Cracking in low molecular PLLA banded spherulites

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Abstract

Banded spherulites and cracks can be formed in some polymers under proper experimental conditions. Lots of studies have been focused on banded pherulites or cracks on spherulites.In order to explore the differences of cracks in bright or dark bands, a kind of banded spherulites of low molecular PLLA was prepared in our study, it is interesting to be found that cracks were more likely to occur on the bright bands during the cooling process occasionally. This study mainly focused on this phenomenon, and the mechanism and correlation between banded spherulites and cracks are investigated.

Keywords

PLLA, Banded spherulites, Cracks.

1. Introduction

PLLA, a kind of material which can be completely derived from renewable resources, has attracted a lot of attentions due to its excellent biocompatibility, mechanical property and biodegradable property. Besides, it is also one of the most widely used biopolymers in biomedical fields, such as scaffold, drug carrier, and so on[1-5]. And the crystallization behavior of PLLA has been widely studied[6-11] due to the property is highly related to the morphology of crystals. Banded spherulites in PLLA have been observed under the isothermal crystallization condition by Xu et al. several years ago[12]. Before their study, banded spherulites can be formed in PLLA only in mixed blends such as poly(3-hydroxybutyrate) [9, 13, 14], poly(ethylene oxide) or in solution cast film and so on[15]. In recent years, the temperature range of forming banded spherulites of PLLA has been studied. Banded structure of PLLA can be formed when the temperature of isothermally crystallized was between 125℃ and 140℃[16]. And the influence of molecular weight to banded structure of PLLA has also been studied[17].

Cracks in spherulites were observed several decades ago. The brittleness of some polymer materials may results from the cracks in spherulites[18]. And the formation of the cracks should also be resulted from different expansion between radial and circumferential directions of spherulites during the cooling progress[19,20]. The cracks can be divided into two broad categories, one is circumferential crack, and the other is radial crack. Different types of cracks can be associated with different materials and different crystallization conditions. In addition, some special cases such as hexagon cracks have also been observed when spherulites are quenched into liquid nitrogen[21]. And some researchers also put forward that the cracks formation of spherulites resulted from the different expansion of polymer and substrates[22]. Fraschini et al. have used different substrates and studied the cracks[23]. The number of cracks in spherulites was slightly different on different substrates. The cracks can be influenced by a lot of factors, such as different substrates[23, 24], crystallization temperature[25], spherulite size[23, 25], sample thickness[26], with or without up covered glass[25], molecular weight and crystallinity[25].

The cracks in PLLA spherulites have been observed in previous reports. Fraschini et al. found the density of cracks per 100 μm increased with PLLA spherulite size, the relationship was nearly linear[23]. Nurkhamidah el al. showed the cracks were highly influenced by molecular weight and crystallinity of PLLA, and up covered glass at the same time showed large influence[25]. In a special issue, two types of cracks both occurred in low molecular PLLA banded spherulites[27]. Radial cracks occurred on the dark bands of spherulites and circumferential cracks occurred between bright and dark bands. This may due to the different lamella types in bright and dark bands, and discontinuity in transporting from bright to dark band regions[27]. When co-crystallization with PHB, cracks could be observed when hold at Tc for long enough time[28]. This fact indicates that cracks are not simply related to cooling-induced concentration: other mechanism involving crystallized lamellae are at work[29]. According to the previous studies, the crack behavior of spherulites involving the mechanism has remained as an elusive issue.

And after spherulites are formed, applying stress would also lead cracks. Only arc-shaped cracks are formed when the spherulites are negative while radial cracks are formed when spherulites are positive due to different crystallized lamellae in positive and negative spherulites[29].

In this study, a kind of relatively low molecular PLLA banded spherulites were prepared under a proper condition. It was found by chance that the cracks induced by cooling tended to locate on the bright band. This phenomenon drives us to conduct this research.

