this field is attributable to the fact that the presence of a filler, especially carbon black (CB), hinders the microscopic observation of the crystallization process.

The purpose of this study was to observe the crystallization behavior and the morphology of PCL/PVB blends containing CB and to compare these results with the crystallization of blends without CB. Since PCL/PVB blends form very

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large spherulites, the nucleation and isothermal crystallization behavior can be observed for blends containing CB. The nucleation and crystallization behavior of crystalline polymer containing CB is investigated by microscopy for the first time in the present study. The article is organized as follows: We discuss the frequency of the primary nucleation and spherulitic growth rate of PCL/PVB blends containing CB as a function of PVB content using a cross-polarizing optical microscope. The distribution of CB in the spherulite is also discussed using atomic force microscopy (AFM). A series of studies dealing with the electric properties of PCL/PVB blends containing CB were also undertaken and will be described in separate articles.

EXPERIMENTAL

Materials and Sample Preparation

The PCL and PVB used in this study were purchased from Polysciences Inc. The PCL had a weight-average molecular weight (M_w) of 35,000 and PVB had an M_w of 100,000. CB (Cabot Co., Vulcan XC-72; average particle size 30 nm) was used as a conductive filler. A PCL master batch containing 40 phr (phr, parts per hundred resin) CB was made using a roll mixer. The CB fraction was reduced to 5 vol % by adding pure PCL to the PCL master batch dissolved in tetrahydrofuran (THF). The PCL/PVB blends with a varying PVB fraction (0–10 wt %) were prepared by dissolving the PCL master batch with 5 vol % CB and PVB in a common solvent, THF. Uniform thin films were prepared by casting the solutions. After the solvent was removed at room temperature, the samples were kept under a vacuum at 40°C for 1 week.

Optical Microscopic Observation

Samples with CB sandwiched between two cover-glasses were observed under a polarizing microscope (OLYMPUS BHA-P) equipped with a temperature controller (LINKAM TH-600). The samples were heated to 80°C for 1 h and then rapidly cooled to the crystallization temperature (T_c). Photographs were taken during the crystallization.

Atomic Force Microscopic (AFM) Observation

A PCL/PVB blend containing 5 vol % CB was diluted with THF to 1 wt %. After the casting of

a drop of the solution onto a glass plate, it was immediately spin-coated at 2000 rpm for 1 min. The sample was heated to 80°C for 1 h and crystallized at 41°C for 24 h. The AFM system used was the SP13700/SPA300 (SEIKO Instruments, Inc.). The image acquisition was in an attractive force mode with a scanning speed of 0.6 Hz.

RESULTS AND DISCUSSION

Primary Nucleation and Morphology

Figure 1 shows a comparison of the frequency of the primary nucleation of PCL/PVB blends with 5 vol % CB with different PVB content. In spite of the presence of CB, the number of spherulites formed in the initial stage of the crystallization process decreased with increasing PVB composition as in the case of the blends without CB [Fig. 1(a)–(c)]. For pure PCL, many crystals nucleated and impinged upon each other immediately [Fig. 1(d)]. The presence of CB makes it impossible to distinguish the spherulites from one another [Fig. 1(c)]. However, as shown in Figure 1(a) and (b), the nucleation frequencies were depressed by blending PVB irrespective of the presence of CB. The nucleation frequency of the sample in Figure 1(a) is smaller by ca. 2 orders of magnitude than that in Figure 1(d). These observations indicate that the presence of CB has almost no influence on the nucleation of PCL crystals in the blends. Only the blending of PVB changes the nucleation frequency.

Figure 2(a) and (b) are polarized optical micrographs of PCL/PVB (95 : 5) blends with 5 vol % CB and without CB crystallized at 41°C, respectively. As shown in Figure 1(c), it is very difficult to distinguish the growing boundary of spherulites from the dark melt phase containing CB. One reason is that the nucleation of many crystals in the early stage makes the size of the spherulites very small ($\sim \mu\text{m}$). Another reason is the poor visual field because of the black CB in the spherulites and in the melt. However, as shown in Figure 2(a), large spherulites with a Maltese cross were observed when the nucleation frequency was suppressed in the blends. The growth front of the spherulite was also clearly observed in spite of the presence of CB. However, we could not observe any extinction rings when CB existed in the spherulite. The result of these microscopic observations during crystallization was used to estimate the spherulitic growth rate, as discussed below.

