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Oscillation effects on the crystallization behavior of *i*PP

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Abstract

The oscillation effects on the crystallization behavior of the *i*PP were studied by shear stage, wide-angle X-ray diffraction and DSC. The effects of strain and frequency on the crystallization behavior and morphology of *i*PP were also investigated. The β form crystals were found after oscillatory shearing at the fixed frequency (2 Hz), and the β crystallinity increased with the strains. At the fixed strain (100%), the β crystallinity changed little with the increased frequencies. The orientation degree of the molecule chains increased with the strains. If the strain is high enough, the fiber crystals emerge. It is difficult to find the effect of frequency on the crystallization morphology of *i*PP. The orientation degree of the molecule chains changed little with different oscillatory frequencies.

Keywords: Oscillation effects; *i*PP crystallization; Strain and frequency

1. Introduction

The isotactic polypropylene is a commonly used semicrystalline polymer and there are many reports on its crystal structure, its properties of the various crystalline phases and the modes of crystallization. Three familiar crystalline modifications of *i*PP have been described in the literature: α (monoclinic), β (hexagonal) and γ (orthorhombic). The β-phase can improve the mechanical performance of the material and benefit its macroscopic toughness. The hexagonal β-modification can be induced in flow fields, in temperature gradients and particularly by nucleants. Varga et al. [1–3] and Hsiao et al. [4,5] lucubrated the effect of shear on the formation of the β-phase *i*PP. They all considered that the induced mechanism is that shear made the molecule chains orient to form α row nuclei and these α row nuclei can induce β-crystals.

Most of the polymers are subjected to intense flow fields when they are processed from melt. In recent years, the study of the effect of flow on polymer quality has aroused a great interest of many scientist [6–12]. Oscillation is one of the flow methods and oscillation has been widely used in scientific research in recent years [13–20]. Linear rheology via sinusoidal oscillation has become a well-established method for determining the mechanical properties of (e.g. polymeric) materials [21]. Pogodina et al. [22] have shown from frequency-dependent isothermal crystallization experiments that isotactic polypropylene undergoes a physical gelation transition at very low crystallinites, ~2%, over a wide range of under-cooling, setting up a kind of structural network through which to guide the subsequent growth of crystallization in polypropylene.

Zhang et al. [23] found that through melt vibration, crystal structure of *i*PP changed from α form to β form and γ form. Zheng et al. [24] also found that crystallite size, crystal structure and crystallinity of *i*PP under vibration and unvibration are different by using DSC, WAXD and POM. In the present work, we investigated the oscillation effect on the content of β-crystals of the *i*PP. The strain and the frequency were set severally to understand which is the primary factor to affect the crystal structure of *i*PP.

2. Experimental section

The isotactic polypropylene used in this work was the same as that in our previous work [25,26]. A Linkam CSS-450 high-temperature shear stage (Linkam Scientific Instruments, Ltd, Tadworth, Surrey, UK) was used in this work. The introduction of this shear stage has also been described in our previous work. The *i*PP was melted at 200 °C for 5 min to erase any thermal and mechanic history, then the samples were cooled to the crystallization temperature 134 °C at a rate of −30 °C/min.

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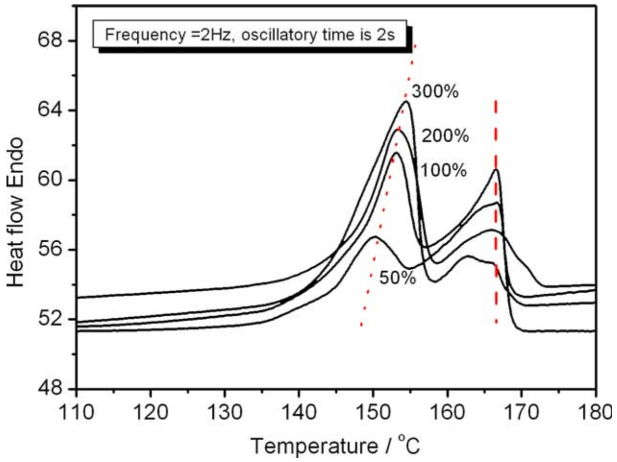

Fig. 1. DSC patterns of *i*PP after oscillatory with different strains at fixed frequency 2 Hz and crystallized at 134 °C.

