

Study on the crystal morphology and melting behavior of isothermally crystallized composites of short carbon fiber and poly(trimethylene terephthalate)

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Abstract The spherulites of the short carbon fiber(SCF)/poly(trimethylene terephthalate)(PTT) composites formed in limited space at designed temperatures, and their melting behaviors were studied by the polarized optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM), respectively. The results suggest that SCF content, isothermal crystallization temperatures, and the film thicknesses influence the crystal morphology of the composites. The dimension of the spherulites is decreased with increasing SCF content, but whether banded or nonbanded spherulites will form in the composites is not dependent on SCF content. However, the crystal morphology of the composites depends strongly on the temperature. When the isothermal crystallization temperatures increase from 180°C to 230°C, the crystal morphology of SCF/PTT composites continuously changes in the following order: nonbanded → banded → nonbanded spherulites. Discontinuous circle lines form in the film when the film thickness increases from 30 to 60 μm. Basing on the SEM observation, it is found that these circle lines are cracks formed due to the constriction difference of the different parts of the spherulites. These cracks are formed when the film is cooled from the isothermal crystallization temperature to the room temperature at a slow cooling rate; while they will disappear gradually at different temperatures in the heating process. The crack will appear/disappear first around the center of the spherulite when the film was cooled/heated. The nontwisted or slightly twisted lamellas will reorganize to form highly twisted lamellas inducing apparent banded texture of the spherulites.

Keywords poly(trimethylene terephthalate), short carbon fiber, banded spherulites, crack

1 Introduction

Poly(trimethylene terephthalate)(PTT) is a member of the aryl polyesters commercialized in 1995. More recently, PTT have drawn attention for its outstanding properties [1–7]. In general, the final properties of a polymer or its composite have close relationship with its crystallinity, crystal morphology, and crystal texture; so, it is very important to study the crystallization behavior of the system. It is generally believed that the extinction bands in banded spherulites are due to the periodic twisting of the lamella along the radial growth direction of the spherulites [6,8]. Chuang et al. [6] studied the PTT spherulites during isothermal crystallization. The morphological changed from an axialite/or elliptical banded spherulite to banded spherulite and then nonbanded spherulite with the temperature decreasing. The lamellar growth mechanism varied at different crystallization temperature. Fibrillation of the edge-on lamella was observed on the surfaces of axialite and the convex bands of banded spherulite. Terrace-like lamellas were observed on the surface of the nonbanded spherulite and the concave bands of banded-spherulite. In thin film crystallization, PTT banded spherulite exhibits a texture of alternate edge-on and flat-on lamella, wavy-like surface, and rhythmic growth. On the other hand, the acceleration of growth rate appears in concave bands with a growth habit of terracelike lamella for emerging valley surface. The alternating growth mechanism of the lamella was considered to be related with the formation of spatiotemporal self-organization patterns far from equilibrium.

Some mechanisms of lamellar twisting within spherulites were given by many researchers [9–19]. Some mechanisms, such as the isochiral screw dislocation mechanism [10,11], are abandoned now. Currently, the mechanism of lamellar twisting within spherulites is

preferred for the unbalanced surface stresses associated with deposition of chains on inclined lamellae [16–19].

The effect of fibers on crystallization of semicrystalline thermoplastics is a major concern in polymer science because of the technical importance of fiber-reinforced composites [20]. The important studies on carbon fiber reinforced polymer composites include carbon fiber/poly(ether ether ketone) [21], carbon fiber/poly(propylene) [22], carbon fiber/poly(ether imide) [23], and short carbon fiber(SCF)/epoxy polymer [24]. However, to our knowledge, few experimental about effects of the short carbon fibers on the crystal morphology of PTT have been reported. Our earlier work [25] prepared the SCF/PTT composites and studied their crystal morphology and nonisothermal crystallization behaviors. It is found that some SCF are served as nucleating agents and increased the crystallization rate of the PTT; the composite with more SCF has higher crystallization ability. When the melt was cooled, banded spherulites formed in both PTT and its composites.

In the present work, the composites of SCF/PTT were characterized for their spherulites texture, surface topography of spherulites formed in limited space, and their melting behavior by using the polarized optical microscopy, atomic force microscopy, and scanning electron microscopy. The effects of the section of SCF, temperature, and the film thickness on the spherulite are investigated in detail.

2 Experimental

2.1 Materials

PTT, named of Corterra 9240, was supplied in pellet form by Shell Chemicals (USA) with an intrinsic viscosity of 0.92 dL/g provided by the producer. The short carbon fibers with epoxy sizing (B-DJ04S) used in our experiment was a PAN-based type supplied by Anbaoli Co. Ltd. (China) with a diameter of 7 μm and an average length of 4 mm. PTT/SCF composites were prepared in our lab [25].

