

Interfacial Banded Transcrystallization of Polyoxymethylene/Poly(butylene succinate) Blends Induced by the Polyamide 6 Fiber

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Electronic Supplementary Information

Abstract Interfacial crystallization of polyoxymethylene/poly(butylene succinate) blends induced by the polyamide 6 (PA6) fiber was investigated. Due to strong heterogeneous nucleating ability, dense nuclei were generated on the surface of the PA6 fiber, which compelled the growth of twisted lamellae perpendicular to the PA6 fiber. As a result, unique interfacial banded transcrystallization was formed, which is rarely found before. Crystallization temperature was dominant in determining the nucleation activity of the PA6 fiber, further affecting the architecture of banded transcrystallization. With the increase of crystallization temperature, the nucleation density decreased to give more growth space for the twisted lamellae around the fiber. The wave-like banded stripes were transformed into fan-like stripes. Accordingly, band spacing and eccentricity respectively showed positive and negative correlation with crystallization temperature. These meaningful results shed light on regulating the architecture of banded crystals in polymer composites.

Keywords Interfacial crystallization; Banded transcrystallization; Heterogeneous fiber; Nuclei density; Polymer blends

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INTRODUCTION

Banded spherulites are special spherulites that show not only Maltese black cross extinction but also periodic alternating bands of light and dark.^[1] The types of banding are diverse, such as circular ring bands, radial-stripe bands, etc.^[2,3] It is controversial whether a universal mechanism accounts for the diversity of banding morphology.^[4] The banding may come from the thickness-related periodic height changes,^[5] periodic variations in composition,^[6] and lamellar twisting.^[7] Despite some debating issues, lamellar twisting has been regarded as a primary cause.^[8] Lotz and Cheng^[9] concluded that the occurrence of lamellar twisting was mainly derived from unbalanced surface stresses from structural features. Apart from the study of banding mechanisms, large efforts are being devoted to regulating the morphology of banded crystals.^[10–12] For example, Li *et al.*^[13] found the single ring-banded poly(ethylene adipate) spherulite was generated *via* controlled stepwise evaporative crystallization. Nagarajan *et al.*^[14] synthe-

sized an aryl polyester and a camellia-flower-like bands morphology was observed at the crystallization temperature of 110–125 °C. These interesting morphologies bring new opportunities and challenges to the study of ring banded spherulites.

Apart from manufacturing high performance polymer materials,^[15,16] blending has also been considered as a stimulating route to create distinctive types of banded morphologies due to various combinations depending on the crystalline/amorphous feature and miscibility of the components.^[17–19] Ye *et al.*^[20] found that the banded morphology of polyoxymethylene (POM) transformed from concentric ring to single spiral when blending with poly(lactic acid) (PLA). It was due to the formation of a continuous phase by excluded PLA. Toda *et al.*^[21] reported that poly(vinyl butyral) enabled poly(ϵ -caprolactone) (PCL) to form large banded spherulites, which did not occur for neat PCL. Generally, the band spacing is reduced by extra surface stresses caused by miscible blends.^[22] But the band spacing became larger for poly(3-hydroxybutyrate)^[23] and poly(butylene succinate) (PBS)^[24,25] after blending with a miscible polymer. It was probably because the reduced melting temperature of blends promoted lamellar thickening to hinder deformation.^[26]

Fiber reinforcement has attracted tremendous attention over decades due to the advantages of high feasibility and

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economy.^[27–29] The efficiency of mechanical enhancement is strongly dependent on interfacial adhesion, which bridges the fiber and the matrix to ensure stress transfer.^[30–33] Thereinto, interfacial crystallization is regarded as one of the desired approaches to improving interfacial bonding.^[34,35] Fu *et al.*^[36] reported that interfacial shear strength between PBS and a surface-modified ramie fiber was increased by 95.6%. They attributed the interfacial mechanical enhancement to the formation of transcrystalline structure induced by the dopamine coating on the surface of the ramie fiber. Li *et al.*^[37] reported that both polyethyleneimine-modified carbon nanotube fiber and polyethyleneimine-modified graphene oxide fiber readily induced the transcrystallization of polypropylene. The interfacial shear strength accessed by the microdroplet test showed 39.5% and 34.5% increase, respectively. Our previous work found that the cylindrites of stereo-complex PLA induced by interfacial shear not only improved the interfacial bonding but also enhanced solvent resistance.^[38]

Till now, researches on banded crystals mainly concentrated on the influence of chain structure, components, and blending ratios on the banded morphology.^[39–42] Considering the significant role of interfacial crystallization, it is of great significance to ascertain how heterogeneous fibers affect or alter banded morphology. In this work, we investigated interfacial crystallization of banded crystals by imbedding a single polyamide 6 (PA6) fiber in POM/PBS blends. The heterogeneous nucleation efficacy of the PA6 fiber as a function of crystallization temperature (T_c) was evaluated. The morphology evolution of banded crystals induced by the PA fiber was tracked by *in situ* polarized light microscopy (PLM). Detailed crystalline structure was observed by scanning electron microscopy (SEM) and two-dimensional wide-angle X-ray diffractometer (2D-WAXD). It is very interesting to discover that unique banded transcrystallization was developed on the surface of the PA6 fiber. The relationship of featured crystalline structure (*i.e.*, band spacing, eccentricity of elliptical bands, and crystal growth rate) with T_c was obtained. These findings are of great significance to tailor banded crystalline morphology in polymer composites.