2. Material and Method

PLLA (Mw 22,000, PDI 1.1) without further purification used in our experiment was purchased from sigma Co. Films were prepared by dropping PLLA solution on clean glasses, using chloroform as a solvent. The thickness of films was controlled by the concentration of solution. And all the samples were crystallized without covered glasses to ensure the stability of films' thickness. Four different thickness of films,5 μm , 12 μm , 25 μm and 40 μm were prepared by four kinds of concentration of solution (2 wt%, 4 wt%, 6 wt%, 8 wt%) , which were coded named sample-5 μm , sample-12 μm , sample-25 μm ,sample-40 μm , respectively. For the banded spherulites, the concentration of polymer was 3.2 wt% and the film thickness was 8 μm. After dropping, the solvent was totally evaporated in atmosphere and dried at 40℃ for 1 h. Then the samples with glasses were heated on a hotstage (Linkam, England) to melt state of 195℃ for 5 min and rapidly cooled to designed temperature for crystallization. To avoid thermal degradation of PLLA, 195 ℃ was set as maximum temperature in this study. After crystallization, the samples were rapidly removed from the hot stage and kept at 4℃ for 10 min to make cracks fully developed. As for real-time observation of cracks, the samples were observed directly under POM on the hot stage which controlled the cooling speed.

The crystalline morphology of polymer was characterized by a polarized optical microscope (POM) equipped with a digital camera. After crystallization, samples were fast cooled on the hot stage and images were taken after removing polarizer on the microscope.

The morphology of cracks and spherulites was also characterized by atomic force microscopy (AFM: Instrument Model: Bioscope Catylyst Nanoscope-V. Produced by Veeco instruments, USA. Image mode: scanAsyst) in tapping mode with a silicon tip (f=150 kHz, k=5 N/m) installed. The scanning range of AFM characterization in this study was 100×100 μm^2. All the films on glass were characterized with an open face directly.

3. Results and Discussion

As shown in Fig.1, the bright and dark alternated bands could be observed clearly under the POM after spherulites of PLLA were prepared under isothermal condition (film thickness was 8 μm, Tc was

134℃). And after cooling, the circumferential cracks could also be observed under the POM and OM. It could be found that the cracks tended to locate on the bright bands. Previous studies has been demonstrated that the altitude of bright was higher than dark bands in banded spherulites[30-32]. It seems that our results were consistent with them, and the results would be shown later by AFM characterization. We tried to explain this phenomenon on perspective of different altitude of the bright and dark bands. In this study, cracks tended to locate on the bright bands during the cooling process. In the previous study[33], a similar result that cracks on bright bands have been shown in PTT banded spherulites by contacting solvent chloroform. The different treatment could include more meaning in deep. The solvent-induced cracks were more associated with lamella, while the cooling-induced cracks were associated with not only lamella but also thermal expansion. Note not all the cracks located on the bright bands, a small amount of cracks also located on the dark bands. When crack occurred on the bright bands, it tended to extend along a circle, while note the bands of the banded spherulites were not totally circle as shown in Fig. 1a. The not completely regular bands of spherulites caused not totally matched of the bands and cracks.

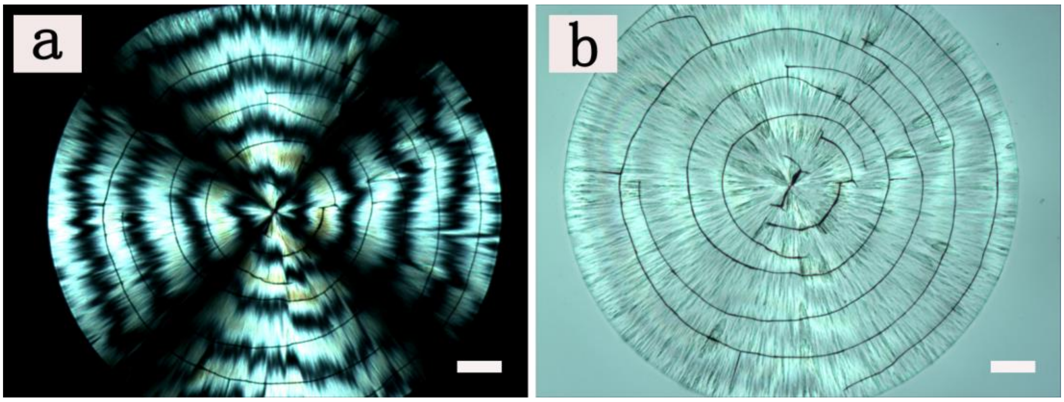

Fig. 1. POM images and the corresponding OM images of the PLLA banded spherulites with cracks, solution concentration= 3.2 wt%, Tc=134℃. The scale bar represents 100 μm.