2.2 Polarized optical microscopy (POM)

Polarized optical microscope (Yongheng 59XA, China) with a digital camera system (Panasonic wv-CP240, Japan) was used for the observation of the crystal morphology. The procedure were taken as follows: samples of pure PTT or SCF/PTT composites were pressed between two glass slides on the hot stage with a distance of about 30 or 60 μm and first melted at 260°C for 5 min to eliminate the thermal history, and, then, quenched to the desired temperature, held for 7 h, and cooled to room temperature at 8°C/min. Afterwhich, photographs of the final spherulites were taken.

In order to observe the changing process of the above

spherulites, the crystallized samples were heated from room temperature to 260°C at a heating rate of 5°C/min, taking photographs at different temperatures.

2.3 Atomic force microscopy (AFM)

The crystalline samples prepared for the POM experiments were observed to study their surface topography by the atomic force microscopy (AFM) (CP-II, Digital Instruments), and all the scans were carried out in a tapping mode. After being quenched under liquid N₂, the glass slide on one side of the sample was removed, and then, the topography of the exposed surface of the sample was observed by the AFM.

2.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (KYKY-2800B, Travor-Norther Co., USA) was also used to study the surface topography at an accelerating voltage of 25 kV. Prior to the observations, the exposed surfaces of the above samples were sputter coated with gold, and the thickness of the thin layer is about 60 nm.

3 Results and discussion

3.1 Spherulites of different composites

The morphological feature of semicrystalline polymers, such as crystalline form and spherulites size, can be affected by filling [26]. Figure 1 shows the POM micrographs of SCF/PTT composites, with film thickness of about 30 μm , isothermally crystallized at 205°C, and then cooled at 8°C/min to room temperature. In the micrographs of all the composites, some SCF (the short black fibers) disperse in the PTT matrix. It can be observed in Fig. 1 that all spherulites in both pure PTT and SCF/PTT composites show well-defined Maltese cross extinction patterns and apparent periodic banding patterns; this banded pattern is predominantly decided by the crystallization temperature. However, the band spacing of the spherulites and the spherulites' size are different in these micrographs. As seen in Figs. 1(a)–(d), the spherulites of pure PTT have a clearer band spacing of about 15 μm ; while the band spacing of the composites becomes narrow and vague gradually with increasing SCF content. Blending reduced band spacing in the blends has been observed in the poly(ϵ -caprolactone)/poly(styrene-co-acrylonitrile) [27] and poly(ϵ -caprolactone)/ethyl cellulose blends [28]. However, why the blending causes narrower band spacing is still unclear. It is known that in pure crystalline polymer, band spacing may depend on the following factors: chain mobility, radial growth rate of the spherulite, degree of super-cooling, surface free energy, lamellar thickness, etc [5,6]. The filling of SCF into PTT

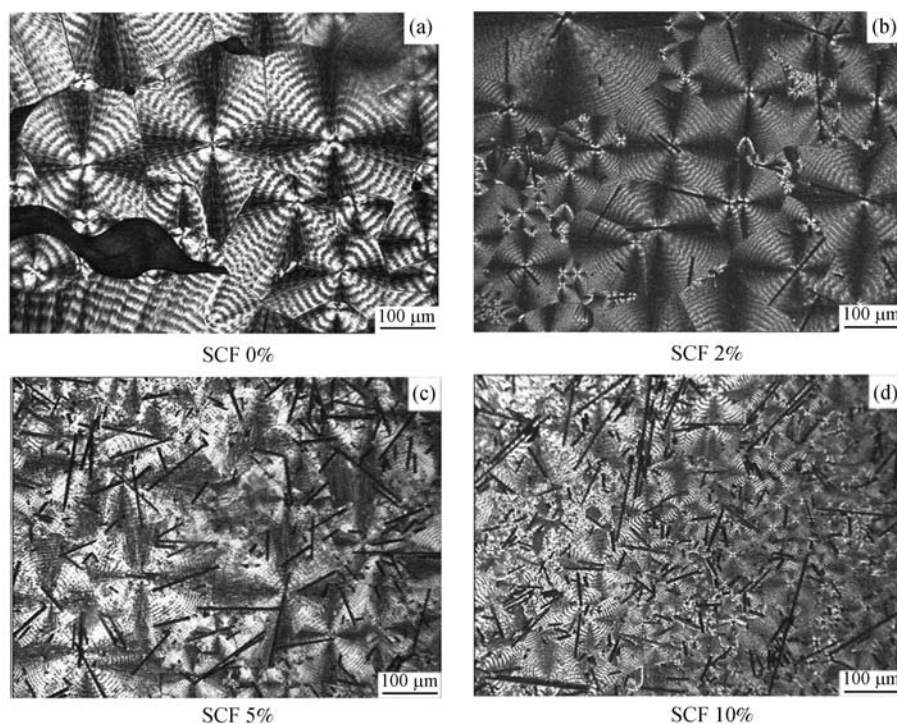


Fig. 1 POM micrographs of the different SCF/PTT composites crystallized from melt at 205°C for 7 h with film thickness of about 30 μm

will surely influence all the above factors, so the band spacing decreases.