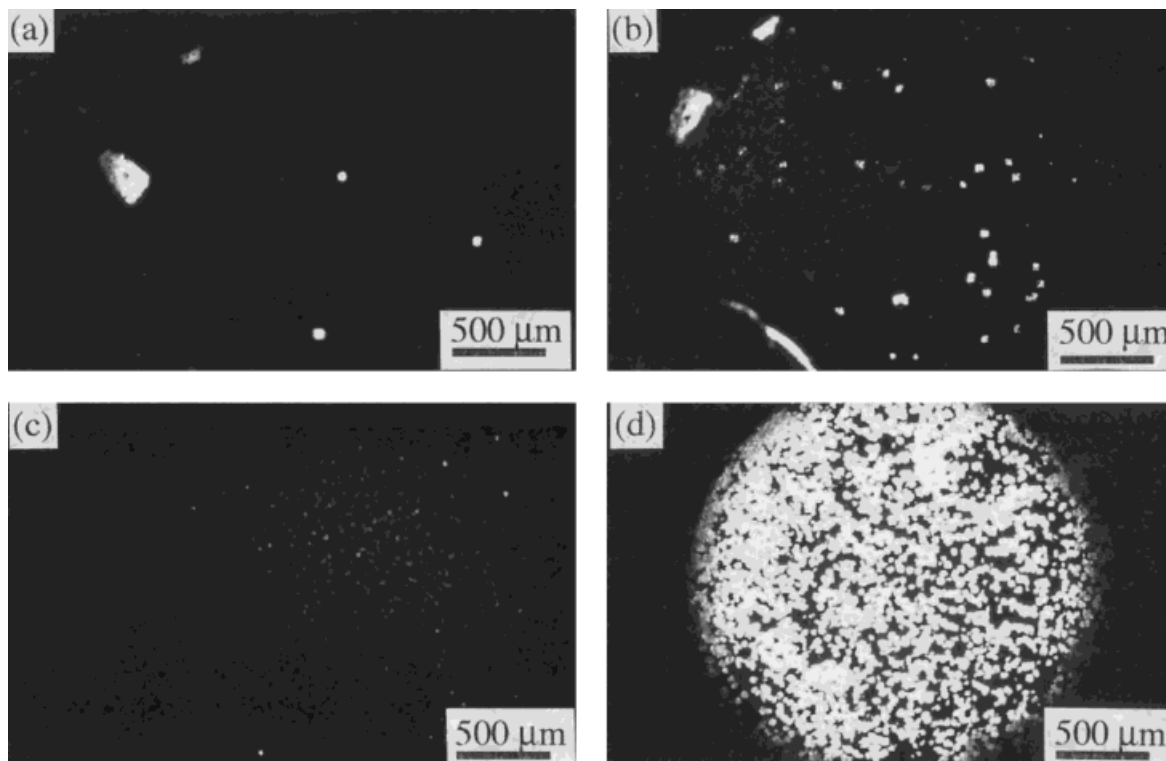


Figure 1 Cross-polarized optical micrographs describing the nucleation frequency of PCL/PVB blends with and without CB in the initial stage of the crystallization processes. The crystallization temperature was 41°C. The nucleation density in (a) decreased by about 2 orders of magnitude compared with (d). (a) PCL/PVB (95 : 5), CB 5 vol %; (b) PCL/PVB (99 : 1), CB 5 vol %; (c) pure PCL, CB 5 vol %; (d) pure PCL, CB 0%.