Fig.2 showed the cracks of different thickness of samples (5 μm, 12 μm, 25 μm, 40 μm, respectively) crystallized at the same temperature (135℃). The upper column showed the POM images and the following column showed the corresponding OM images of the spherulites after cooled at 4℃ to make cracks fully developed. It could be clearly observed that the density of cracks decreased with the thickness of samples. In the previous study[26], the density of cracks of PTT spherulites firstly increased with samples' thickness, while the density decreased when the thickness continued to increase. At last, no cracks occurred after cooling when samples were thick enough. In this study of PLLA, it showed a similar but different result. The density of cracks continuously decreased with the increase of samples' thickness. Except for different materials, another possibility might be the different span range of thickness of studying. In Fig. 2a and Fig. 2e, no radial cracks could be observed. The visual field was dominated by circumferential cracks. While in Fig. 2b, 2c, 2d and Fig. 2e, 2f, 2g, some radial cracks directed by the centre of spherulites were observed. And the length of the radial cracks increased with the thickness of film. It could be concluded that radial cracks could be more easily formed in relatively thick films under the same Tc in this study. A crystallization nucleus nucleated in the centre of the sphere and crystals were aligned to the radial directions[34, 35]. Therefore, a spherulite was formed with a unique crystallography: both the radial direction and the direction perpendicular to it are associated with the crystal cells[20]. Hence, defects could exist between the crystal cells, including radial and perpendicular. And these defects could lead cracks during the cooling process due to the spherulites possessing different radial and circumferential thermal expansion coefficients which generate large internal stresses. And the radial cracks in thicker films might result from different stress forms compared to thin films. The volume of thick films was larger than thin films. Thus, cooling would lead larger volume contraction. Therefore, the tensile stress induced by cooling in thicker film was larger than the thin films. Then the larger tensile stress toward the centre of spherulites led cracking of centre, resulting in radial cracks.

From Fig. 2a to Fig. 2d, the density of the cracks on the spherulites decreased in turn. And this could result from the higher strength of thicker films. While the depth and the width showed increasing trend. This fact could be associated with larger volume contraction or tensile stress.

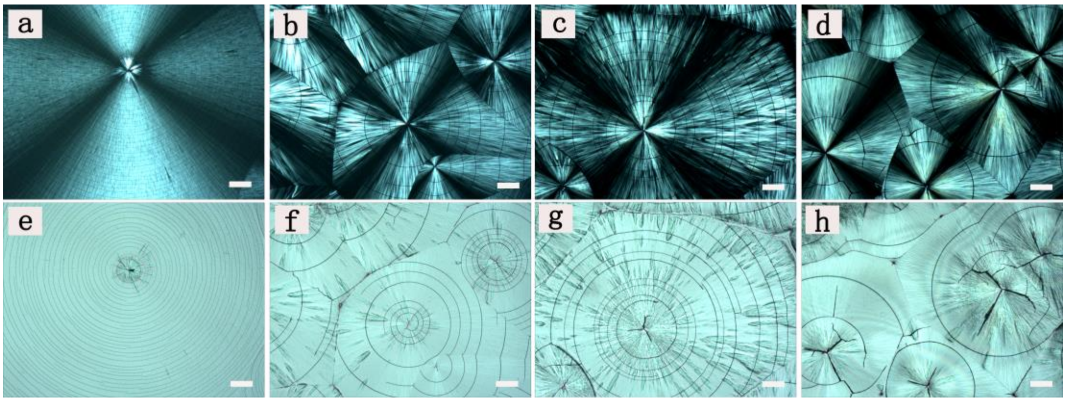

Fig. 2. POM and the corresponding OM images of different samples with different thickness isothermally crystallized at the same temperature 135℃. (a) and (e) sample-5 μm : (b) and (f), sample-12 μm: (c) and (g), sample-25 μm: (d) and (h), sample-40 μm. The scale bar represents 100 μm.

The detailed depth and width of the cracks were shown in Fig. 3 by AFM characterization. In Fig. 3a, it was difficult to see the cracks, indicating small width and depth. The depth and width was increased with thickness of samples. The following column showed the AFM height profile of the topology of the cracks on spherulites. A concave part where the cracks located could be easily seen on the height profile. For more precise data, each crack was measured for three times on different position randomly. From the three profiles, the depth and width of cracks on the samples were relatively uniform with small fluctuation. Fig. 4 showed the average depth and width of the cracks. The width and the depth both showed increasing trend. And from sample-5 μm to sample-25 μm, the increasing trend was relatively smaller compared with the trend from sample-25 μm to sample-40 μm. From sample-5 μm to sample-40 μm, the width and depth of cracks both showed a huge increasing trend, it was from about 1 μm in width and 13 nm in depth at the beginning (sample-5 μm) to about 2 μm in width and 1450 nm in depth (sample-40 μm). The depth increased by about one time and the width increased by about 110 times.