Moreover, the spherulites' dimension is also decreased with the increasing content of the SCF due to the nucleating effect of the SCF in PTT matrix [25]. As seen clearly in Fig. 1(b), most spherulites are grown with the SCF as the nuclei, i.e., a part of the SCF is served as nuclei for the crystal growth of the PTT. However, it should be noted that not all of the SCF are acted as nucleating agents in the matrix because some of the SCF does not exist in the center of the spherulites. This may be because some of the SCF with epoxy sizing have a weak interaction with the PTT molecular chains.

3.2 Effect of the temperature on spherulites

The relationship between the temperature and the spherulites in SCF/PTT composites (SCF 2%) was studied from the viewpoint of crystallization-temperature dependency [2,5]. Figure 2 shows a series of POM micrographs for spherulites crystallized at various isothermal melt-crystallization temperatures from 180°C to 230°C.

The well-defined Maltese cross extinction without banded patterns appeared at 180°C, as shown in Fig. 2 (a). After isothermally crystallized at 190°C for 7 h, as shown in Fig. 2(b), the spherulites still show well defined Maltese cross extinction but with narrow faintness periodic banded patterns. With increasing temperature to 200°C, the

banded spherulites are clearly observed in Fig. 2(c) with the band spacing increasing greatly to about 10 μm . In Fig. 2(d), the band spacing is increased to about 20 μm at 210°C; however, the regular banded morphology had changed to irregular zigzag mode. At 220°C and 230°C (Figs. 2(e) and (f)), the spherulites lost its birefringence gradually, and the Maltese cross extinction faded away progressively. The banding begins to break down as the temperature was increased to 230°C. Apparently, the loss is due to poor orientation of the lamellae along the radial direction of the spherulite. In conclusion, in the temperature range of 180°C–230°C, the spherulites of the SCF/PTT composites changes with the temperature in the following order: from nonbanded \rightarrow banded \rightarrow serrated-type \rightarrow nonbanded spherulites, or clear Maltese cross extinction \rightarrow weak Maltese cross extinction \rightarrow non-Maltese cross extinction; there is a dependence of the spherulites on the temperature.

3.3 Effect of the film thickness on spherulites

To investigate the effect of the film thickness on the spherulites, samples with film thickness of 60 μm were studied under the POM and optical microscopy (OM). Figure 3 shows the spherulites micrographs of A1-A4 composites isothermally crystallized at 205°C, respectively.