EXPERIMENTAL

Materials

Polyoxymethylene (POM, MC90) with M_w of 1.74×10^5 g/mol and M_w/M_n of 2.19 was obtained from Shenhua Co., China. Poly(butylene succinate) (PBS) with M_n of 6×10^4 g/mol was offered by SHOWA Highpolymer Co., Japan. Polyamide 6 (PA6) fibers were obtained from Guangzhou Xinhui Meida Co., Ltd. The diameter of a single PA6 fiber was 15.7 μm (Fig. S1a in the electronic supplementary information, ESI) and the corresponding 2D-WAXD pattern was shown in Fig. S1(b) (in ESI).

Sample Preparation

POM/PBS (1 g, W/W=20/80) blend was completely dissolved in 15 mL of hexafluoroisopropanol under vigorous stirring at ambient temperature. The mixed solution was coated onto a glass substrate drop by drop to obtain ~ 25 μm thin films and dried in vacuum at 80 $^\circ\text{C}$ for 12 h to remove any residual solvent. The as-prepared films were kept in a dryer before use.

Polarized Light Microscopy (PLM) Observation

A single PA6 fiber was sandwiched between two thin films and interfacial crystallization was observed using a BX51 PLM (Olympus Co., Tokyo, Japan) equipped with a Linkam CSS450 hot stage. The thermal procedure was described as follows and depicted in Fig. S2 (in ESI): (1) Heat to 200 $^\circ\text{C}$ at a rate of 30 $^\circ\text{C}/\text{min}$ and maintain for 3 min to remove previous thermal history; (2) Cool to the crystallization temperature ($T_c=145, 148, 150, 152, 155, 158, \text{ and } 160$ $^\circ\text{C}$) at the rate of 30 $^\circ\text{C}/\text{min}$; (3) Keep for 60 min when the temperature reached T_c and micrographs were taken per minute using a computer-controlled digital camera.

Scanning Electronic Microscopy (SEM) Observation

Interfacial crystalline morphology of POM/PBS blends induced by a single PA6 fiber was observed by a Nova NanoSEM450 field-emission SEM (FEI, USA). The accelerating voltage was 5 kV. All the film specimens were sputtered with a thin golden layer before observation.

Scanning Microbeam Two-dimensional Wide-angle X-ray Diffraction (2D-WAXD) Measurement

High-resolution scanning microbeam 2D-WAXD measurement was conducted at the beamline BL15U1, Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China) with an SX165 X-ray CCD detector (Rayonix Co., Ltd. USA). The X-ray beam had a wavelength of 0.124 nm and was concentrated in a region of 3 $\mu\text{m} \times 2.7$ μm (length $\times$ width). The distance from the sample to the detector was 158.9 mm. The schematic diagram of micro-focus scanning was illustrated in Fig. S3 (in ESI). The step size was 5 μm and the arrow indicated the scanning direction.

RESULTS AND DISCUSSION

Interfacial Crystalline Morphology Induced by the PA6 Fiber

Fig. 1 shows the crystalline morphology evolution of POM/PBS blends induced by a single PA6 fiber at different T_c . A large number of nuclei congregate along the fiber surface, while sporadic nuclei are randomly distributed in the region away from the fiber (Figs. 1a₁–1d₁). It verifies that the PA6 fiber has a strong heterogeneous nucleation ability for POM/PBS blends. Considering the T_c in this work is higher than the melting point of the PBS phase (113.1 $^\circ\text{C}$), the nuclei and subsequent crystallization are only relevant to the POM phase. DSC results also support the time-resolved PLM observation (Fig. S4 in ESI). During non-isothermal crystallization, the initial crystallization temperature rises significantly with the increase of PA6 fiber content (Fig. S4a in ESI). Accordingly, the exothermic peak becomes sharper and shifts to a higher temperature, indicating that the non-isothermal crystallization is advanced. During isothermal crystallization, the onset crystallization time goes forward and the total period is shortened with the fiber content (Fig. S4b in ESI). These results powerfully demonstrate that the PA6 fiber promotes the nucleation and crystallization of POM/PBS blends effectively.

