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The effect of thermal history on crystalline structure and mechanical properties of $\beta$-nucleated isotactic polypropylene

Yefei Tian$^1$, Jian Zhou$^1$ and Jiachun Feng$^2$

$^1$ School of Materials Science and Engineering, Chang’an University, Xi’an, Shaanxi 710064, People’s Republic of China

$^2$ State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People’s Republic of China

E-mail: yftian@chd.edu.cn

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Abstract

The effect of thermal history on $\beta$-nucleated iPP was systematically investigated by comparing the variance of crystalline microstructures and mechanical property of stepwise crystallized sample and annealed sample, which experienced different thermal history. The mechanical property tests exhibit that the toughness of stepwise crystallized sample and annealed sample were both decreased compared to control sample, while the tensile strength of the stepwise crystallized sample increased slightly. Structure investigation showed that the $\alpha$-relaxation peak, which is related to the assignment of chains in rigid amorphous phase, moved to the high temperature region for stepwise crystallized sample, while it moved to the low temperature region for annealed sample. The results indicated the weakening in rigid amorphous fraction (RAF) and the increase in lamellar thickness of $\beta$-iPP after stepwise crystallization treatment. For annealed sample, the RAF strengthened and lamellar thickness decreased slightly after thermal treatment. A mechanism of crystalline microstructures evolution of restricted area between the main lamellar under different treatments was proposed.

1. Introduction

Isotactic polypropylene (iPP) shows a high performance with low cost, but its poor toughness, especially in the low temperature, largely limits its scope of application. Hence, how to improve the impact resistance of iPP is always the most important problem to be solved in both industry and academia. As a typical polycrystalline polymer, iPP has three common polymorphs, which are $\alpha$-, $\beta$- and $\gamma$-form [1, 2]. The iPP of $\alpha$-form is the most thermodynamically stable, which exhibits higher elastic modulus and yield strength than the other two modifications of iPP. Compared to the iPP of $\alpha$-form, $\beta$-form iPP exhibits enhanced impact resistance, which is usually attributed to the phase transition from $\beta$- to $\alpha$-form and the intrinsic loose structure of $\beta$-crystals that are in favor of energy dissipation [3, 4]. In this aspect, $\beta$-form iPP shows superior performance than $\alpha$-form, especially its excellent property of rigidity-toughness balance. The $\beta$-form is thermodynamically metastable, which can be obtained under special conditions such as crystallization under a temperature gradient, under shearing, or in the presence of specific $\beta$-nucleation agent. Due to there are an obvious growth competition between $\alpha$- and $\beta$-crystals, the iPP with high content $\beta$-crystals can only be obtained in a specific temperature range, which is between the high critical temperature and the low critical temperature for the growth of $\beta$-crystals [5, 6]. Moreover, because of its thermodynamically metastable characteristics, $\beta$-crystals are highly prone to take a $\beta$-to-$\alpha$ phase transition during heating and tensile process [7, 8]. Many efforts have been made to obtain high content and stable $\beta$-form iPP. Lotz et al found that the specific thermal treatment, such as stepwise crystallization, could inhibit the $\beta$-to-$\alpha$ phase transition during next melting process [9, 10]. In a typical thermal protocol of stepwise crystallization, crystallized sample would be following kept at a lower temperature to continue secondary crystallization. The sufficient crystallization greatly eliminate the residual $\alpha$-grains, which can act as $\alpha$-nuclei during the melting process and lead to a significant $\beta$-to-$\alpha$ phase transition. Therefore, stepwise crystallization treatment is an effective way to obtain high content $\beta$-iPP with high toughness. On the other
hand, it is demonstrated that annealing can induce a dramatic improvement of fracture resistance of polypropylene or polypropylene composites [11–13]. Compared with annealing and stepwise crystallization treatment, samples are both subjected to a similar certain holding temperature (lower than its crystallization temperature). The only difference is the experienced thermal history of samples. We expect to explore the effect of thermal history on the crystalline structure and properties of \( \beta \)-nucleated iPP through comparing the differences of the crystalline structure and properties between stepwise crystallized sample and annealed sample.