For the film with thickness of about 60 μm , the banded

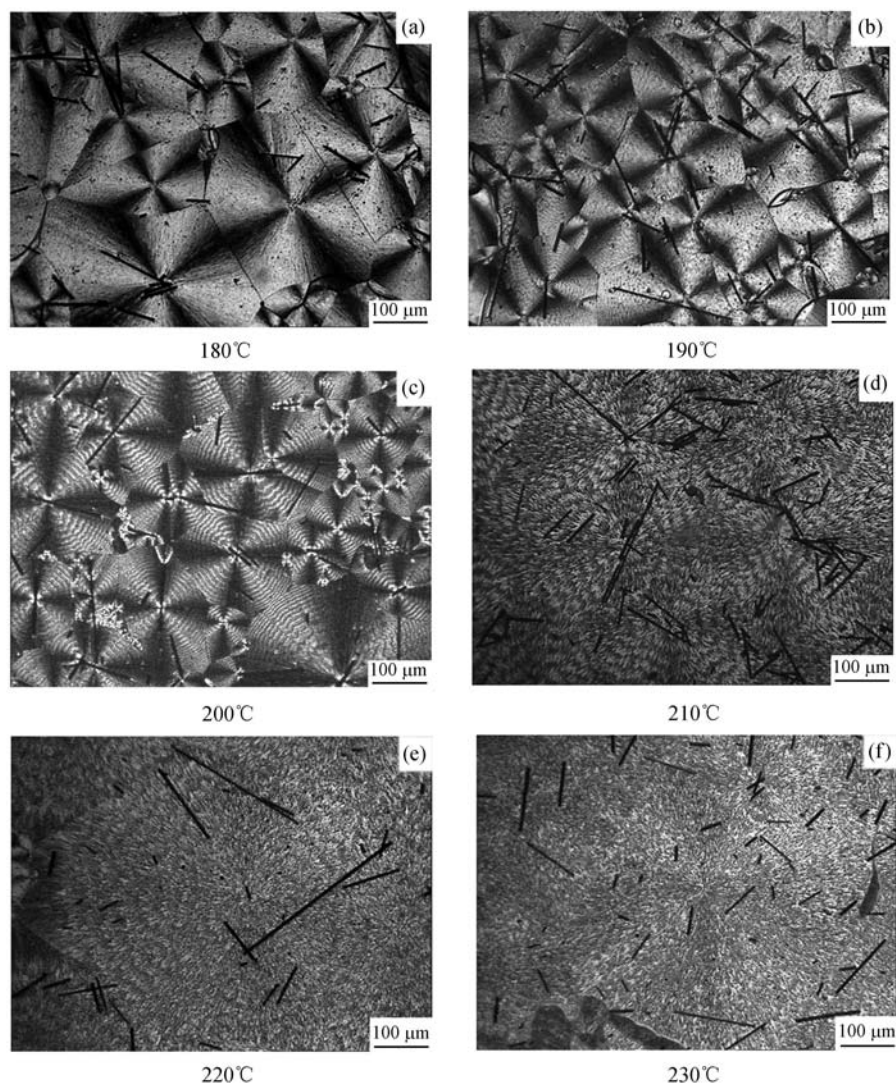


Fig. 2 POM micrographs of the composites (SCF 2%) crystallized from melt at a variety of temperatures for 7 h with film thickness of about 30 μm

spherulites with Maltese cross-extinction pattern and alternative extinct zones were observed clearly in Fig. 3 (a). After careful observation, some discontinuous homocentric circle lines are shown in the micrograph. These discontinuous homocentric circle lines can be observed more clearly under optical microscopy, as shown in Fig. 3 (b). However, the circle lines space is not as uniform as those band spacing; the circle lines space is in the range of 15–30 μm, while the band spacing is about 15 μm. Some circle lines are located in the black bandings (as marked by the white arrows), while others are in the white bandings. Within one spherulite, the propagation of some circle lines is stopped or interrupted by the short carbon fibers or its minute scraps. On the other hand, the circle lines propagate and stop at the boundary of the spherulite, i.e., the lines of different spherulites do not intercross each other. It should be noted that the circle lines are observed forming

gradually in the cooling process (8°C/min) after the sample isothermally crystallized at 205°C for 7 h; the lines appear first in the center of the spherulite, and then gradually formed from the center to the fringe of the spherulite. However, when the crystallized sample is cooled fast (above 80°C/min), the circle lines could not form. Some previous research works [29–32] also found the homocentric lines in different polymer spherulites; they believe that these lines are cracks, but there are no detailed characterizations of these cracks. We will study these lines in next part in detail.

With the SCF content increasing, as shown in Figs. 3 (b)–(h), the spherulites show the similar changing tendency, i.e., the band spacing becomes faintly, and the spherulites' size decreases gradually. At the same time, the homocentric circle lines still appears clearly in these figures, especially under the optical microscopy, although