The thickness of the samples is 100 μm. As soon as it reached 134 °C, the oscillatory shear applied to the *i*PP and the oscillation time was 2 s. First, we set the fixed oscillation frequency at 2 Hz and changed the strain from 50 to 300%, then changed the frequency from 1 to 9 Hz with the fixed strain 100% for the oscillatory shear experiments. After the oscillation shearing, the *i*PP was kept at 134 °C for a few hours to crystallize entirely and then was investigated by ex situ WAXD and DSC. The WAXD measurements were carried out at room temperature with a Rigaku D/max 2000V PC diffractometer with curved graphite crystal filtered Cu K_α radiation source ($\lambda = 0.154$ nm) at 40 kV and 200 mA. The peak-fit procedure used in this work was the same as that used before [25]. DSC measurements were carried out with a Perkin–Elmer DSC 7 instrument. The samples were melted at a moderate rate (10 °C/min) in the heating up to 200 °C in a nitrogen environment.

In order to observe the morphology development of the crystals and orientation degree of the *i*PP molecule chains after oscillation, we changed the oscillation method and crystallization temperature. The *i*PP was melt at 200 °C for 5 min to erase any thermal and mechanic history, then began to oscillation at 200 °C for 10 min and kept oscillation during cooling to the crystallization temperature 150 °C. When the temperature reached 150 °C, oscillation ceased and the

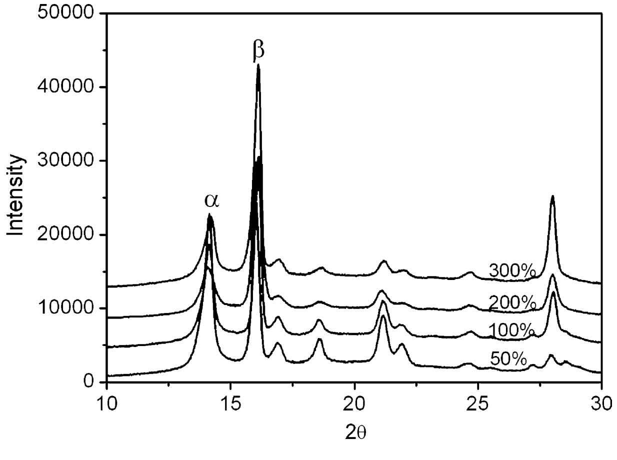

Fig. 2. WAXD patterns of *i*PP after oscillatory with different strains at fixed frequency 2 Hz and crystallized at 134 °C.

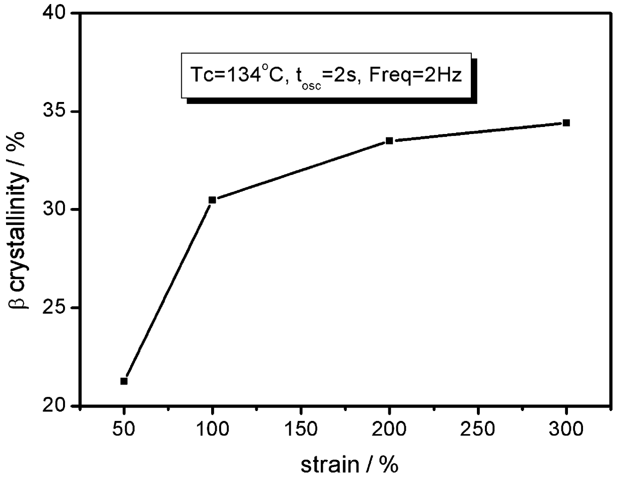

Fig. 3. Strain dependence of β crystallinity for *i*PP at 134 °C.