Due to the exceeding heterogeneous nucleation activity of the PA6 fiber, the nuclei density on the interface is high enough to hinder the multi-direction development of POM crystals (Fig. 1a₁). As a result, crystallization is forced to develop perpendicularly to the axial direction of the fiber. It is inter-

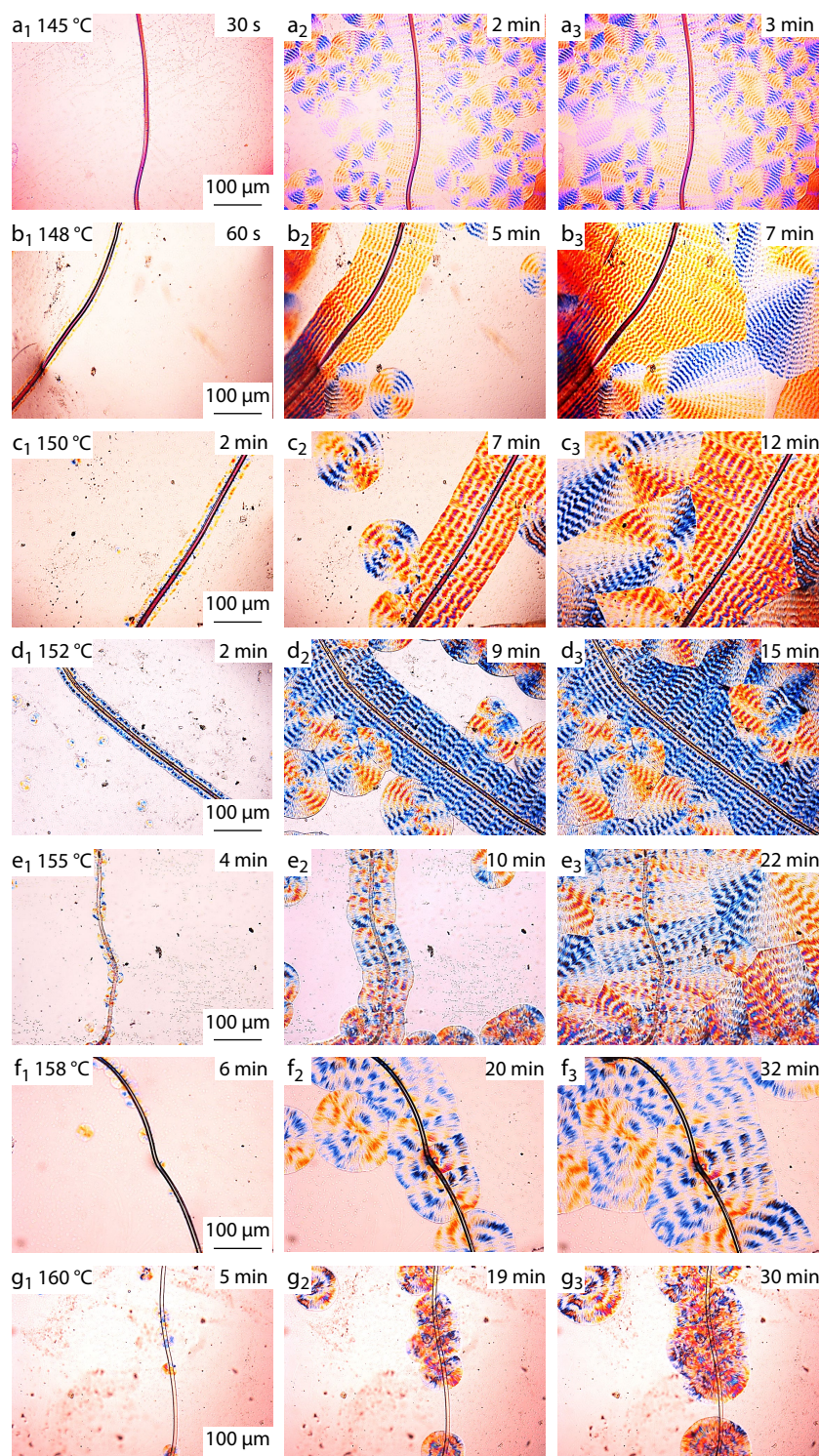


Fig. 1 PLM images showing the banded morphology evolution of POM/PBS blends induced by a single PA6 fiber as a function of time at T_c of (a₁–a₃) $145\text{ }^{\circ}\text{C}$, (b₁–b₃) $148\text{ }^{\circ}\text{C}$, (c₁–c₃) $150\text{ }^{\circ}\text{C}$, (d₁–d₃) $152\text{ }^{\circ}\text{C}$, (e₁–e₃) $155\text{ }^{\circ}\text{C}$, (f₁–f₃) $158\text{ }^{\circ}\text{C}$, and (g₁–g₃) $160\text{ }^{\circ}\text{C}$.

esting to note that periodic extinction occurs along the radial direction. As a result, unique banded transcrystallization of POM/PBS blends is cultivated on the PA6 fiber (Fig. 1a₂). As the crystallization time prolongs, the interfacial banded transcrystallization and banded spherulites grow larger until they impinge against each other (Fig. 1a₃).

