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# Evidence for the formation of interpenetrated spherulites in poly(butylene succinate-*co*-butylene carbonate)/poly(L-lactic acid) blends investigated by atomic force microscopy

Takayuki Ikehara[a,*], Yuko Nishikawa[b], Toshio Nishi[c]

[a]*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*
[b]*Asahi Kasei Electronics Co., Ltd, 2-1, Samejima, Fuji, Shizuoka 416-0934, Japan*
[c]*Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152-8552, Japan*

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**Abstract**

The spherulitic morphology in poly(butylene succinate-*co*-butylene carbonate)/poly(L-lactic acid) (PEC/PLLA) blends was investigated by atomic force microscopy (AFM) to obtain direct evidence for the formation of interpenetrated spherulites (IPS), where the spherulites of PEC penetrate into PLLA spherulites. The observation actually revealed that PEC crystals penetrated into interfibrillar regions of edge-on lamellae in a PLLA spherulite. The penetration process was also investigated by AFM with a temperature controller. An edge-on PLLA lamella or a fibril that ran nearly perpendicular to the growth direction of a PEC spherulite obstructed the growth of PEC spherulite. The PEC crystals filled the blocked space after growing around the PLLA lamella. These results showed that the spherulites of PEC and PLLA grow on the same layer instead of forming a layered structure of two spherulites. All the results supported the formation of IPS.

*Keywords:* Poly(butylene succinate-*co*-butylene carbonate); Poly(L-lactic acid); Interpenetrated spherulites

## 1. Introduction

Various properties of amorphous/amorphous and crystalline/amorphous blends are widely investigated. In contrast, only a small number is reported so far on crystalline/crystalline blends that are miscible above the melting points $T_m$ of the two components [1–5]. In crystalline/crystalline systems, the difference in $T_m$ of the two components is usually about 100 K. The component with higher $T_m$ therefore crystallizes first in the crystallization process of these blends. It usually influences the crystallization behavior of the other component. Spatially restricted crystallization of the lower-$T_m$ component takes place at lower temperature.

Our group has reported that poly(butylene succinate-*co*-butylene carbonate)/poly(L-lactic acid) (PEC/PLLA) blends are miscible crystalline/crystalline polymer blends in which the two components simultaneously crystallize [6]. The difference in $T_m$ is 34 °C. The spherulitic growth rate $G$ of the higher-$T_m$ component (PLLA) is slower than that of the lower-$T_m$ component (PEC). This enables the simultaneous spherulitic growth of the two specimens.

Moreover, these blends were found to form interpenetrated spherulites (IPS), where PEC spherulites penetrate into PLLA spherulites. The penetration of a spherulite of a different polymer has also been reported in three other blend systems so far [7–12].

In crystalline/amorphous polymer blends, the amorphous component act as impurity to crystallization of the crystalline component, and expelled into interlamellar, interfibrillar, and interspherulitic regions [13]. Interlamellar and interfibrillar amorphous melt must play an important role especially in the formation of IPS since it eventually crystallizes.

The simultaneous crystallization and the formation of IPS in PEC/PLLA have been analyzed by optical microscopy. The discussions on the change in birefringence

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[*] Corresponding author. Tel: +81-45-481-5661x3849; fax: +81-45-413-9770.

*E-mail address:* ft101651@kanagawa-u.ac.jp (T. Ikehara).

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indicated the formation of IPS [6]. However, direct observation of IPS in PEC/PLLA at the lamellar or fibrillar level has not been demonstrated yet. The aim of this paper is to investigate the structures of IPS in PEC/PLLA by AFM and to study the formation process of IPS at the lamellar or fibrillar level.

## 2. Experimental

PEC is a commercial polymer IUPEC-350 ($T_m = 106\,°C$, $T_g = -26\,°C$, $M_w \approx 10^5$) provided by Mitsubishi Gas Chemical Company Inc. PLLA ($T_m = 140\,°C$, $T_g = 40\,°C$, $M_w = 2000$) was purchased from Polysciences Inc. Both polymers are biodegradable. Blends were prepared by dissolving the two components into mutual solvent chloroform. The details of the sample preparation were described elsewhere [6]. The blend composition for AFM observation was PEC/PLLA = 8/2.