In this study, the final heat treatment temperature of stepwise crystallized sample and annealed sample was set at 120 °C. The mainly difference between two samples was that the stepwise crystallized samples were cooled to this temperature after primary crystallization, while the annealed samples were heated up to this temperature from room temperature. For semi-crystalline polymer, the heating and cooling process is actually a competitive process of melting and crystallization. The crystalline structure of semi-crystalline polymer is irreversible during the heating and cooling process, which means that the crystalline structure at the same temperature in heating process and cooling process is not exactly the same. For example, under the temperature at 160 °C, iPP is just about to melt and most of the lamellar structure still exists during the heating process; while during the cooling process, iPP has not yet began to crystallize in the cooling process, the system is still in the melt state. According to the difference of crystalline structure in the process of heating and cooling, they divided the temperature range into three stages, in which the higher temperature range was the primarily irreversible district, corresponding to the formation and melting of main lamellar of the polymer system. During this stage, the long period and lamellar thickness of polymer in heating and cooling process had most significant difference. The medium temperature range was the secondary irreversible district, corresponding to the structure evolution of the restricted area between the main lamellar during the thermal treatment. At the secondary irreversible stage, the difference of the long period and lamellar thickness in heating and cooling process was relatively minor. The low-temperature range was a reversible district. In this range, a small amount of reversible ordered structure formed, which had no dependence on the thermal history. This small ordered structure maintains exactly the same during either heating or cooling process. Based on the above theory, the two thermal treatments in this work can only influence the structure evolution of restricted area between the main lamellar, which may correspond to the secondary irreversible stage evolution. Herein, two thermal treatments were used to regulate the different parts of iPP crystalline structure. The effect of thermal history on \( \beta \)-nucleated iPP was systematically investigated and a mechanism of crystalline microstructures evolution of restricted area between the main lamellar under certain treatment was proposed.

2. Experimental procedure

2.1. Materials and sample preparation

Ziegler–Natta isotactic polypropylene (F401) used in this study was supplied by Yangzi Petrochemical Co., SINOPEC (Nanjing, China). The weight-average molecular weight (Mw) obtained from the gel permeation chromatography (GPC) was 22.0 × 10⁴ and the polydispersity index was 4.85. The peak melt point obtained from differential scanning calorimetry (DSC) was 167 °C (samples were heated from 25 to 200 °C at a rate of 10 °C min⁻¹). The \( \beta \)-nucleating agent was aryl amide compounds (TMB-5), which was supplied by Shangxi Institute of Chemical Industry (Taiyuan City, China). The iPP was melt mixed with TMB-5 in torque rheometer to prepare \( \beta \)-nucleated iPP containing 0.05 wt% \( \beta \)-nucleating agent. The rotor speed was set at 80 rpm, and samples were blended at 180 °C for 8 min. The blended mixtures were molded into 0.4 mm-thick sheets in a hot press at 200 °C under a pressure of 15 MPa, and then cooled naturally to room temperature.

2.2. Thermal-treatment protocol

The specific thermal treatment was carried out in the Hot Press. Two kinds of samples experienced different thermal history, but finally annealed under the same condition, were prepared to compare the influence of thermal history on iPP crystalline structure. The thermal-treatment protocol for various samples are as follows: (1) Stepwise crystallized samples: samples were first heated to 200 °C and kept there for 5 min to erase previous thermal history, and fast cooled down to 135 °C at rate of 30 °C min⁻¹ and kept there for 30 min to complete primary crystallization. Then the samples were rapidly cooling to the annealing temperature of 120 °C and kept there for 30 min, then cooled naturally to room temperature. (2) Annealed samples: samples were first heated to 200 °C and kept there for 5 min to erase previous thermal history, and fast cooled down to 135 °C at rate of 30 °C min⁻¹ and kept there for 30 min to complete primary crystallization. Then samples were cooled naturally to room temperature, and subsequently heated up to the annealing temperature of 120 °C and kept there for 30 min to experience thermal treatment. At last, the samples were cooled naturally to room temperature. (3) Control samples: samples were first heated to 200 °C and kept there for 5 min to erase previous thermal history,
and fast cooled down to 135 °C at rate of 30 °C min⁻¹ and kept there for 30 min to complete primary crystallization, then cooled naturally to room temperature.