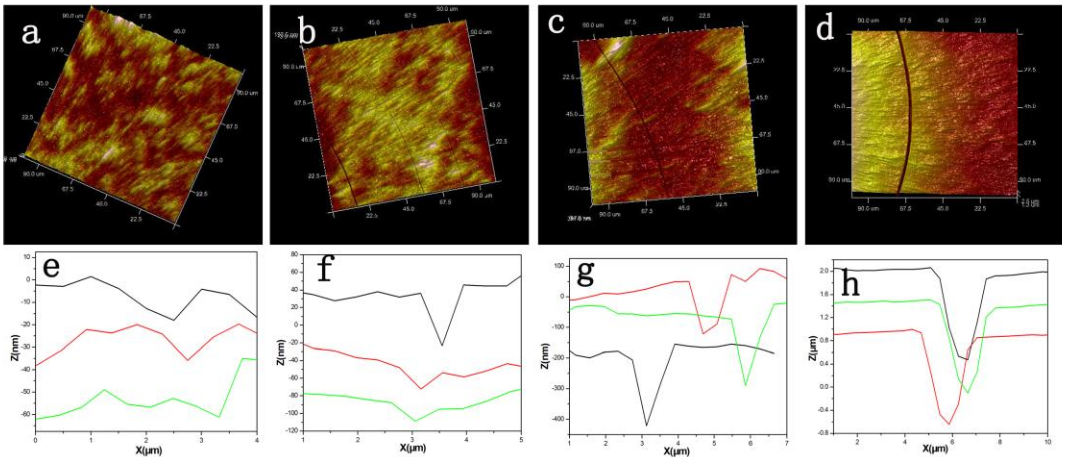

Fig. 3 (a), (b), (c), (d), AFM images of the cracks on spherulites in Fig. 2: (a) sample-5 μm : (b), sample-12 μm: (c), sample-25 μm: (d), sample-40 μm: (e), (f), (g), (h) were the corresponding height profiles.

Moreover, the process of the cracks forming was observed for real-time by a slow cooling speed (3℃ /min). It was found when different samples with different thickness were under the same condition (the same crystallized temperature), the first crack on spherulites occurred at different temperature. As shown in Fig. 5, when the film was thicker, the cracks tended to occur at higher temperature. The first crack occurred at 87℃, 77℃, 52℃ when the films were 40 μm, 25 μm, 12 μm respectively. The cooling speed was out of control by the hot stage when below 40℃. The dotted line was used to illustrated that the cracks did not occur when cooling to 40℃ for sample-5 μm. When cooling to the same temperature, the thicker spherulites would be under larger tensile stress. Thus, cracks tended to occur at higher temperature in thicker films.

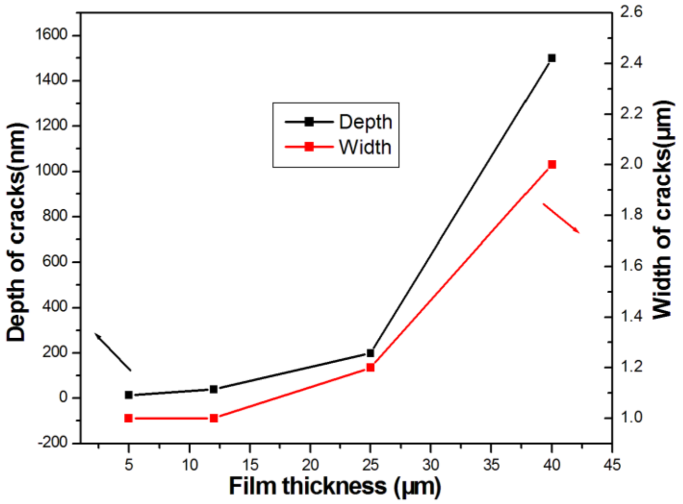

Fig. 4. Relationship between depth and width of cracks and film thickness.

