Special Issues –International Symposium on Polymer Crystallization 2007– Solvent Induced Cracking and Morphology in Banded Spherulite of Poly(trimethylene terephthalate)

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The crack formations in the banded and non-banded poly(trimethylene terephthalate) (PTT) spherulite by dipping into chloroform were observed. The former showed multiple circular cracking pattern which seemed correlating with the banded pattern when observed under polarized light microscope (PLM). The retardation profiles in the radial direction of the banded spherulites were estimated by the parallel Nicol method under PLM and compared with the position of the cracks. As the result, PTT showed an optically uniaxial spherulite and it was observed the cracks were mainly formed at the higher birefringent region in the banded spherulite, that is, flat-on lamellae region. Based on these results, the correlation between cracking and the banded patterns is discussed.

KEY WORDS: Crack Formation / Banded Spherulite / Poly(trimethylene terephthalate) / Birefringence / Retardation /

In polymer materials, environmental stress cracking is sometimes observed by the combination of effect of residual stress in the materials, external stress and solvents. When a spherulite of semicrystalline polymer is formed on a substrate, crack formation is also sometimes observed during crystallization, cooling processes or by contacting with a solvent etc.^{1–4} In the case of poly(3-hydroxybutyrate), two types of cracking had been reported, cracks in the radial direction of spherulite and circumferential cracks.^{1,2} The former was observed at lower crystallization temperature and the latter in the cooling process of the spherulite crystallized at higher temperature. It was proposed that such circumferential cracks might have originated from the residual stress induced by the difference in coefficients of thermal expansion (CTE) between radial and circumferential direction during the cooling process of the spherulites from the higher crystallization temperature to room temperature. The residual stress stored during the cooling process is due to the difference of CTE between the radial and tangential directions of the spherulite.

Poly(trimethylene terephthalate) (PTT) is a suitable material to observe the spherulite under polarized light microscope (PLM) because it can easily form a high birefringent banded spherulite with the diameter more than several hundred micrometers.⁵ PTT spherulite also occasionally shows cracking after crystallization and cooling processes. Under a given set of conditions, it seems that the morphology of the PTT spherulite affects the cracking pattern. To our knowledge, such a correlation has not been reported in detail, therefore, the correlation between the morphology observed under PLM and the cracking pattern was investigated in this study.

EXPERIMENTAL

PTT was first dried at 80 °C for 6 h in vacuum before

sample preparation. A small fragment of PTT was put on a cover glass and covered with a polyimide film followed by another cover glass. A thin layer specimen of the thickness of about 10 to 20 μm was prepared by pressing the PTT fragment between the two cover glasses at 270 °C. After the specimen was melted at 270 °C for 5 min, it was rapidly transferred onto a hot stage preset at the crystallization temperature (160 °C or 195 °C) and isothermally crystallized for 1 h. After the crystallization process, the sample was quenched to room temperature and both the upper cover glass and the polyimide film were removed from the sample carefully. Cracks are occasionally formed in the as-crystallized spherulite but most of the PTT spherulite on the substrate does not show cracking. To accelerate the crack formation, the as-crystallized spherulite was dipped in chloroform for 1 s. The cracks were formed in the spherulites.

The PTT spherulite before and after dipping in the solvent was observed under PLM (Olympus BH2-BHSP) in the cross Nicol configuration. The retardation of the spherulite was estimated by the parallel Nicol method under the PLM in the parallel Nicol configuration.

Measurement of Retardation

Retardation $\Delta n \cdot d$ (Δn : birefringence, d : film thickness) at a given point in the spherulite was estimated by the parallel Nicol method. Detail of the method is as follows: Transmitted light intensity of a birefringent material between two polarized plates in the parallel Nicol configuration is expressed by the following equation:

$$I_{tr} = I_{in} \left[\cos^4(\theta - \phi) + \sin^4(\theta - \phi) + \frac{1}{2} \sin^2 2(\theta - \phi) \cos\left(\frac{2\pi}{\lambda} Re\right) \right], \quad (1)$$

where I_{tr} and I_{in} are intensities of transmitted and incident light,

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Figure 1. Experimental setup for retardation measurement by the parallel Nicol method.

respectively, θ is the rotation angle of the polarizing plates from the initial position, ϕ is the angle between the transmission axis of the polarizing plates and one of the principal axes of refractive index of the sample, λ is wavelength of light and R_e is the retardation of the sample. When λ is known and I_{tr} dependence on angle θ is measured at more than three angles, R_e can be estimated by fitting the parameters with eq 1.