2.3. Mechanical property testing
Dynamic mechanical analysis (DMA) testing was conducted using a NETZSCH 242 C DMA analyzer. Specimens with approximate dimensions of 10.0 × 4.0 × 0.4 mm³ were slightly surface-polished to eliminate shrinkage, and then were used to perform the test under tensile mode at a vibration frequency of 1 Hz in nitrogen atmosphere. The testing temperature was selected from −50 °C to 150 °C at a heating rate of 2 °C min⁻¹.

The dog-bone specimens used for tensile test were cut from the 0.4 mm-thick sheets. The tensile testing was conducted on a SANS CMT-6503 universal testing machine (Shenzhen, China) with a cross head speed of 20 mm min⁻¹ according to GB/T1040-92. Notched Izod impact tests were carried out using an XJJ impact tester (Changchun, China) followed to ASTM D 256-04. All specimens were placed at room temperature (23 ± 0.5 °C) for 12 h before testing. These values were measured under the same conditions and each reported mechanical result was an average value of at least 6 measurements.

2.4. Thermal property characterization
A Mettler DSC-1 apparatus was used to analyze the thermal properties. Calibration for the temperature scale was performed using indium (Tm = 156.60 °C and ΔHf₀ = 28.45 J g⁻¹) as standard to ensure reliability of the data obtained. The accuracy of measured temperature was ±0.05 °C. All the experiments were carried out in nitrogen atmosphere. To investigate the thickness of crystalline lamellar, the samples were heated from 25 to 200 °C at a rate of 10 °C min⁻¹ and the melting traces were recorded.

2.5. Fourier transform infrared spectroscopy (FTIR)
A Nicolet Nexus 470 Infrared Spectrometer (Thermal Nicolet, America) was used to collect the IR spectra in the region of 4000–500 cm⁻¹. Thin film samples were fixed in a KBr tablet for FTIR measurements. All time-resolved FT-IR spectra at different temperatures were recorded on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm⁻¹, and 32 scans were available for an acceptable signal-to-noise ratio. Time dependent spectra were collected at 120 °C for various duration. Raw spectra were baseline corrected by the software Omnic.

3. Results and discussion

3.1. Mechanical performance for two samples under different thermal history
The typical stress-strain curves of stepwise crystallized sample, annealed sample and control sample were shown in figure 1. It can be seen that the tensile elongation at break for stepwise crystallized sample and annealed sample were both decreased greatly compared to control sample, which indicating the toughness decreasing of β-nucleated iPP after stepwise crystallization treatment and annealing treatment. Besides, the tensile strength of stepwise crystallized sample increased slightly compared to annealed sample and control sample. To verify the toughness decreasing of samples experienced thermal treatment, we further investigated the notched Izod impact strength of three kinds of samples. As shown in figure 2, the notched Izod impact strength of stepwise crystallized sample, annealed sample and control sample are 2.73 kJ m⁻², 3.59 kJ m⁻² and 7.95 kJ m⁻²,
respectively. It is obvious that the toughness of samples experienced stepwise crystallization treatment or annealing treatment has fallen sharply. As for semicrystalline iPP, the difference in mechanical properties among three kinds of samples was possibly caused by the structure evolution of crystalline region and amorphous region of samples during thermal treatment.