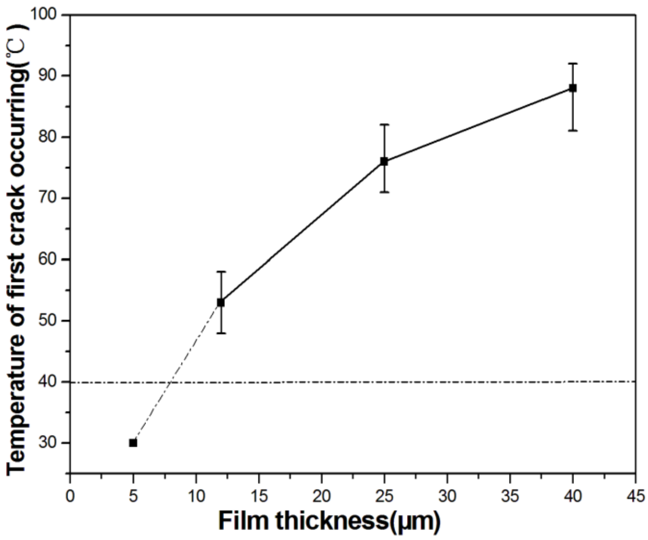

Fig. 5. Relationship between temperature of first crack occurring and film thickness.

More clear observations were conducted in our experiment. A spherulite with different thickness was designed as shown in Fig. 6. Different thickness of spherulites showed different birefringence [36,37]. The left side showed higher birefringence than the right under the POM meaning that the left side was thicker. During the cooling process, cracks occurred on the thicker side while there were no cracks on the thinner side at relatively high temperature. When continuing to cool, on the right side, the thinner side, cracks occurred. During the cooling process, the cracks occurred on the spherulite, and then broke along the direction of a circle, forming a completed circle crack. And the first crack occurred randomly on the radius. Namely, the first crack could be formed near the spherulites centre or near the edge of the spherulites randomly. During the cracks forming process, the relationship between fracture rate and temperature was shown in Fig.7. Here the fracture rate meant the proportion of total current cracks' length to the final cracks' length. As temperature decreased, the fracture rate became larger, meaning more cracks were developed. If suddenly stopped cooling during the cooling progress, the cracks could still extend, and reached an equilibrium state. But the cracks were still less than the final state. And continuing to cool, more cracks could be developed. As we know, most polymers were brittle under low temperature. Here, it showed more cracks under lower temperature. This fact seemed support the view that polymer brittleness was caused by the cracks in spherulites.

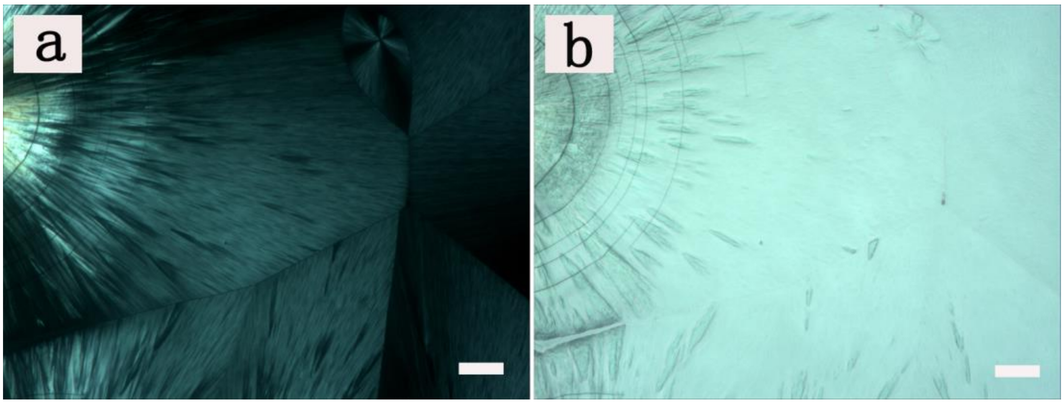

Fig. 6. Different thickness was designed on one spherulite, and the (a) POM images: (b) the corresponding OM images were taken at relatively high temperature on the hot stage. The scale bar represents 100 μm.