The experimental procedure by the parallel Nicol method in this study was as follows: The sample was observed in the parallel Nicol configuration under PLM with an interference

color filter of 550 nm and the CCD camera images of the PTT spherulite were recorded by a computer as shown in Figure 1. In this study, the images at θ of 0° , 30° , and 60° were recorded. Brightness at an arbitrary point of the three images was extracted from the images and the retardation at that point was estimated by fitting the data with eq 1. The estimated value of retardation is up to half wavelength of the incident light because the value of $\cos(\frac{2\pi}{\lambda} R_e)$ takes the value from 1 to -1 at the region of $0 < \lambda < \pi$, $\pi < \lambda < 2\pi$ and every cycle of 2π . The PTT spherulite has high birefringence and the retardation of the $20\mu\text{m}$ thick film is about 1000 nm. It is, therefore, difficult to estimate the exact value of the retardation only from the parallel Nicol method. The real value of retardation is roughly measured by the Berek compensator under PLM. While it is hard to measure the position dependence of retardation by the compensator, the retardation values estimated by the parallel Nicol method were calibrated by the values measured by the Berek compensator.

RESULTS AND DISCUSSION

Crack Formation in Banded Spherulites in Thin and Thick Films

PTT spherulites were isothermally crystallized at 195°C in films with thickness of about 5, 10 and $20\mu\text{m}$, respectively and dipped into chloroform to cause cracking. As shown in Figure 2, banded pattern was observed in the spherulites and those in thinner films (Figure 2(a) and 2(b)) were less ordered. Cracking pattern was concentric; however, the number of cracks in the thinner films was much more than that in the thicker one, that is, the spacing between cracks increased monotonically with increase of the thickness of PTT specimen

Figure 2. Polarized light micrographs under cross Nicol configuration of cracked PTT spherulite isothermally crystallized at 195°C . Film thickness is (a) about $5\mu\text{m}$, (b) about $10\mu\text{m}$ and (c) about $20\mu\text{m}$.

Figure 3. Polarized light micrographs under cross Nicol configuration of cracked PTT spherulite isothermally crystallized at 160 °C (a) before and (b) after crack formation. White arrows point out the cracks. Retardation profiles on the dashed lines are plotted in Figure 6.

Figure 4. Polarized light micrographs under cross Nicol configuration of cracked PTT spherulite isothermally crystallized at 195 °C (a) before and (b) after crack formation. White arrows point out the cracks. Retardation profiles on the dashed lines are plotted in Figure 6.

(Figure 2). The cracks in the 20 μm thick film seem to correlate with the banded pattern of the spherulites, while those in the thinner film did not. Such thickness dependence of cracking pattern must come from the difference of CTE between the PTT spherulite and the glass substrate. The CTE of polymers is about one order of magnitude larger than that of a glass substrate and the stress stored near the surface of PTT during crystallization and cooling processes is different from that near the interface between PTT and the substrate. When the film thickness is small, the slope of difference of stress between the surface and the interface is larger than that in a thick film. Therefore, the number of cracks in the thinner film was more than that in the thicker one as shown in Figure 2. As mentioned above, the cracking pattern in the spherulite of about 20 μm thick film seems to correlate with the banded pattern under PLM. Therefore, 20 μm thick films were used in the following observation.

Crack Formation in Banded and Non-banded Spherulites

To check the correlation between the existence of banded pattern and the cracking pattern in the PTT spherulite, PTT was isothermally crystallized at 160 °C and 195 °C as shown in Figures 3 and 4, respectively. The non-banded spherulites were formed at 160 °C, while the banded spherulites were formed at 195 °C. Moreover, just after dipping into chloroform, only one circular crack was observed in the non-banded spherulite, while multiple circular cracks were concentrically formed in the

banded spherulite. For both spherulites, brightness of the grayscale images of PTT spherulites in the radial direction (that is, the dashed lines shown in Figures 3 and 4) was plotted in Figure 5(a) and 5(b), because interference color under PLM in the cross Nicol configuration should reflect the retardation. The non-banded spherulite shows almost constant brightness independent of radius and is slightly convex upward, while the banded one shows the periodic change. All of the positions where the cracks were formed in the banded spherulite were the bright region in the banded pattern and we can clearly see the correspondence between the morphology observed under PLM and the cracking pattern.