Spherulitic Growth

Since the nucleation frequency of PCL was strikingly depressed in the blends, isothermal spherulitic crystallization proceeded until the diameter of the spherulites reached 2 mm as measured under the polarizing optical microscope. Figure 3 shows the PVB content dependence on the growth rate of the spherulites in the blends with and without CB. A straight line was obtained for each blend, and from the slope of each line, the growth rate $G = dR/dt$ (R denotes the radius of a spherulite) was determined. The value of G was independent of the size of the spherulites during the crystallization. It decreased with increasing PVB composition. Microscopic observation showed that the crystallization of the PCL/PVB blend is retarded by the addition of PVB, while CB has no effect on the nucleation of PCL or the spherulitic growth rate.

If noncrystallizable material is rejected by the growing lamellae, the growth rate should decrease during crystallization because of the increase of the diluent concentration at the growth front.^{10,11} As the spherulites grow, the diluent con-

centration increases rapidly around the impinging spherulites. This causes a marked reduction in the growth rate and the flattening of the round spherulite profile. However, such flattening was not observed in this study. This implies that the concentration of the crystallizable component at the growing front remains constant throughout the spherulitic growth. In PCL/PVB blends, a polar interaction between PCL and PVB prevents strong segregation of PVB. Therefore, PVB is not expelled from the spherulites and remains mainly in the amorphous layer between the PCL lamellae. Although these observations gave us a very important insight into the behavior of the blended polymers, we obtained no information on the distribution of CB in the spherulites because the size of CB is too small to be observed by optical microscopy. We observed it using the AFM as described in the next section.

AFM Observation

In the early stage of the mixing of the CB-polymer composite, CB generally exists as aggregates;

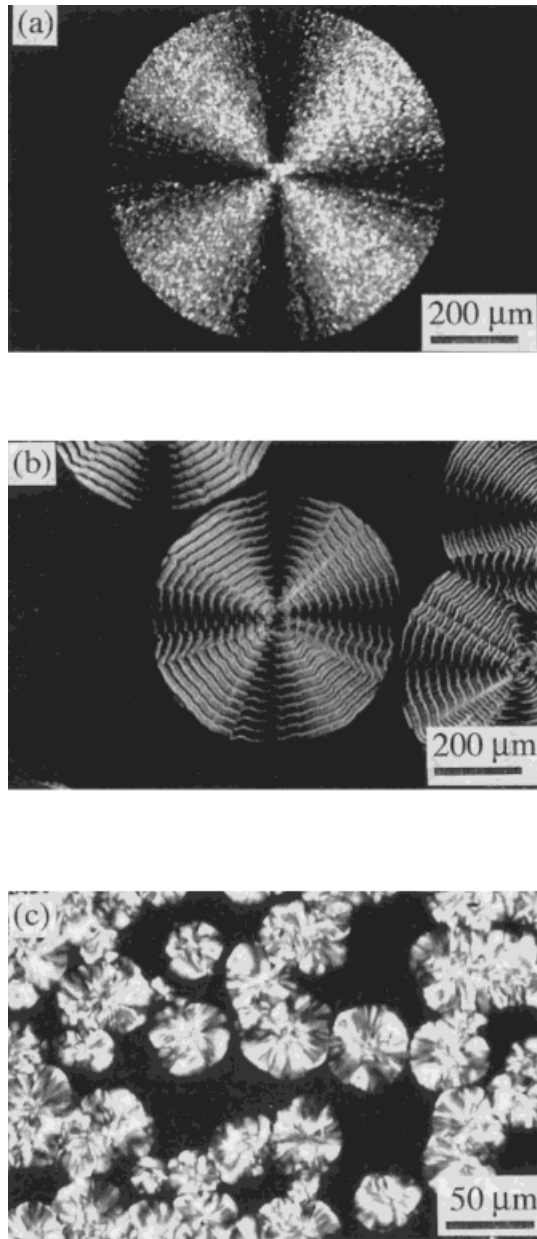


Figure 2 Cross-polarized optical micrographs describing the spherulitic structure of PCL/PVB blends grown at 41°C (the scale is different for each micrograph): (a) PCL/PVB (95 : 5); CB 5 vol %; (b) PCL/PVB (95 : 5), CB 0%; (c) pure PCL, CB 0%.