T_c has a profound influence on crystalline growth and resultant morphology since nucleation and crystal growth rates of the polymer strongly depend on the temperature.^[8,43,44] When T_c increases from $145\text{ }^{\circ}\text{C}$ to $152\text{ }^{\circ}\text{C}$, the nucleation and crystallization growth are remarkably prolonged (Figs. 1b₁–1d₁). It is because the nucleation is limited by a

high nucleation energy barrier at a lower supercooling degree, which retards the formation of nuclei. Even so, the nuclei density at the interface is predominant (Figs. 1b₂–1d₂). In addition, the width of transcrystallization thickens with T_c (Figs. 1b₃–1d₃) due to the reduced lamellar growth rate.

As the T_c increases to 155 °C, the density of crystal nuclei

decreases significantly, which hardly covers the entire surface of the PA6 fiber (Fig. 1e₁). Prior studies suggested that the essence of transcrystallization was an accumulation of squeezed spherulites along a specific direction.^[45,46] The decrease of the nuclei density makes the lateral extension of spherulites easier. Thus, the development of banded lamellae

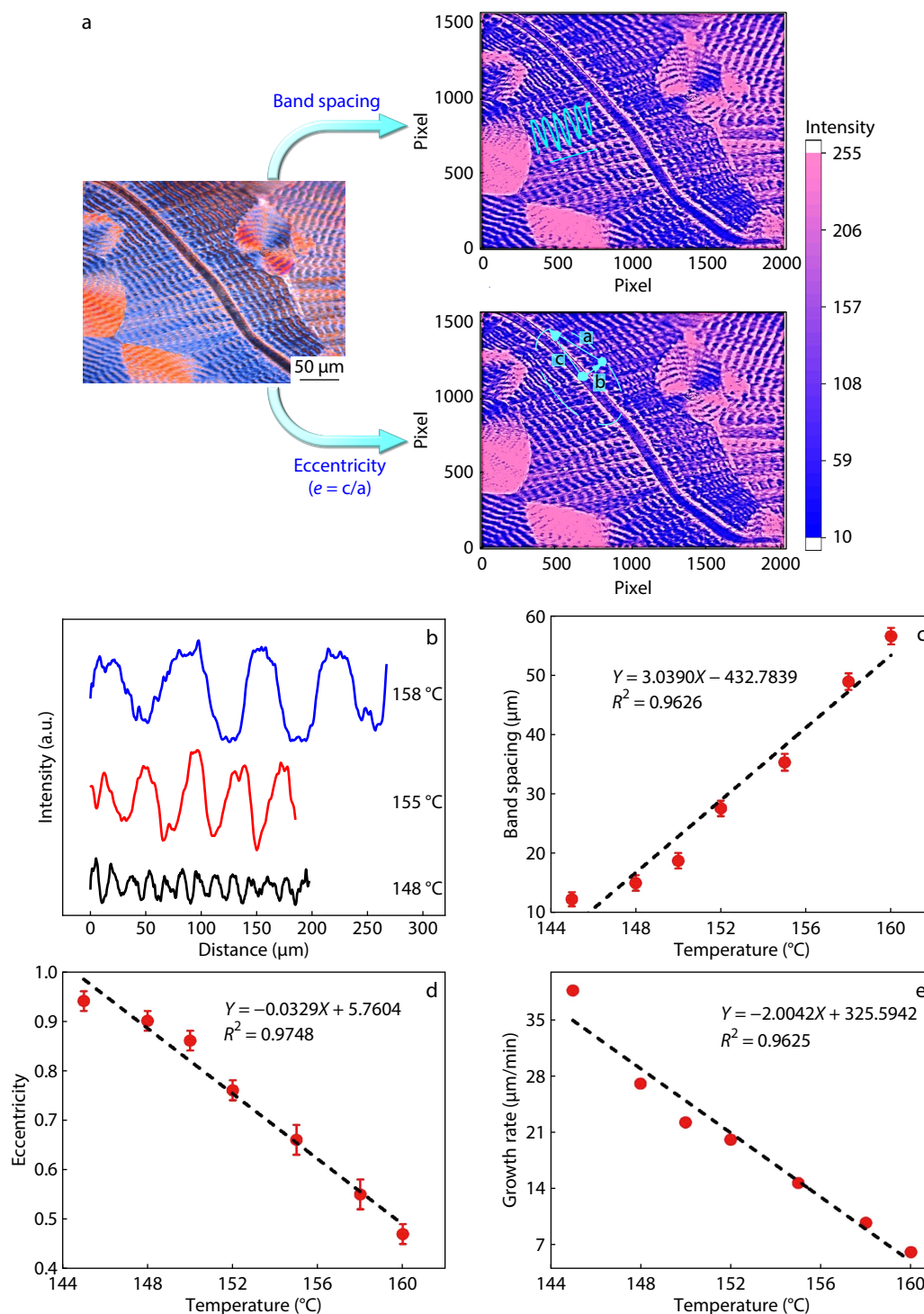


Fig. 2 Schematic showing (a) the measurement of band spacing and elliptical eccentricity from the HSI-converted PLM image; (b) The intensity variation of the band as a function of distance from the central PA6 axis to the outside; The relationship between (c) band spacing, (d) elliptical eccentricity, and (e) crystal growth rate of banded transcrystallization with T_c .

enables the banded transcrystallization in a fan-like shape (Fig. 1e₂). When further rising T_c to 158 °C, the spherulite is barely formed in bulk, a nucleation-controlled crystallization occurs, where nucleation is predominately induced by the PA6 fiber. Consequently, the sparse nuclei generate semi-circle-shaped transcrystallization (Fig. 1f₁–1f₃). At the T_c of 160 °C, the density of nuclei is too low to hinder spatial extension of lamellae. A shish-calabash-like interfacial banded transcrystallization is formed (Figs. 1g₁–1g₃).