### 3.2. The difference of crystalline structure between two samples under different thermal history

Two kind of samples experienced different thermal history were firstly isothermal crystallized at 135 °C. The relationship of relative crystallinity and crystallization time during isothermal crystallization process was shown in figure 3. It can be seen that the crystallization half-time for samples isothermally crystallized at 135 °C is around 10 min. Hence, isothermally crystallized at 135 °C for 30 min, the samples have crystallized completely. To find out the reason caused performance difference of three samples, the melting curves of stepwise crystallized sample, annealed sample and control sample before and after tensile test were compared in figure 4. The two melting peaks represent the melting of β- and α-iPP, respectively [3, 14]. It is obvious that the control sample after tensile test owns a large melting peak of α-iPP, while the α-crystal melting peaks of stepwise crystallized sample and annealed sample after tensile test seems less obvious. Many previous studies suggested that β-iPP could take a β-α phase transition when undergoing tensile, impact or other external force, which absorbed large amounts of energy and gave rise to the good toughness of β-iPP [15, 16]. The DSC results correspond well with the tensile test and the notched Izod impact strength that either stepwise crystallization or annealing significantly suppressed the β-α transition of β-iPP and resulted in the decrease of tensile elongation at break and toughness. As for samples before tensile test, the main melting peaks (β-crystal) of stepwise crystallized sample, annealed sample and control sample were located at 157.5, 156.9, and 157.2 °C, respectively. Since melting point can reflect the lamellar thickness, as the higher melting point indicating thicker lamellar [17]. The stepwise crystallized sample shows the highest melting point, which may be due to the thickening of lamellar during the secondary crystallization. The reinforcement of crystalline lamellar strcure resulted in the increase of tensile strength for stepwise crystallized sample, which is in consistent with the machnical performance results.
To compare the structure difference of two samples which experienced different thermal history, we investigated the dynamic mechanical properties of stepwise crystallized samples, annealed samples and control samples, as shown figure 5. It can be found that there are two distinct maxima in the curves of $\tan \delta$, corresponding to the relaxation transition. The relaxation peak at the low temperature (about 18 °C) is $\beta$-relaxation, corresponding to the glass transition of mobile amorphous fraction (MAF) [16]. The relaxation peak at the high temperature is $\alpha$-relaxation [18, 19], while the internal mechanisms of $\alpha$-relaxation are still controversial. Many studies suggest that the $\alpha$-relaxation corresponds to the change in the structure of the crystalline region. For instance, Men et al [20] proposed that the sliding of the small crystal blocks between primary lamellar was the main reason to cause the $\alpha$-relaxation. However, some researchers argue that the $\alpha$-relaxation should involve both crystalline and amorphous phases [19]. For example, the segment diffusion between the crystalline and the amorphous phases has been considered to be the $\alpha$-relaxation [21]. The chain rearrangement in rigid amorphous fraction (RAF) is the main cause of $\alpha$-relaxation, which seems more reasonable in most cases and has been adopted in many literatures [16, 17, 22–24]. From figure 5, it was found that the $\alpha$-relaxation peak of control sample, stepwise crystallized sample and annealed sample located at 109.2 °C, 96.4 °C and 115.9 °C, respectively. The $\alpha$-relaxation peak of annealed sample moved to high temperature compared to control sample, which means the decrease of mobility of chains in RAF, namely, both of the number of polymer chains in RAF and the order degree of chains in RAF were increased. The strengthening of RAF area was mainly due to the transition of crystalline structure near the primary lamellar from mesomorphic phase to $\beta$-crystal and the formation of the secondary lamellar. During these processes, many flaws would be introduced into the newly formed secondary lamellar, which made the energy required for the $\alpha$-relaxation greatly increase and caused the $\alpha$-relaxation peak moves to high temperature [25]. In contrast, the $\alpha$-relaxation peak of stepwise crystallized sample obviously moved to the low temperature region, suggesting that stepwise crystallization enhanced the mobility of chains in RAF. The weakening of RAF area might be due to the decline of the chain segments in RAF district. According to the DSC and mechanical performance results, the

![Figure 4. DSC heating curves of stepwise crystallized sample, annealed sample and control sample before and after tensile test.](image)

![Figure 5. Temperature dependence of the loss factor ($\tan \delta$) of stepwise crystallized sample, annealed sample and control sample.](image)
lamellar thickness of stepwise crystallized sample increased, indicating more chains arranged into lamellar that giving rise to the weakening of RAF area simultaneously.