tens of CB particles cling to one another. They are broken up gradually during the mixing process. Finally, the aggregates are distributed in the composite with various sizes, from the size of an unbroken aggregate to that of a single CB particle. Figure 4 shows AFM images of the PCL/PVB blend (99 : 1) containing 5 vol % CB. The specimen was cast onto a glass plate and then crystallized at 41°C for 24 h. Figure 4(a) shows bright spots

of CB aggregates having different sizes in the spherulites and radial lamellar growth from a center of a spherulite (A) (scan size: $150 \times 150 \mu\text{m}^2$). The fibrils of the lamellar crystals avoid CB aggregates which are in the way of the growing fibrils. Figure 4(b) shows the magnified image of the lower left corner (B) of Figure 4(a) (scan size: $40 \times 40 \mu\text{m}^2$), where two spherulites impinged against each other. Radially grown fibrils and the dark boundary can be seen. Since AFM generally detects the depth profile, the dark phase appearing in Figure 4(b) corresponds to the ravinelike structure between the two impinged spherulites. This structure is caused during isothermal crystallization by the incorporation of PCL into the growth front, where PCL is packed more tightly than in the melt. An AFM top view of the ravine gives a dark phase, whereas fibrils and CB in the spherulites give a bright phase. Although several CB aggregates exist in the spherulites, no aggregates do so on the boundary. However, CB particles or smaller CB aggregates can be observed. Figure 4(c) shows a magnified image of the center of Figure 4(b). The scan size is $10 \times 10 \mu\text{m}^2$. It is clearly visible that the aggregates which are smaller than those in the spherulites exist on the boundary. Since the diameter of

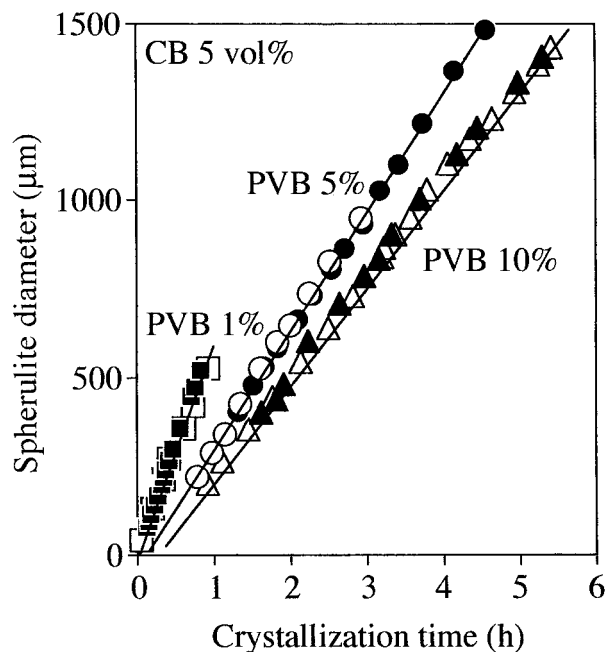


Figure 3 Size of spherulites vs. crystallization time for PCL/PVB blends with different PVB content. The crystallization temperature was 41°C. (\square, \blacksquare) PCL/PVB (99 : 1); (\circ, \bullet) PCL/PVB (95 : 5); ($\nabla, \blacktriangledown$) PCL/PVB (90 : 10). Solid symbols denote the samples containing 5 vol % CB; open symbols denote those without CB.