Quantitative Data Analysis of Banded Transcrystalline Morphology

To establish a quantitative relationship between transcrystalline microstructure and T_c , the PLM images were transformed using the hue-saturation-intensity (HSI) model (Fig. 2a). The featured structural parameters of interfacial banded transcrystallization, such as band spacing and eccentricity of elliptical bands, were measured from the converted digital images. Fig. 2(b) plots the change of intensity in the HSI model along the radial direction of banded transcrystallization at different T_c . The sinusoidal profile corresponds to periodic alternating bands of light and dark. By measuring the distance between the neighboring sinusoidal peaks (or valleys), the band spacing was acquired. Interestingly, the band spacing increases linearly with T_c (Fig. 2c). This is because the dense nuclei on the interface give birth to additional interfacial instability and aggrandize the unbalanced surface stress for lamellar twisting. However, as the T_c drives up, the nuclei density on the fiber surface decreases, which contributes to the alleviation of torsional stress. Besides, lamellar thickening at low undercooling impedes lamellar twisting.

It can be seen that the fronting of the banded transcrystallization grows into an elliptical shape along the fiber axis. The eccentricity defined as c/a in Fig. 2(a) is a way of measuring how much an orbit deviates from a perfect circle. Herein, the eccentricity of the elliptical bands was used to

evaluate the band deformation, where a higher eccentricity means a larger deformation of the circular bands. The eccentricity shows a negative correlation with T_c , indicating less band deformation (Fig. 2d). The crystalline growth rate at different T_c s is obtained by measuring the width of banded transcrystallization as a function of crystallization time. The low supercooling aggravates the chain detachment with the rise of T_c . As a result, the growth rate decelerates linearly with T_c (Fig. 2e).

Microscopic Morphology of Banded Crystals Induced by the PA6 Fiber

Figs. 3(a₁)–3(c₁) displays enlarged PLM images of interfacial banded transcrystallization. It can be seen that the banded pattern varies at different T_c s. To observe the detailed lamellar morphology, SEM observation was performed. At T_c of 148 °C, the banded stripes develop like parallel waves from the fiber surface (Fig. 3a₂). At higher magnification, rich nuclei localize the PA6 fiber surface at T_c of 148 °C. The lateral extension of lamellae is confined by a spatial hindrance, forcing the growth of lamellae nearly perpendicular to the fiber axis (Fig. 3a₃). As the T_c increases to 155 and 158 °C, the banded stripes transform into a fan-like shape (Figs. 3b₂ and 3c₂). It manifests that the transformation of banded stripes is defined by the density of nuclei along the surface of the PA6 fiber. The reduced nucleation density at high T_c provides more available space for lamellae to grow in a multi-direction manner (Figs. 3b₃ and 3c₃). It explains the formation of shish-calabash-like banded transcrystallization.

Crystalline Structure of Banded Transcrystallization Induced by the PA6 Fiber

The crystalline structure of banded transcrystallization induced by PA6 fibers at different T_c s was studied by micro-focus 2D-WAXD. Fig. 4 shows the 2D-WAXD patterns of banded crystals scanned radially from the center of the fiber at 5 μ m steps. The