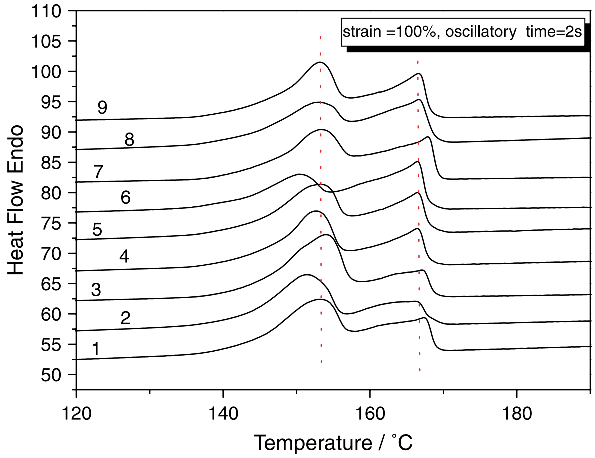

Fig. 4. DSC patterns of *i*PP after oscillatory with different frequency at fixed strains 100% and crystallized at 134 °C, oscillatory time is 2 s.

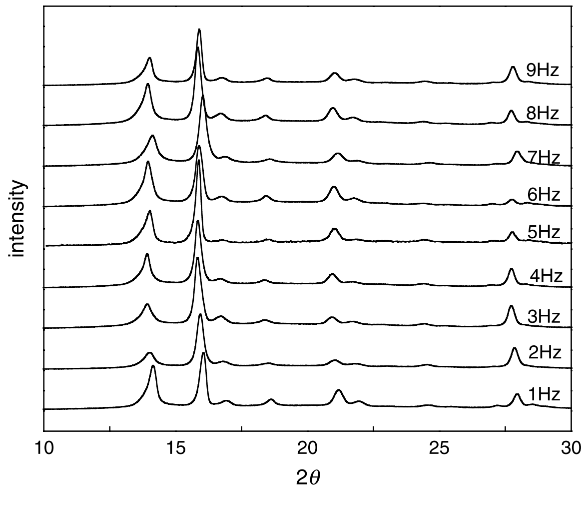

Fig. 5. WAXD patterns of *i*PP after oscillatory with different frequency at fixed strains 100% and crystallized at 134 °C, oscillatory time is 2 s.

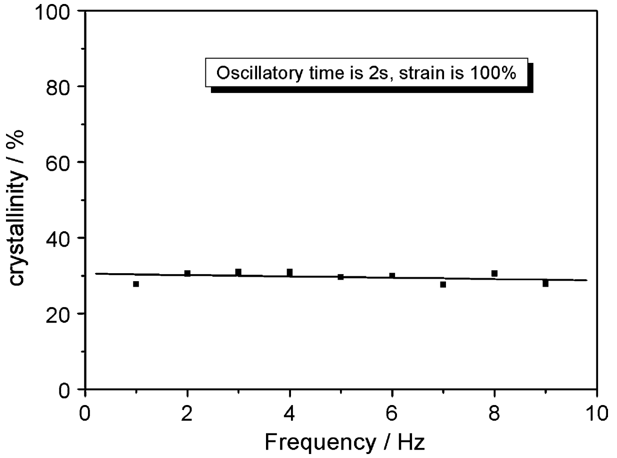

Fig. 6. Frequency dependence of β crystallinity for *i*PP at 134 °C, oscillatory time is 2 s.

morphology transformation of the *i*PP was observed by polar optical microscope.