The AFM instrument was JSPM4210 of Jeol equipped with a thermal control unit to enable temperature control of a sample. The cantilevers were OMCL-AC160TS purchased from Olympus Optical with the nominal spring constant 42 N/m and the resonant frequency 300 kHz. All observation was performed in the non-contact mode, and topographic and phase images were obtained simultaneously.

Cast films of the blends were prepared on glass substrates. The film thickness was about 1 μm. They were first kept at 170 °C for 3 min to obtain homogeneous melt, and then quenched to a desired isothermal crystallization temperature $T_c = 70\,°C$ at $-100\,°C/min$. The AFM observation was carried out at room temperature after crystallization was complete for crystallized samples. In situ observation of isothermal crystallization was also performed on the AFM sample stage with a temperature control unit. In this case, only PEC in the crystallized blend was first melted at 125 °C, then it was cooled to 95 °C on the sample stage. This crystallization temperature was chosen to realize a slow spherulitic growth rate for in situ AFM.

## 3. Results and discussions

Fig. 1 shows an AFM result of the in situ crystallization process of neat PEC at 90 °C. Most of the lamellae were flat-on except for a small amount of edge-on lamellae. It also showed some screw dislocations. The structures around the center of a neat PLLA spherulite after crystallized at 90 °C are shown in Fig. 2. The lamellae were edge-on at the center of the spherulite, i.e. they were edge-on at the primary nucleation of the crystal. As shown in figure, they changed into flat-on in the growing process.

Fig. 3 shows an AFM topography of a PEC/PLLA = 8/2 blend. It was crystallized at 70 °C before AFM measurements and was observed at room temperature. A center of a PEC spherulite exists at the lower right-hand corner. The other small spherulites are PLLA. A boundary between PEC spherulites runs nearly vertically on the left-hand side of the picture.

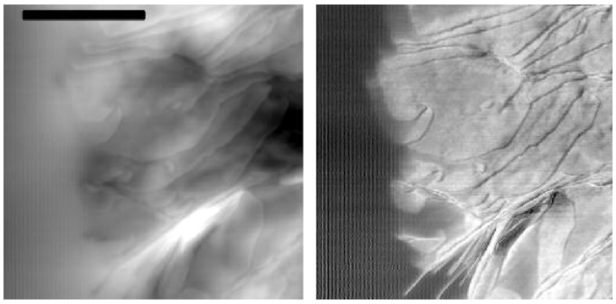

Fig. 1. In situ AFM result of the crystallization process of neat PEC crystallized at 90 °C. Left is topography and right is a phase image. Most of the lamellae were flat-on. Bar represents 2 μm.

In PEC/PLLA blends, the spherulitic growth rate $G$ of the higher-$T_m$ component PLLA was slower than the lower-$T_m$ component PEC. When the two components crystallized simultaneously, small PLLA spherulites and large PEC spherulites were observed under most conditions. The number of PEC spherulites, however, was smaller than that of PLLA. One factor for this is the difference in the degree of supercooling of the two components. Another possible factor is the difference in the nucleation rate itself of the two components. The interaction between a polymer and a substrate also affects the nucleation rate.

The enlarged topographic and phase images of the squared area (a PLLA spherulite) in Fig. 3 are displayed in Fig. 4. The left-hand and right-hand sides of the PLLA spherulite were flat-on and edge-on, respectively. These images, especially the phase image, clearly show that the crystals of PEC penetrated between the edge-on fibrils of PLLA.