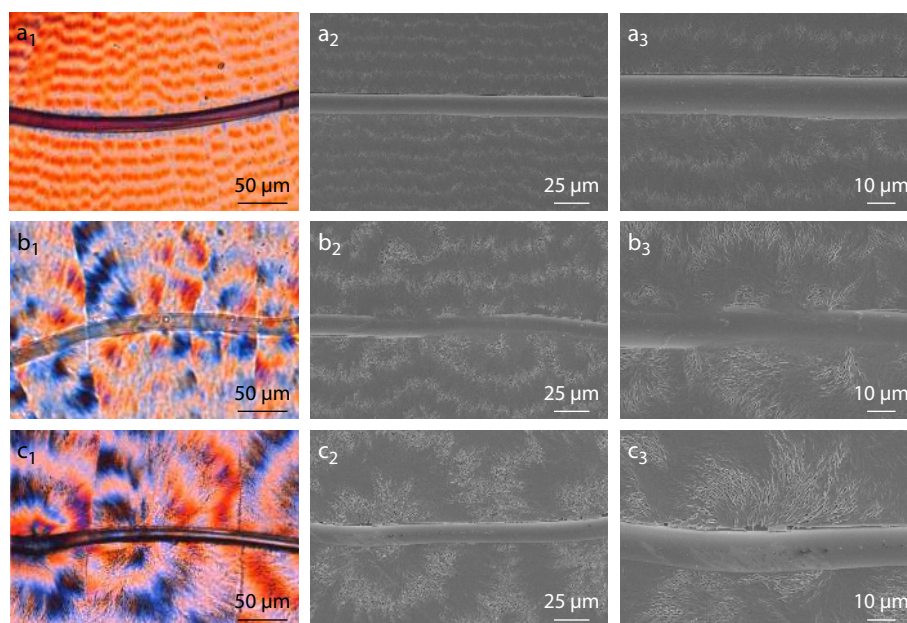


Fig. 3 PLM (a₁–c₁) and SEM (a₂–c₃) images of detailed crystalline morphology of banded transcrystallization induced by the PA6 fiber at T_c of (a) 148 °C, (b) 155 °C, and (c) 158 °C after isothermal crystallization for 60 min.

high anisotropic diffraction signal in the center is attributed to the strong orientation of the PA6 fiber itself, consistent with the result shown in Fig. S1(a) (in ESI). The asymmetrical spots are derived from the tilt angle between the PA6 fiber and the X-ray direction, since the micro-focus scanning has a very small-size light spot and the PA fiber is curly with a small diameter. This phenomenon sometimes occurs for the microfocus WAXD technique.^[47] The two weak diffraction signals in the middle are (021) and (020) crystal planes of the PBS phase, respectively. And the strongest diffraction is the overlap of (110) crystal plane of the PBS phase and (100) plane of the POM phase.^[48–50]

The 1D-WAXD curves at different T_c s were resolved from 2D-WAXD patterns, as shown in Figs. 5(a)–5(f). The diffraction peaks for (110) crystal plane of PBS and (100) crystal plane of POM are very close at $2\theta \sim 18.4^\circ$, making it hard to distinguish each other. While the other two weak peaks at $2\theta = 15.8^\circ$ and 17.9° belong to the (020) and (021) crystal planes of PBS, respectively. The peak position does not change and no new

diffraction peak appears, indicating the T_c does not affect the modification of POM and PBS, but it is worth noting that the peak intensities of both POM and PBS crystals fluctuate from the inside out. It reveals the spatial distribution of the lamellae along the radius of transcrystallization. More explicit results can be found in Fig. 6. The crystallinity of PBS changes periodically as a function of the distance away from the fiber. The variation period increases with T_c , which is in accordance with the band spacing as measured from PLM images (Fig. 2c). In fact, the fluctuation of PBS crystals results from the fluctuation of POM crystals, since both of them constitute a thin film. The rhythmic growth is reported as another mechanism for banded crystals, but it usually matches the sample with a very thin thickness (less than several μm). In this work, the sandwiched film has a thickness of $\sim 50 \mu\text{m}$. Thus, lamellar twisting is suggested to dominate the generation of banded transcrystallization.