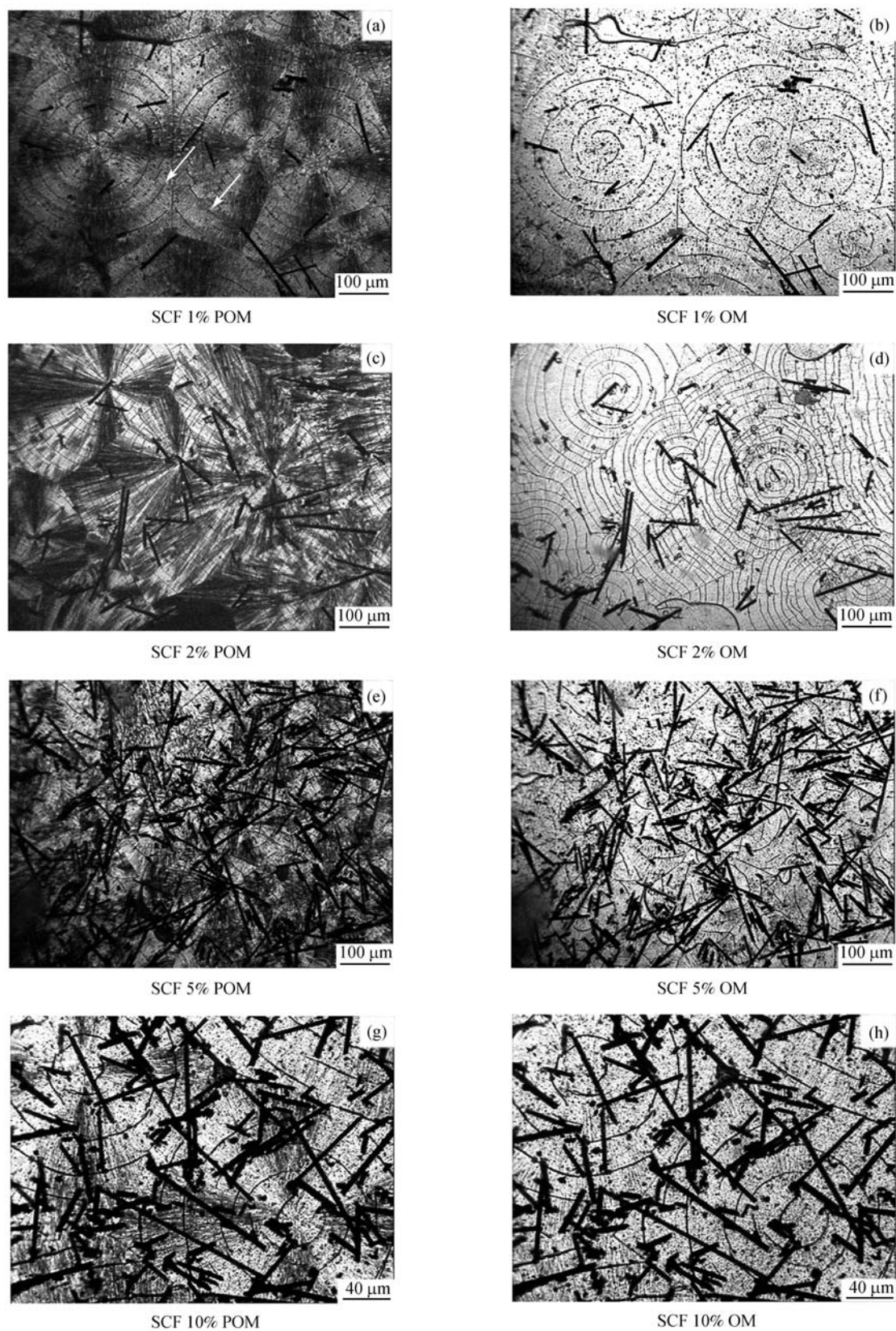


Fig. 3 POM and OM micrographs of different composites after isothermally crystallized from melt at 205°C for 7 h; the film thickness is about 60 μm

they are more frequently interrupted by the increasing content of SCF in the matrix. In order to see the circle lines clearly in the composite with SCF 10%, the POM and OM micrographs were further magnified with $250\times$, as shown in Figs. 3(g)–(h). The circle lines can also form with a lot of SCF, but they are more discontinuous due to the disturbance of the SCF. Comparing the spherulites in Fig. 2 with those in Fig. 1, it is found that no circle lines appeared in Fig. 1, i.e., when the film thickness is $30\ \mu\text{m}$ the circle lines can not form in the spherulites.

3.4 Surface topography of the composite's spherulites

In order to investigate the detailed morphology of the discontinuous circles lines appeared in Fig. 3, SEM and AFM measurements were carried out to observe the surface topography of the spherulites, as shown in Fig. 4. Before the observation, the glass slide on one side of the

crystallized film was disclosed to expose the surface of the spherulites. Figure 4(a) shows a surface topography of the crystallized composite under SEM, and many discontinuous circle lines appeared homocentrically (as marked by the black arrow). These discontinuous circle lines look like cracks of the film. At the same time, some bulgy SCF covered by gold or polymer are also appeared in the micrograph (as marked by the three white arrows). Moreover, it can be seen that the cracks stop propagation when they come into touch with the SCF.

When the circle lines in Fig. 4(a) are magnified under SEM, as shown in Fig. 4(b), the circle lines are clearly seen as a piece of crack with the maximum width of about $1\ \mu\text{m}$; within the crack, a mass of cilia or microfibers are seen perpendicular to the direction of the line (or parallel to the radial direction). Moreover, some cilia are ruptured, while others were continuous. This result indicates that the crystalline film was somewhat toughness. The formation of