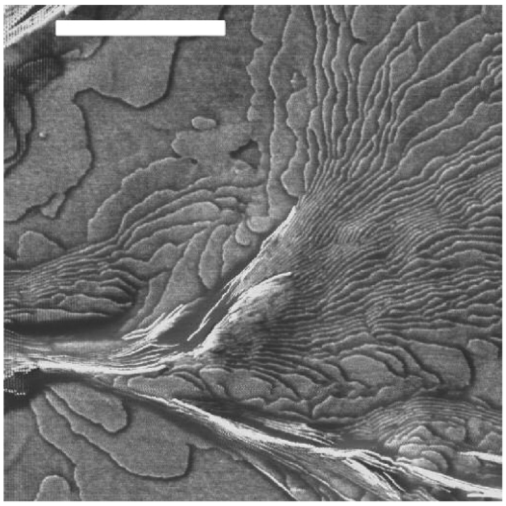

Fig. 2. The phase image of neat PLLA crystallized at 90 °C. The center of the spherulite is located near the lower left corner. The lamellae were edge-on near the center, and changed into flat-on in the growing process. Bar represents 1 μm.

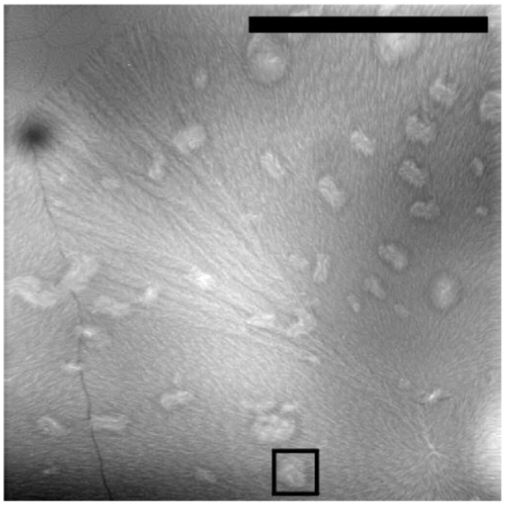

Fig. 3. AFM topography of a PEC/PLLA = 8/2 blend crystallized at 70 °C. A large spherulite with its center close to the lower right corner is a PEC spherulite. The other small spherulites are PLLA. Bar represents 50 μm.

Fig. 4 indicates the following situation. The lamellae of PEC grow from the right to the left since the center of the PEC spherulite is located at the right of the PLLA spherulite as shown in Fig. 3. The PLLA lamellae were still edge-on when the PEC lamellae reached the PLLA spherulite from the right. The PEC crystals penetrated between the fibrils of PLLA crystals. The PEC crystals fixed the edge-on structure in the right half of the PLLA spherulite at this stage. When PEC crystals reached the center of the PLLA spherulite, the lamellae of PLLA on the left side could still continue to grow, and they changed into flat-on as in Fig. 2. This process can explain the structure of the PLLA spherulite, namely edge-on in the right half and flat-on in the left half.

Fig. 5 shows the height profile along the line in Fig. 4(a). The thickness of the fibril pointed by the markers was about 60 nm. The thickness of a thicker fibril was more than 100 nm in Fig. 4. If we assume a typical thickness of a lamella to be of the order of 10 nm, a stack of several lamellae constructs the observed edge-on structure. However, the lateral size in an AFM result is strongly affected by the radius of an AFM tip, especially when the size of interest is close to or smaller than the tip radius $r$ (usually about 10 nm). The nominal (typical) radius of a tip in this work is 6.8 nm. We can obtain the real thickness by subtracting $2r$ from the observed value as a rough estimation. This effect is intrinsically inevitable in the estimation of a size in the lateral direction by AFM.

There is also a problem whether the observed edge-on structures are comprised of lamellae or fibrils. Considering the characteristic sizes discussed above, we concluded that the structures are more probably made up of fibrils than lamellae.

Fig. 6 displays the penetration process of a PEC spherulite into a PLLA spherulite observed at 95 °C by in situ AFM, i.e. the sample was crystallized on a temperature controller on the AFM sample stage, and the real-time crystallization process was observed. The four pictures are