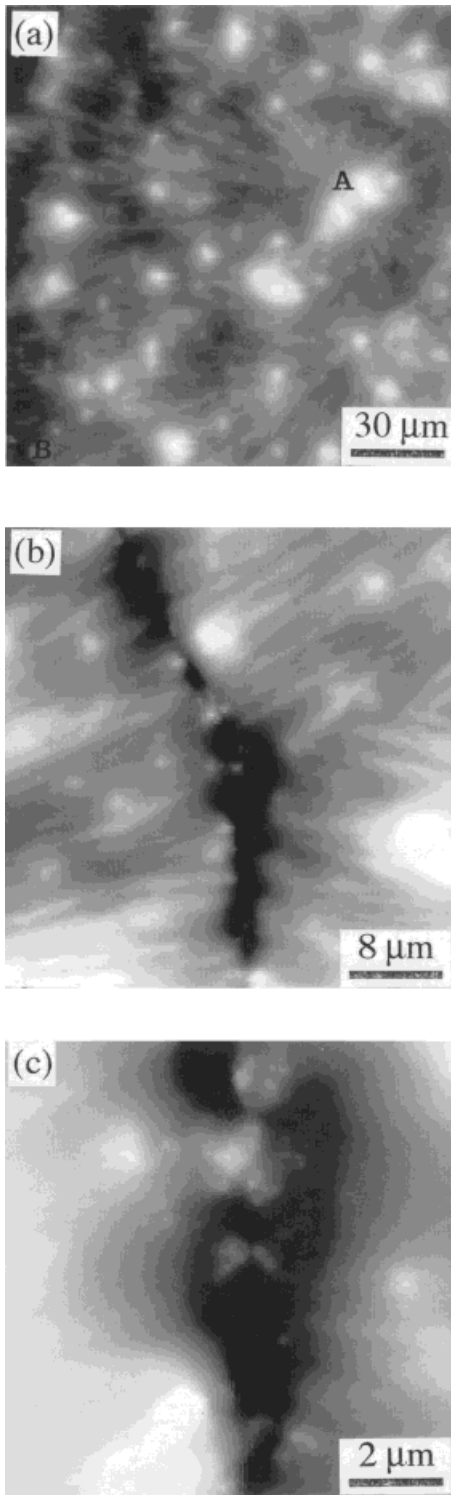


Figure 4 AFM images of spherulites of PCL/PVB (99 : 1) with 5% CB grown at 41°C for 24 h. Scan sizes are (a) $150 \times 150 \mu\text{m}^2$, (b) $40 \times 40 \mu\text{m}^2$, and (c) $10 \times 10 \mu\text{m}^2$.

a CB particle is of the order of 30 nm, the small spots in Figure 4(c) should be the CB particles or broken CB aggregates expelled from the spherulites during crystallization.

From the results of these AFM observations, the distribution of CB in the spherulites is considered as follows: (a) Owing to their large size, CB aggregates remain in the spherulites. Fibrils of PCL avoid these aggregates when they grow radially. (b) CB particles and small broken CB aggregates are expelled onto the boundary of impinged spherulites during crystallization. However, the fraction of CB existing as particles or small broken aggregates is much smaller than the total amount of the CB aggregates. Therefore, although some parts of the CB particles or small broken aggregates are expelled from the spherulite during crystallization, the amount is too small to dilute the concentration of PCL at the growing front of the spherulite. This explains the time-independent growth rate of the spherulites as shown in Figure 3.

CONCLUSIONS

1. The presence of CB has no influence on the nucleation frequency of the PCL/PVB blends. Owing to the reduction of nucleation density in the blends, very large spherulites (\sim several millimeters) were formed during isothermal crystallization even for the blends containing CB. This is the first time that the crystallization process of polymer blends with CB was observed by a cross-polarizing optical microscope.
2. In PCL/PVB blends containing CB, the spherulitic growth rate was influenced only by PVB content and is independent of the presence of CB. The growth rate remains constant throughout the crystallization process and is not affected by the existence of CB.
3. The linear growth rate of spherulites in the blends containing CB implies that the concentration of PCL at the growing front is unchanged during the whole crystallization process. From the results of AFM observations, CB aggregates exist mainly in the spherulites and the amounts of expelled CB particles on the boundary of impinged spherulites are too small to dilute the concentration of PCL.
4. Drastic morphological changes observed in PCL/PVB also affect the distribution of CB in the spherulite. The electric property of the specimen (PTC phenomenon) will be discussed in part II with these results.

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