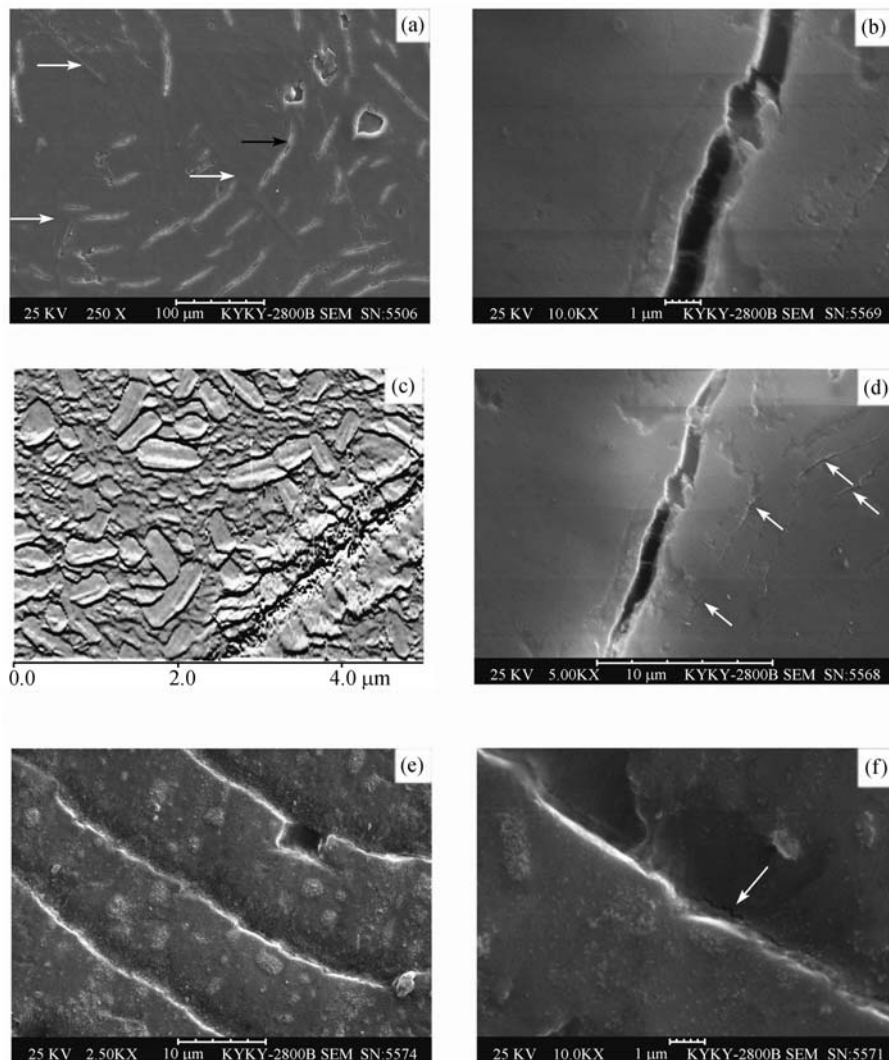


Fig. 4 SEM and AFM micrographs of circle lines on the composite's film surface with different magnifications. (a) SEM, $250\times$; (b) SEM, $10000\times$; (c) AFM, $10000\times$; (d) SEM, $5000\times$; (e) SEM, $2500\times$; (f) SEM, $10000\times$

the crack is proposed to the difference of the constriction coefficients of the spherulites film along the radial and the tangential direction of the spherulite during the cooling process [30,31]. It should be noted that for the pure PTT, the cracks do not appear under the same film thickness and cooling rate. Thus, besides the effect of the film thickness on cracks, we believe that SCF is another factor for causing the cracks.

However, the surface of the film is nearly smooth, and no apparent concave and convexity morphology appeared besides the cracks. The image in Fig. 4(c) is the further features of the film surface observed by AFM. A part of the crack is seen at the lower right corner of the image; however, no detailed characters within the crack can be seen under the AFM. While much of the irregular terraces-like structure can be seen in the image. We believe that they are multiple lamellar crystal of the spherulite.

In Fig. 4(d), some microterraces-like morphologies are also seen on the right of the crack, as marked by the white arrows; the height of the terraces increased along the radius, and the width of the terraces are different from each other; furthermore, the terrace was acclivitous from the spherulites center to the circumference. We believe that this structure is related with the film surface of the sample that has been formed between the two glass slides. Xu et al. [33] reported that the surface topography of spherulites is acclivitous terraces, which is low in center and high in circumference; the growth of terrace takes turns from inside to outside.

Other magnified terraces are seen under SEM in Fig. 4(e); it can be seen that they are homocentric with the terrace width of about 12–15 μm . Chuang et al. [6] also reported that the terrace-like lamella was observed on the surface of the nonbanded spherulite. When the terrace was further magnified, as shown in Fig. 4(f), there is a primary crack at the bottom of one terrace (as marked by the white arrow). The crack propagates along the bottom of the terrace, forming the discontinuous circle lines. However, no cracks are seen on the top surface of the terraces.

The reason why the crack appeared between the different terraces is that this part is the weakest part of the banded spherulites. During the crystallization process of the sample, the terraces formed with different thicknesses, i.e., the farther the terrace formed to the center of the spherulite, the thicker the film is. Thus, the unbalanced stress will be produced by the different constriction coefficients between different film thicknesses. If the inner stresses overstep the strength of the lamellas, lamellas will split at the bottom of the terrace. For different parts of the bottom that suffered different stress, the discontinuous circle lines were formed. Of course, as the crack propagates, if it meets with the SCF, then the crack will stop growing. Therefore, we believe that the difference of the constriction coefficients between different parts of the spherulites film with various thicknesses is an important reason for forming a crack. On the other hand,

we believe that the inner stress is lower than the strength of the lamellas when the film thickness is 30 μm , so the cracks will not form in these spherulites in Fig. 2.

According to the above results, some reasons are believed important for the crack: (1) Whether a crack will appear or not in the film is dependent on the difference between the inner stress and the film strength. (2) No cracks will form in pure PTT with any film thickness. PTT is different to PLLA although similar cracks are also widely reported in poly(L-lactic acid) (PLLA) with no fibers or other polymers [29–32]. The film strength and the constriction difference of these polymers are all different to PTT. (3) When the SCF/PTT film is about 30 μm , no cracks will form in the film; however, when the film is 60 μm , cracks will form easily in the film. Therefore, we believe that the film thickness is one of the reasons for crack. (4) When pure PTT film thickness is 60 μm , no cracks will form in the film, so we suppose that SCF is another reason for crack. (5) When the isothermally crystallized film was cooled rapidly (such as in ice water), no cracks will form; however, when it is cooled slowly, cracks will form gradually. Therefore, the cooling rate is also a reason for crack. In other words, film thickness, fibers, and cooling rate are all reasons for crack in SCF/PTT composite. All these conditions will influence the constriction of the film, which will further induce the inner stress of the film.