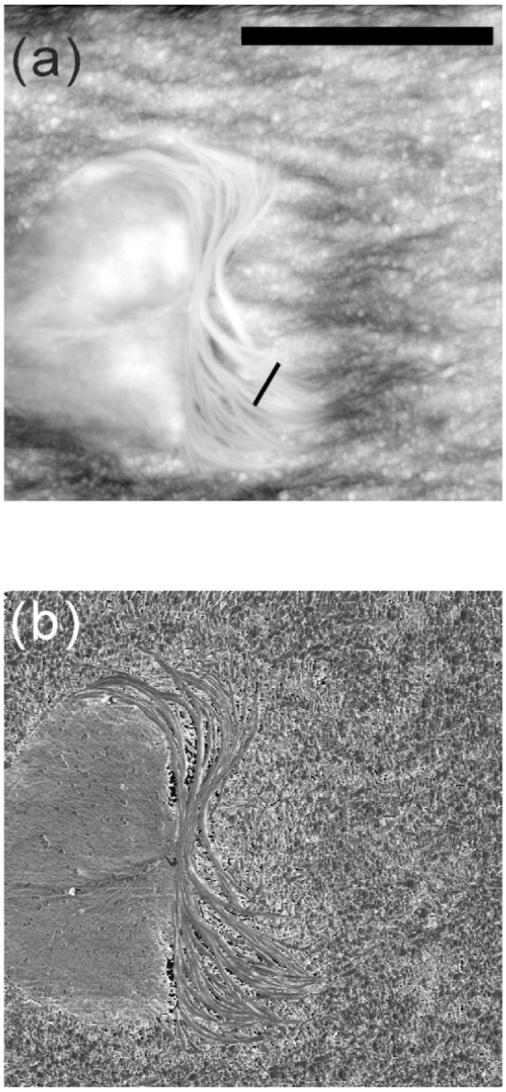

Fig. 4. The enlarged scan of the squared area of a PLLA spherulite in Fig. 3. (a) Topography and (b) phase image. Bar represents 5 μm. The height profile along the fine line in (a) is discussed with Fig. 5.

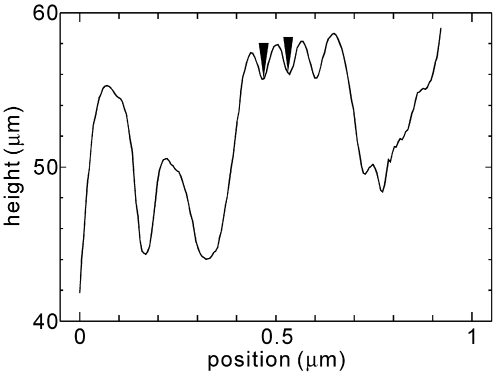

Fig. 5. The height profile along the line in Fig. 4(a). The spacing between the markers was 60 nm.

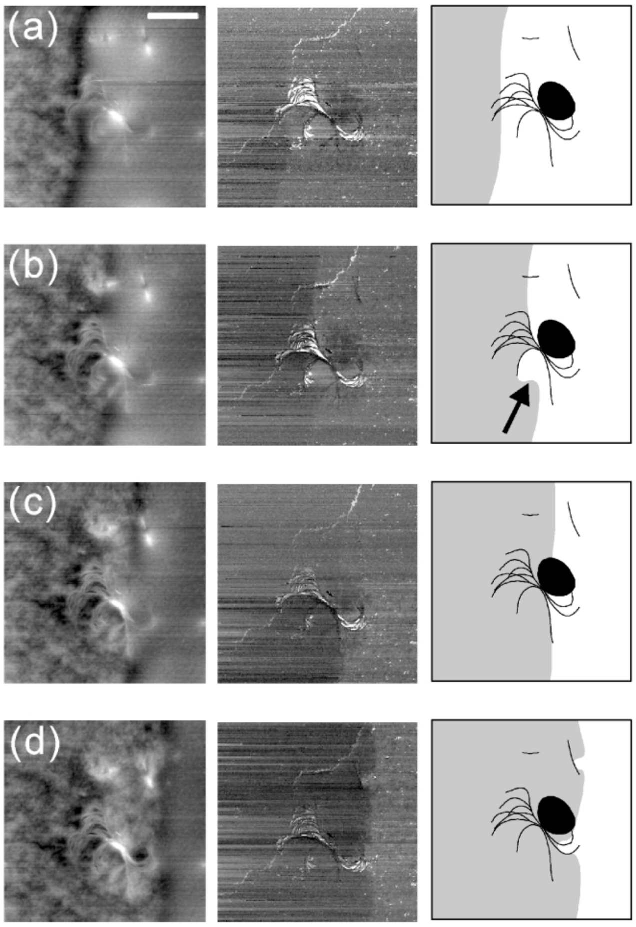

Fig. 6. The penetration process of a PEC spherulite into a PLLA spherulite at 95 °C obtained by in situ AFM. The four figures (a)–(d) are successive scan results with a scanning time about 3 min. Left: topography, middle: phase images, and right: schematic figures. Bar represents 5 μm. The arrow in (b) indicates the area where the growth of PEC was obstructed by PLLA lamellae.