To better understand the difference of structure evolution during thermal treatment under 120 °C between stepwise crystallized samples and annealed samples, we investigated the changes of the helical conformation band of iPP by FTIR in situ. FTIR has a high sensitivity for the conformation changes of polymer, which has been successfully applied in the study for the conformational change of iPP molecular chain during crystallization and thermal treatment [26–29]. The time-dependent FTIR spectra and difference spectra of stepwise crystallized sample and annealed sample during thermal treatment at 120 °C were shown in figure 6. The peaks around 973, 998, 841, 1165 and 1220 cm\(^{-1}\) are the distinct bands corresponding to the helical conformation with the number of repeating units which are 5, 10, 12, 12–14 and 14, respectively. The 973 cm\(^{-1}\) band corresponds to the short sequence with less degree of order in amorphous phase. The differential spectrum was used to magnify the changes of peak strength. The intensity of distinct bands around 841, 998, 1165 and 1303 cm\(^{-1}\) increased greatly for both samples, which meant that the degree of order for the helical conformation for two samples both increased. However, there were significant differences of the changes of the band around 1256 cm\(^{-1}\) between the stepwise crystallized sample and the annealed sample. The intensity of 1256 cm\(^{-1}\) band for the annealed sample increased greatly, while the intensity for stepwise crystallized sample was almost unchanged. According to the statement of Zichy et al, the distinct band around 1256 cm\(^{-1}\) corresponds the helical conformation with less degree of order [30]. Mechanical properties and DMA data have shown that, for the stepwise crystallized sample, its crystalline region strengthened and the primary lamellar thickened during the thermal treatment at 120 °C, while its rigid amorphous region decreased. For the annealed sample, its rigid amorphous region strengthened during the thermal treatment at 120 °C, while its primary lamellar were almost unchanged. Hence, we consider that the 1256 cm\(^{-1}\) band is mainly corresponding to the helical sequence with less degree of order in RAF.

Based on the above experimental results, we proposed a model to describe the structural changes of the two samples during the thermal treatment at 120 °C, which was shown in scheme 1. For the semi-crystalline iPP, its structure can be divided into the lamellar structure, the mobile amorphous fraction with high molecular chain activity and the rigid amorphous fraction near the primary lamellar which chain activity is highly restricted. During the thermal treatment at 120 °C, the stepwise crystallized sample which was directly cooled from the main crystallization temperature down to 120 °C, showed the weakening of RAF and the thickening of primary lamellar, resulting in the increase of tensile strength. However, the annealed sample which was firstly cooled down to room temperature and then heated up to 120 °C, showed a great strengthening of RAF.

Figure 6. Time-dependent FTIR spectra and difference spectra (obtained by subtracting the spectra recorded at 0 min) in the wave number range of 1350–750 cm\(^{-1}\) for the stepwise crystallized sample (a) and the annealed sample (b) during thermal treatment at 120 °C.
4. Conclusions

In this work, we compared the changes of the crystalline microstructures and mechanical properties of two samples with different thermal history of \(\beta\)-nucleated iPP. The mechanical performance tests showed that the toughness of stepwise crystallized sample and annealed sample were both decreased compared to control sample, while the tensile strength of the stepwise crystallized sample increased slightly. Structure characterization showed that, after thermal treatment at 120 °C for 30 min, the \(\alpha\)-relaxation peak of the stepwise crystallized sample moved to the high temperature, while the \(\alpha\)-relaxation peak of the annealed sample moved to the lower temperature. As the \(\alpha\)-relaxation mainly corresponds to the rearrangement of chain segments in rigid amorphous fraction (RAF), according to the FTIR data, it can be inferred that the RAF area of the stepwise crystallized sample decreased while the RAF area of annealed sample increased.

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ORCID iDs

Yefei Tian © https://orcid.org/0000-0002-1165-2851

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