3.5 Effect of the temperature on circle lines and the spherulite

The crystallized composites (SCF 5%) film with discontinuous circle lines were also heated continuously in situ on a hot stage from 200°C to 260°C; and the changing of the circle lines were observed by POM. At 205°C, the circle lines are clearly seen in Fig. 5(a). When the temperature is increased to 210°C, the lines located closer to the center of the spherulite disappear first; those located farther to the spherulite center, as marked by the white arrow, become narrow.

As seen in Figs. 5(a)–(f), the line become narrow gradually and disappeared at last when the temperature increased from 205°C to 227°C. Because different parts of the spherulite have different constriction coefficients during the cooling process, they will also have different expansible coefficients during the heating process; therefore, different lines will disappear at different temperatures, i.e., if the crack disappears at the highest temperature, the terraces on both sides of the crack have the lowest expansible coefficients among the spherulite.

When the above film was further heated, the spherulites will change gradually, as shown in Fig. 6. When the temperature was increased from 244°C to 251°C, as shown in Figs. 6(a)–(d), the banded texture of the spherulites are observed from slightly clear to clear. There may be a melting-recrystallization-remelting process that occurs in

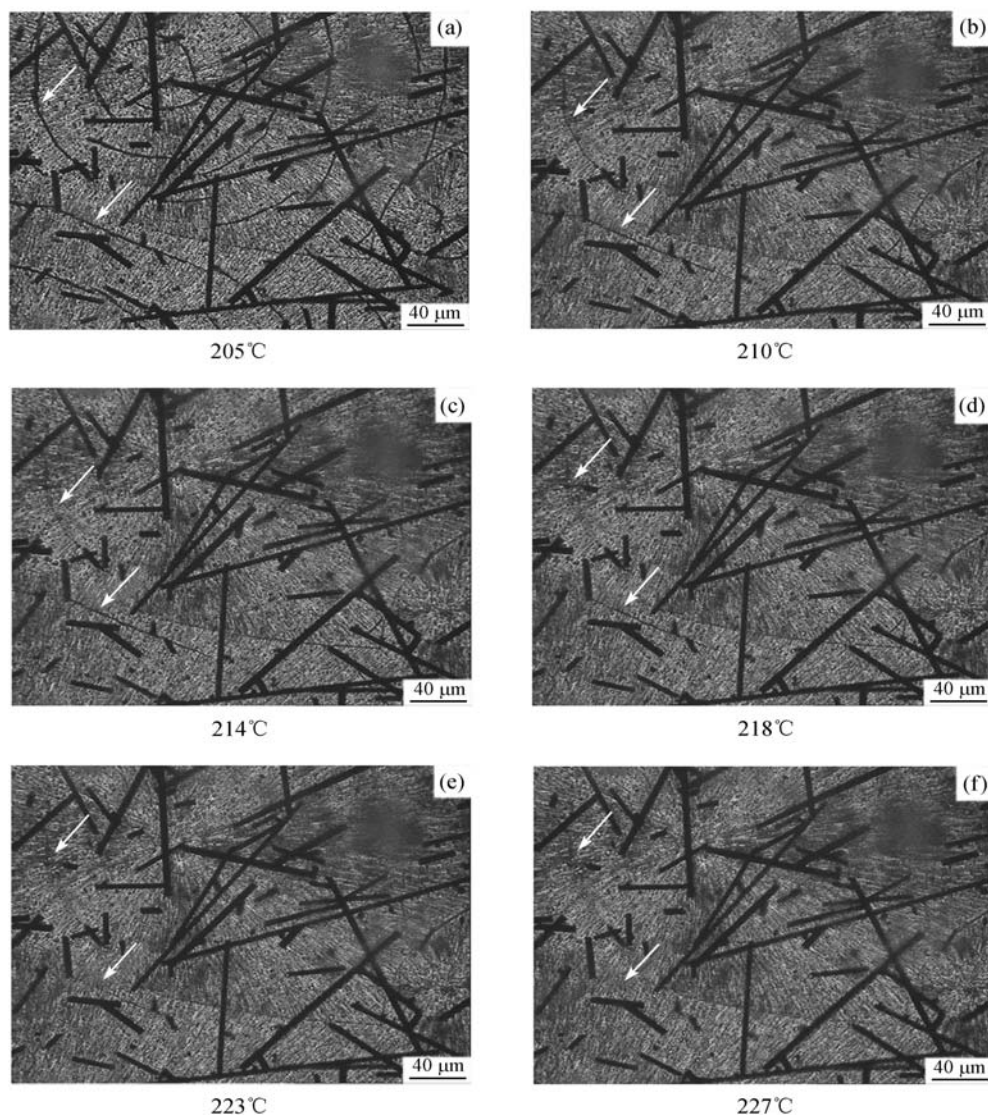


Fig. 5 POM micrographs of the changing process of the circle lines in spherulites film with thickness of about 60 μm at a heating rate of 5°C/min