To check the relation between the brightness and the retardation in detail, the retardation dependence on the position in the PTT spherulite was estimated by using the parallel Nicol method and calibrated by using the Berek compensator. The retardation profiles on the PTT spherulites are shown in Figure 6. The retardation dependence on the spherulite radius in the non-banded spherulite showed an inverse relation with respect to the brightness as shown in Figures 5(a) and 6(a). The retardation dependence in the banded one did not show such an inversion, but the values of retardation around the cracks did not decrease and showed maximum values. The results indicate that the retardation does not necessarily correspond one-to-one with the brightness, though the brightness correlates to some extent with the retardation. One of the reason why the brightness did not correspond to the retardation may be the

Figure 5. Brightness profiles of PLM images of PTT spherulite crystallized at (a) 160 °C and (b) 195 °C before and after crack formation. Arrows indicate positions of cracks.

Figure 6. Retardation profiles of PLM images of PTT spherulite crystallized at (a) 160 °C and (b) 195 °C before and after crack formation. Arrows indicate positions of cracks.

large retardation in the PTT spherulite which was much larger than the half wavelength of the incident light, because the brightness under the cross Nicol configuration does not increase monotonically with the retardation at the higher retardation. Consequently, it is more important to estimate the real value of retardation than measuring the brightness when the retardation of the sample is larger than the half wavelength.

The color of banded spherulite under the cross Nicol configuration gradually changes in the order corresponding to red, yellow, green, and blue in the radial direction. Comparing the morphology of the banded spherulite under PLM (Figure 4) with the retardation profile (Figure 6(b)), it is clear that the region with red interference color shows maximum value of retardation and the region with blue color shows the lowest. This feature suggests that the crystal lamellae seem optically uniaxial though unit cell of PTT crystal is triclinic and optically biaxial. To check the validity of the retardation estimated by the parallel Nicol method, the refractive index of the unit cell was calculated. The calculation of the refractive indices of PTT unit cell was performed by using the Lorentz-Lorenz equation and bond polarizabilities proposed by Bunn.⁶ The PTT spherulite grows along the direction of *a*-axis of PTT unit cell and then the axis of rotation is also *a*-axis if the crystal lamellae twist in the banded spherulite. The details of calculation are reported in our previous paper.⁷ The birefringence when the unit cell is rotated around *a*-axis was calculated and plotted in the Figure 7. The value of birefringence sinusoidally changes and shows two cycles during rotating 360° around the *a*-axis. This result indicates that the PTT banded spherulite is optically

Figure 7. Birefringence when PTT unit cell is rotated around *a*-axis.

uniaxial. This is attributable to the fact that one of the optical principal axes of PTT unit cell is almost parallel to the *a*-axis. It indicates that the PTT crystal grown along the radial direction of the spherulite can be regarded as approximately optically uniaxial.

As for the position of the cracks, they were observed mainly in the red region with maximum retardation in Figures 4(b) and 6(b) when the number of cracks formed in the spherulite was low. Here, the relation between the retardation and the direction of the PTT unit cell at each position is considered. When *x* axis in the Cartesian coordinate system is taken parallel to *a*-axis and *y* axis in the *ac*-plane, the refractive indices are $n_x = 1.528$, $n_y = 1.754$, $n_z = 1.643$.⁷ From these values, we can easily estimate the birefringence and the values are $\Delta n_{xy} = -0.23$, $\Delta n_{xz} = -0.12$, respectively. In other

words, $|\Delta n_{xy}|$ is larger than $|\Delta n_{xz}|$ and this means that the region with maximum retardation in the PTT banded spherulite corresponds to the flat-on lamellae crystal region and the lowest retardation matches with the edge-on, because the growing direction of lamellae crystal in the PTT spherulite is a -axis direction. These facts indicate that the crack is formed easily in the flat-on crystal lamellae region than in the flat-on. If the banded spherulite is three-dimensionally formed, there is no reason why the lamellae periodically brakes at the particular positions. Therefore, it is considered that the correlation between the cracking and the banded patterns originates in the interaction between the substrate. In the case of PTT spherulite, it is considered that the stress stored in the lamellae does not depend on the radius but the strength in the direction of stress depends on the radius. That is, the flat-on lamellae may be weaker than the edge-on ones for the difference of residual stress between the surface of PTT spherulite and the glass substrate because the thickness of the lamellae is thinner than the width of it.

CONCLUSIONS

In the PTT banded spherulite, the concentric multiple cracks were formed periodically correlating with the banded pattern under PLM. It was confirmed that the cracks were mainly formed at the flat-on lamellae region and the mechanism of the

crack formation was discussed. In contrast with the PTT banded spherulite, the non-banded one did not show the multiple cracking. In our previous work, TEM observation of the spherulites was performed and the lamellae in the banded one formed thick lamellae bundles, while it did not happen in the non-banded one. The flexibility of the lamellae bundle may be less than one lamella and the stress stored in the non-banded spherulite during the crystallization and the cooling process was smaller than that in the banded one.

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