3. Results and discussion

Fig. 1 shows the DSC patterns of the samples crystallized after oscillation at different strains, the fixed frequency is 2 Hz and oscillatory time is 2 s. It was noted that each pattern has two melt peaks, the first peaks of all the patterns were between 150 and 154 °C and the second peaks were all at about 168 °C. By all appearances, the first peaks relate to the melt peak of the β crystals and the second melt peak is the α crystals'. This shows that β form crystals can be induced by oscillation in *i*PP crystallization. Zhou et al. [27,28] also found vibration induced β form crystals in polypropylene crystallization. But they did not explain the reason why oscillation induced β crystals. We think the main reason is that oscillation made the molecule chains oriented to form α row-nuclei and the oriented α row-nuclei were in favor to induce β crystals. From Fig. 1, we see that the β melt peak area became bigger with the increased strain, which indicates that the content of the β crystals increased with the strain. We also found that the melting temperature of the β crystals was increased with the strains but the melt temperature of the α crystals did not change. This result indicates that the thickness of the β lamellar crystal increased with the strains but the thickness of the α lamellar crystal did not change. Zheng et al. [24] investigated the crystal structure changed of *i*PP under different vibrated amplitudes through DSC. But they only found that the crystallinity of β form increased with amplitudes, the melting temperature of β crystals did not change.

Fig. 2 shows the WAXD patterns of the samples crystallized after oscillation with a different strain, the fixed frequency is 2 Hz and oscillatory time is 2 s. From Fig. 2, one can easily find the oscillation effects on *i*PP crystallization. The peaks at $2\theta = 21.0$ are the co-diffractions of α phase and β phase and they are not so easy to analyze in detail. In WAXD profile, 2θ at about 16° is the characteristic reflection peak of the β crystals. Although the strain is as low as 50%, the β marker peak was very obvious. This result also shows that oscillation can induce to form β crystals. From Fig. 2, we see that the height of the β marker peak increased with the strains. After using peak-fit procedure, the function of the β crystallinity changed with the strain was shown in Fig. 3. This result is consistent with that of Fig. 1. The β crystallinity of *i*PP increased with strain after

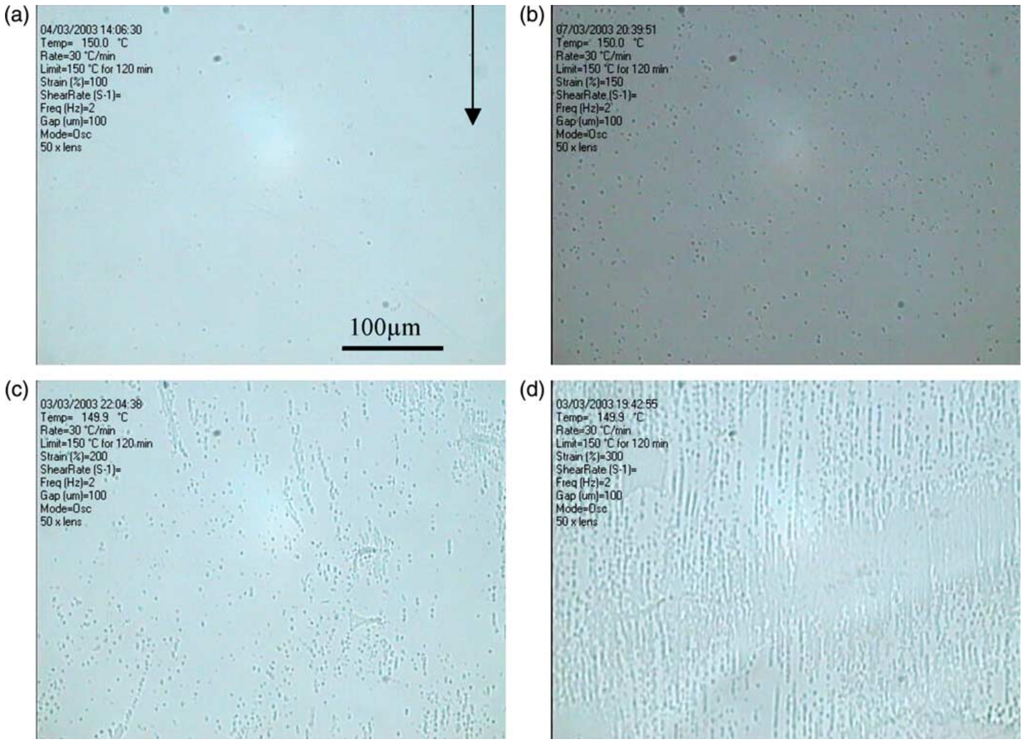

Fig. 7. POM microphotograph of *i*PP crystallized at 150 °C under oscillatory with (a) 100%, (b) 150%, (c) 200%, (d) 300% and 2 Hz at 210 s.