the heating process. What occurred is supposed that the nontwisted or slightly twisted lamellas reorganize to form highly twisted lamellas during heating process, so the apparent banded texture of the spherulites are observed clearly. When the temperature was further increased to 253°C and 255°C, as shown in Figs. 6(e)–(f), banded spherulite began to melt and disappeared at last.

4 Conclusions

The effects of SCF, isothermally crystallization temperatures, the thicknesses of the film, and the heating on the spherulites in SCF/PTT composites were investigated in this work. The results suggest that the spherulites are

dependent on all the above factors. When the isothermal crystallization temperatures increase from 190°C to 225°C, PTT spherulites continuously change as follows, nonbanded \rightarrow banded \rightarrow nonbanded spherulites, which is similar to the results of pure PTT. The SCF additives reduce the dimension of the spherulites. Furthermore, discontinuous homocentric cracks formed in the spherulites film due to the constriction difference between the different parts of the spherulites. Different cracks will appear/disappear at different temperatures during the slow cooling/heating process. Some terraces are observed in some part of the film, and some cracks are located at the bottom of the terrace. During the heating process, the nontwisted or slightly twisted lamellas reorganize to form highly twisted lamellas inducing apparent banded texture of the spherulites.

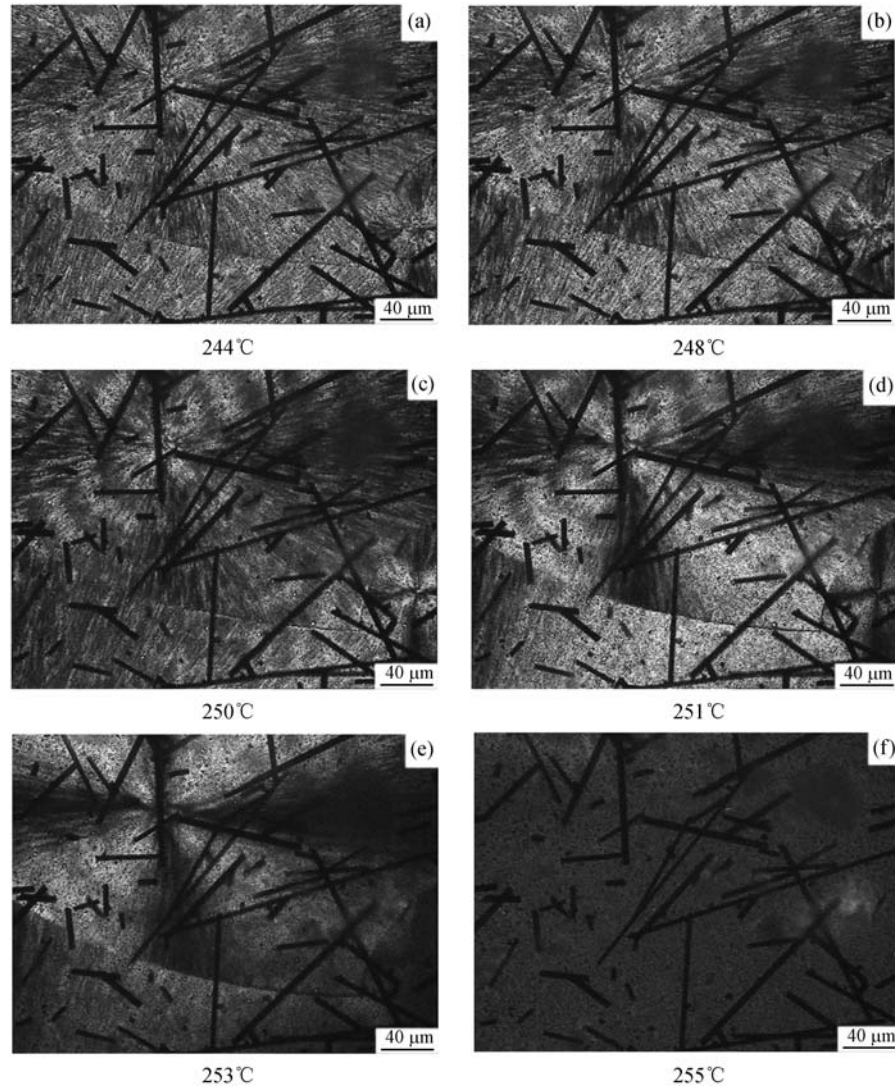


Fig. 6 POM micrographs of the changing spherulites with thickness of about 60 μm at a heating rate of 5°C/min

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