successive scan results with a scanning time about 3 min. When the temperature controller was used, relatively worse quality of the AFM images was inevitable than those without temperature control because of the instability arising from the heat flow from the heater to the sample, cantilever, air, and piezoscanner. The almost vertical line indicates the growth front of the PEC spherulite, and it grew from the left to the right. A PLLA spherulite is located at the center. The figure indicates in (b) that an edge-on PLLA fibril nearly perpendicular to the growth direction of PEC obstructed the growth of PEC in the area indicated by an arrow. This phase image more apparently indicates this situation. The PEC crystals filled the blocked area after growing around the PLLA lamella in (c). On the other hand, PLLA fibrils that are nearly parallel to the growth direction of PEC do not hinder the growth of PEC as indicated by the several fibrils in the upper part. Blocking the growth of PEC indicates that PEC crystals actually penetrated between PLLA fibrils, instead of forming a layered structure of two spherulites of PEC and PLLA. If the layered structure were formed, the fibrils of PLLA would not obstruct the growth of PEC since one spherulite is placed on the other spherulite. The topographic results in Figs. 4 and 6 showed no clear step in height on the boundaries between PEC and PLLA spherulites either. This situation was the same in the AFM analysis of IPS in poly(butylene succinate)/poly(vinylidene chloride-*co*-vinyl chloride) blends [9].

We discuss the formation of IPS here. First, the two components must simultaneously crystallize. Second, as in the discussions in our previous works [8,11], PEC is expelled from the PLLA crystals, and remains amorphous in interlamellar and interfibrillar regions, where the concentration of PEC is higher than the overall PEC concentration in the sample. When the growth front of a PEC spherulite contacts with a PLLA spherulite, the PEC crystals can still continue crystallization with residual amorphous PEC in those regions. Third, a PLLA spherulite must contain sufficiently large amorphous regions required for the crystalline growth of incoming PEC crystals as in the edge-on region in Fig. 4. These three factors should at least be met for the formation of IPS.

When PLLA lamellae are edge-on, the penetration of PEC lamellae can obviously be confirmed as shown in Fig. 4, where the PEC lamellae penetrated between the edge-on lamellae or fibrils of the PLLA spherulite on the right-hand side. On the other hand, the penetration is less clear in the flat-on region of Fig. 4 since AFM provides the information of a surface. However, if the flat-on region is comprised of a stack of PLLA crystals and amorphous melt, PEC crystals can penetrate into the amorphous zones. PEC lamellae have actually a good probability to penetrate into the flat-on region since the film thickness here is of the order of 1 μm and that of a fibril is less than about 100 nm as observed in the edge-on region. The discussions on birefringence in the previous work actually showed that the whole region of a PLLA spherulite is penetrated by PEC [6].

## 4. Conclusions

The spherulitic morphology in PEC/PLLA blends was investigated by AFM to obtain direct evidence for the formation of IPS. It actually revealed that PEC crystals penetrated between edge-on fibrils of a PLLA spherulite. The estimation of the width of a fibril by AFM indicated that the penetration could also take place in the flat-on regions of a PLLA spherulite. The formation process was also investigated with an AFM with a temperature controller. An edge-on PLLA fibril that ran nearly perpendicular to the growth direction of a PEC spherulite blocked the growth of a PEC spherulite. PEC crystals filled the blocked area after growing around the PLLA fibril. These results showed that the spherulites of PEC and PLLA grow on the same layer instead of forming a layered structure of two spherulites. All the results obtained in this work clearly show the formation of IPS in PEC/PLLA blends.

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