oscillated, the oriented degree of the molecule chains increased. Therefore, the larger the strain is, the higher the oriented degree is. This oriented molecule chains formed α row-nuclei and the oriented α row-nuclei can induce to form β-crystals. So the β crystallinity increased with strains.

Fig. 4 shows the DSC patterns of the samples crystallized after oscillation with different frequencies, where the fixed strain is 100% and oscillatory time is 2 s. It was also noted that each pattern has two melt peaks too. The first melt peaks are at about 154 °C, and the second ones are at about 168 °C, almost the same as that in Fig. 1. But in each pattern, the areas of the β melt peaks are almost the same, which is different from Fig. 1. This result shows that the changed frequency has nearly no effect on the crystal structure and the β crystallinity of the *i*PP, which indicates the oriented molecular chains, is nearly in the same degree if the strain is same. We also found that the melt temperature of the β crystals and the melt temperature of the α crystals do not change much with frequencies, Zhang et al. [23] also observed this experimental phenomena.

In order to understand the results in Fig. 4, we tested the samples prepared under the same condition by wide angle X-ray diffraction. Fig. 5 shows the result of the WAXD patterns. It was noted that the height and the area of the β diffraction peak are nearly the same for all the frequencies. Fig. 6 shows the function of the β crystallinity and the oscillatory frequencies. From Fig. 6, we found that the β crystallinity has nearly no change with the increased frequencies. From Figs. 4 to 6, we know that the effect of the oscillatory frequency on the *i*PP crystallization is faint. We think the reason is that the strain is fixed when the frequencies changed and the degree of molecule chains oriented did not change much with the frequency.

For the sake of understanding the change of the oriented degree of the *i*PP after oscillation, we observed the morphology transformation of the *i*PP by polar optical microscope. At the low crystallization temperature 134 °C the crystal growth rate and the nucleation density are high, the observation of the crystallization morphology is too difficult. In order to observe conveniently, the crystallization temperature of the *i*PP we choose is 150 °C at which the crystal growth is relatively slow. At a high crystallization temperature, the *i*PP melt relaxed quickly, so we changed the oscillatory method to keep