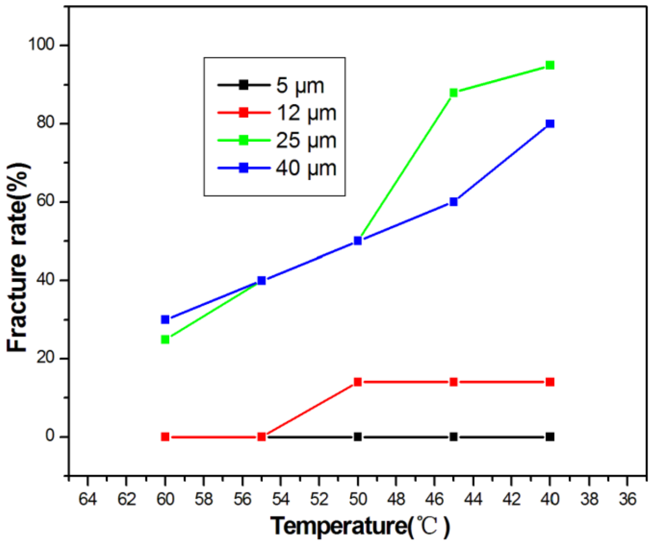

Fig. 7. The relationship between fracture rate by real-time observation and temperature.

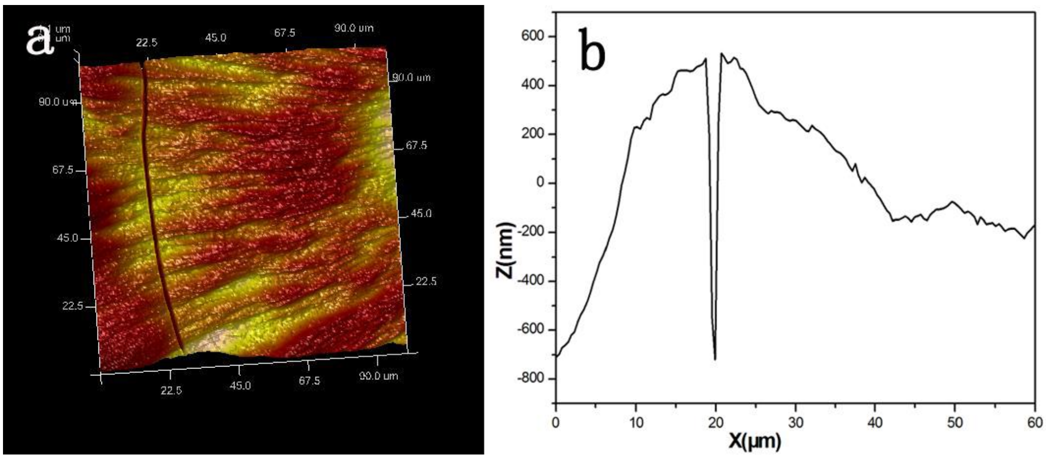

Fig. 8. (a). AFM images of banded spherulite with cracks: (b) height profile of the banded spherulites with cracks.

In the above, the relationship between cracks' density, cracks' depth, cracks' width, the temperature of first crack occurring and thickness of spherulites was investigated. Generally, as the spherulites thickness increased, cracks' density decreased, cracks' depth and width increased, the temperature of first cracks occurring increased.

In addition, Fig.1 has been proved that on the banded spherulites of PLLA, cracks tended to locate on the bright bands. Then, Fig. 8 showed the AFM images of the banded spherulites with cracks. The altitude of bright bands was about 600 nm higher than dark bands. And it could be seen clearly the cracks located on the higher bright bands. From the results above, on one spherulite, cracks would occur firstly on higher altitude and then occurred on lower altitude. There was wave-like structure on the banded spherulites. When cracks occurred on the bright bands (higher altitude), the cracks absorbed energy for cracking, thus avoiding cracks occurred on dark bands. Therefore, the cracks tended to occur on the bright bands, rather than dark bands.

4. Conclusion

In our study, we found an interesting view by chance that the cracks tend to occur on the bright bands of a kind of low molecular PLLA banded spherulites during the cooling process .And this study attributed this phenomenon to different altitude of bright bands and dark bands of banded spherulites.

POM and AFM results indicated that the density of cracks was decreased with increasing of thickness of spherulites, Besides, the depth and width of cracks and the temperature of first crack's occurring were increased with the increasing thickness of spherulites. The different types of cracks on spherulites with different thickness may be associated with different volume contraction. And more cracks are developed as the temperature decreases. Our study proved that cracks were more likely to occur on higher altitude of the spherulites ,it can be propsed that on the banded spherulites, the cracks occur on the higher altitude bright bands and absorb energy for cracking, thus avoiding occured on the dark bands.

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