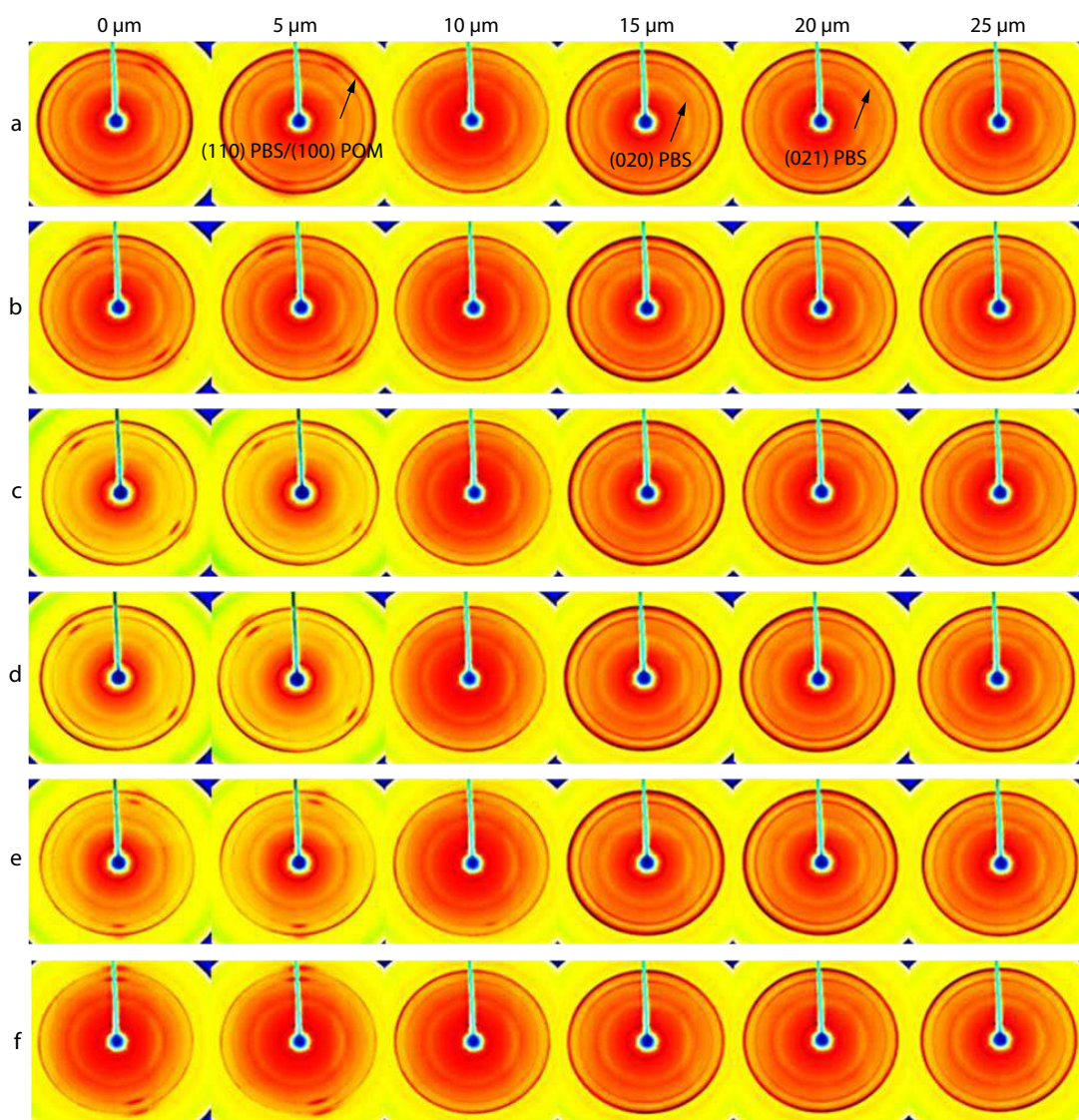


Fig. 4 Selected scanning microbeam 2D-WAXD patterns away from the central fiber at T_c s of (a) 148 °C, (b) 150 °C, (c) 152 °C, (d) 155 °C, (e) 158 °C, and (f) 160 °C.

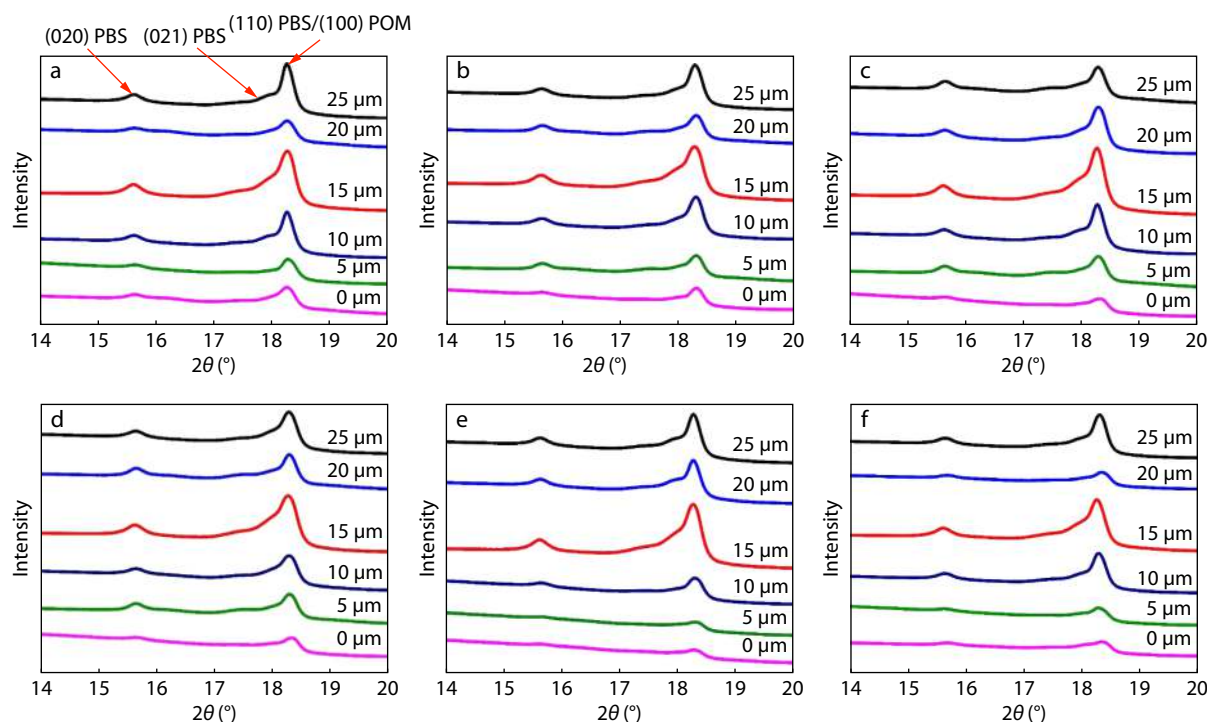


Fig. 5 1D-WAXD intensity profiles of the samples at T_c s of (a) 148 °C, (b) 150 °C, (c) 152 °C, (d) 155 °C, (e) 158 °C, and (f) 160 °C.