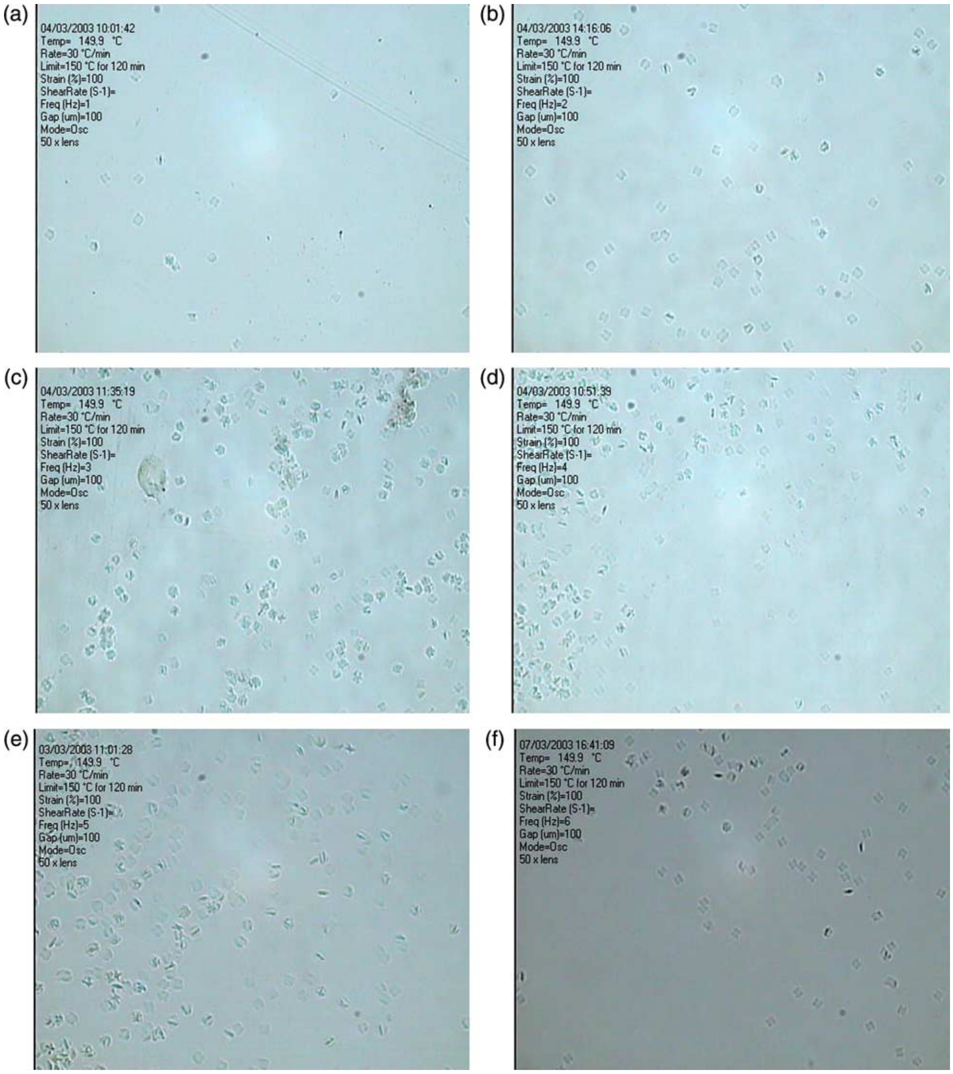

Fig. 8. POM microphotograph of *i*PP crystallized at 150 °C under oscillatory with (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6 Hz and the strain is 100% at 490 s.

the effect of the oscillation on the *i*PP:*i*PP was oscillated with different strains and frequencies at 200 °C for 10 min and then cooled to the crystallization temperature with the cooling rate at 30 °C/min under oscillating. Fig. 7 shows the polarized light optical micrographs of the crystals of *i*PP grown from the melt after oscillating from 200 to 150 °C with different strains at the fixed frequency 2 Hz and the crystallization time is 210 s. From Fig. 7 it is noted that the nucleation density increased with the strain, and when the strain reached 200%, the fiber crystals emerged. After the strain reached 300%, we see that the oriented fiber crystals are much longer than that of 200%, and the nucleation density is too high to impact. This result shows that the increased strain was in favor of the orientation degree of the molecules chains. The oriented molecule chains may be induced to form β crystals.

Fig. 8 shows the morphology change of the *i*PP of different frequencies at the fixed strain 100%, with the crystallization time at 490 s. It was noted that the crystal morphologies are all spherulites under different oscillatory frequencies, and that the spherulite density had almost no change with the increased frequency. This result shows that the orientation degree of the molecule chains changed little with the oscillatory frequencies. This is the reason why the β crystallinity had nearly no change with the oscillatory frequencies.

4. Conclusions

In this work, we investigated the oscillation effect on the crystallization behavior of the *i*PP. Our major concluded remarks can be summarized as follows:

1. Oscillatory shear may induce to form β crystals, at the fixed frequency (2 Hz), the β crystallinity increased with the strains.
2. At the fixed strain (100%), the β crystallinity changed little with the increased frequencies.
3. The effect of strain on the crystallization morphology is obvious. The nucleation density and the orientation degree of the molecule chains increased with the strains. If the strain is high enough, the fiber crystals emerge.
4. There is nearly no effect of frequency on the nucleation density and the orientation degree of the molecule chains of *i*PP.

Acknowledgements

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