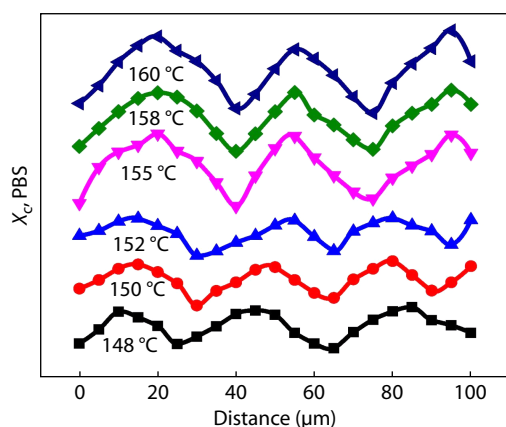


Fig. 6 Crystallinity distribution as a function of distance from the central PA6 fiber to outside at different T_c s.

Formation Mechanism of Interfacial Banded Transcrystallization

Given the above results, the evolution of nucleation and morphology/structure of banded crystals induced by the PA6 fiber is schematically depicted in Fig. 7. T_c is a substantial factor to determine the number of nucleation sites of the PA6 fiber. At low T_c , the nucleation ability of the PA6 fiber is strong enough to induce dense row-nuclei on the interface. Due to spatial obstruction, the lamellae are forced to grow perpendicular to the fiber axis. When the torsional stress caused by the growth and branch of lamellae exceeds a threshold value, lamellae twisting occurs to evolve a periodic banded structure. Finally, unique interfacial banded transcrystallization is formed (Fig. 7a). The increase of T_c weakens the nucleation on the fiber surface.

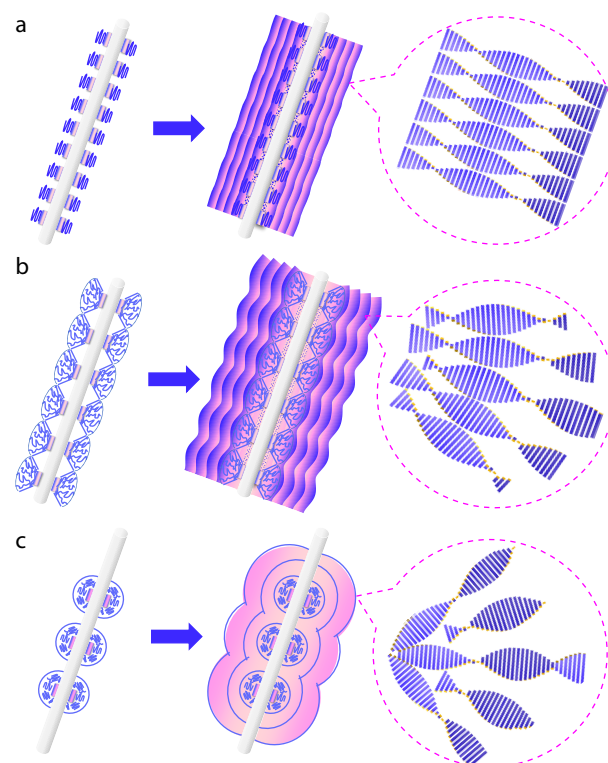


Fig. 7 Schematic for the formation of interfacial banded transcrystallization induced by the PA6 fiber: (a) wave-like interfacial banded transcrystallization at low T_c , (b) fan-like interfacial banded transcrystallization at medium T_c , and (c) shish-calabash-like banded transcrystallization at high T_c .

More available space is reserved for lamellar growth, allowing the formation of a fan-like banded transcrystallization (Fig. 7b). As T_c increases further, only sparse nuclei appear on the fiber surface. Under this circumstance, the lamellae develop divergently without hindrance to form a shish-calabash-like banded transcrystallization (Fig. 7c).

CONCLUSIONS

Interfacial banded transcrystallization of POM/PBS blends was induced by the PA6 fiber, which acted as a strong heterogeneous nucleating template to facilitate twisted lamellae grown perpendicular to the fiber axis. Crystallization temperature plays a pivotal role in determining the heterogeneous nucleation efficacy of the PA6 fiber. With increasing crystallization temperature, the nucleation density on the interface showed a decreased trend. Correspondingly, the wave-like banded stripes transformed into a fan-like shape, and diverse interfacial banded transcrystallization was obtained. The band spacing increased, associated with a linear descent of the eccentricity with crystallization temperature. It was mainly due to the alleviated steric hindrance by decreased nucleation density. The current effort enriches the means to regulate the architecture of banded crystals in polymer composites.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2684-6>.

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