Exploring the Effects of Stereo-Defect Distribution on Nonisothermal Crystallization and Melting Behavior of $\beta$-Nucleated Isotactic Polypropylene/Graphene Oxide Composites

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ABSTRACT: In this work, using two isotactic polypropylene (iPP) resins with similar average isotacticity and molecular weight but different uniformities of stereo-defect distribution, the $\beta$-nucleated iPP/graphene oxide ($\beta$-iPP/GO) composites (NPP-A and NPP-B) were prepared to investigate the effect of stereo-defect distribution on the nonisothermal crystallization kinetics and polymorphic melting behavior of the composites by means of scanning electron microscopy, wide-angle X-ray diffraction, and differential scanning calorimetry. The results showed that more uniform stereo-defect distribution led to a slight increase of the crystallization rate and decrease of the crystallization activation energy $E_c$. NPP-B with more uniform stereo-defect was more favorable for the formation of a large amount of $\beta$-phase. Moreover, the role of the cooling rate was also discussed and it was found that the higher the cooling rate, the higher the $\beta$-phase content and the smaller the crystalline sizes, meanwhile, the higher the amount of $\beta$-phase with relatively lower thermal stability that will take part in $\beta\rightarrow\alpha$ recrystallization during the subsequent melting process. For $\beta$-iPP/GO composites, although the cooling rate greatly influences the polymorphic behavior and crystalline structures of the composites, the uniformity of stereo-defect distribution was found to be the first factor determining the formation of the $\beta$-phase.

1. INTRODUCTION

Since the first time, in 1954, polypropylene (PP) was synthesized by Natta et al. in the laboratory and industrialized in 1957, PP has been widely used for its excellent thermal and mechanical properties. With the development of catalyst technology, the improvement of catalyst activity and selectivity and the improvement of catalyst morphology have greatly simplified the production process of PP and greatly reduced the production cost, which has promoted the rapid development of the PP industry. In just 60 years, PP has become one of the fastest growing, most productive, and most diverse types of plastics. It is widely used as pipes, packaging materials, and separator materials.

The good properties of isotactic polypropylene (iPP) materials are directly related to their crystal form. Isotactic PP (iPP) is a typical polymorphic polymer with different crystal forms including $\gamma$, $\beta$, $\alpha$, and $\gamma$-phase, exhibiting great differences in properties. Among these crystal forms, the $\alpha$-phase is the most stable and commonly seen modification and can be obtained under practical processing conditions, whereas the $\beta$-phase is a thermodynamically metastable crystalline form, whose toughness is higher than the $\alpha$-phase and can only be formed through particular methods, such as crystallization in the melt shear field, in a temperature gradient field, or in the presence of $\beta$-nucleating agents ($\beta$-NA). In these methods, adding $\beta$-NA is the most efficient and simplest way to acquire high content of $\beta$-form. After the addition of a small amount of $\beta$-NA, the impact strength of $\beta$-iPP is improved evidently compared with $\alpha$-iPP. However, the rigidity and yield strength are reduced. Some scholars have found that the growth of $\alpha$- and $\beta$-crystals has a competitive relationship. The growth of $\beta$-crystals needs to be in a specific temperature range. At this time, the growth rate of $\beta$-crystals is higher than that of $\alpha$-crystals and $\beta$-crystals can be formed. When the temperature exceeds the critical temperature, the growth rate of the $\alpha$-crystal is higher than that of the $\beta$-crystal and only the $\alpha$-crystal can be formed. In addition, the $\beta$-crystal is in a thermodynamic metastable state and its thermal stability is not as good as that of the $\alpha$-crystal. The $\beta\rightarrow\alpha$ phase transition might occur during the heating process. To enhance the stiffness of $\beta$-iPP, the composite modification of iPP using a reinforcing filler may be a possible way to balance the rigidity and toughness.

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In 2004, Andre Geim et al. first produced graphene by the adhesive method. Graphene, as a two-dimensional atomic crystal composed of a single atomic layer of carbon atoms connected by sp² hybridization, is only 0.34 nm thick which is the thinnest known material. This special structure gives graphene many excellent properties, such as outstanding electrical conductivity, thermal conductivity, high elastic modulus, larger specific surface area, and fractional quantum hall effect. However, the strong van der Waals force of graphene results in the characteristics of hydrophobicity and easy agglomeration, and the application of graphene is greatly limited. Graphene oxide (GO), as a precursor of graphene, has a structure similar to graphene and can be used as the preferred choice for reinforcing polymers, benefiting from its carboxyl groups and carbonyl groups at the edge and hydroxyl groups and epoxides groups on the matrix. The existence of these functional groups improves the hydrophilicity of GO and can react with polar polymers such as polyamide, poly(vinyl alcohol), and poly(methyl methacrylate). For nonpolar polymers, functional groups are introduced to modify the surface of GO. Surface-functionalized GO has good interfacial compatibility in nonpolar polymers such as iPP and poly-styrene. Composite modification of iPP with GO is an important way to make high performance iPP materials. To make β-iPP gain high toughness and high strength at the same time, it has always been the key and difficult point to manufacture iPP/GO composite materials with a high content of β-crystals. However, GO has a strong effect of α-nucleation in this composite system, which is not conducive to the formation of β-crystals.

The chain tacticity parameters of iPP are important factors affecting the crystallization behavior, including the stereo-defect distribution and the average isotacticity caused by multiple active sites on heterogeneous Ziegler–Natta catalysts. The uniformity of stereo-defect distribution greatly affects its properties and crystallization, especially the selectivity of α- and β-crystals. Since it is important to study the relationship between the crystallization behavior and the molecular tacticity of iPP, many researchers have studied the relationship between crystallization behavior, average isotacticity, and the final mechanical behavior in the past few decades. However, due to the complexity of Ziegler–Natta polymerization, it is not easy to adjust the polymerization conditions and to obtain ZN-iPP with similar average isotacticities and molecular masses but different stereo-defect distributions. Therefore, the role of stereo-defect distribution on the crystallization and mechanical properties is still not clear, as far as we know.

Recently, by using two kinds of Ziegler–Natta catalysts with different catalytic activities in the polymerization process, we synthesized two kinds of iPP samples with different stereo-defect distributions. Their polymorphic composition, crystallization behavior, and mechanical properties were studied in previous studies. It was found that the mechanical properties and β-phase crystallization of β-iPP are closely related to the uniformity of stereo-defect distribution.

The aim of this study is to further investigate the crystallization process of the β-iPP/GO composites, the nonisothermal crystallization kinetics of β-iPP/GO composites with different distributions of stereo-defects were compared by cooling at different rates. From the application point of view, the nonisothermal crystallization process is close to the actual operating conditions, so the study of nonisothermal crystallization kinetics also has practical significance.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

The iPP resins (PP-A and PP-B) used in this study were obtained using two kinds of Ziegler–Natta catalysts (ZN-A and ZN-B, the activity of ZN-A was higher than that of ZN-B) in the polymerization process, keeping other polymerization conditions unchanged as described in our previous works. A brief introduction of their microstructures is provided in Table 1. As can be seen from Table 1, the weighted average molecular weight $M_a$ and the average isotacticities of samples are nearly the same, suggesting that the total defects of PP-A and PP-B are similar. However, compared with PP-B, PP-A has a more high-isotacticity component ("mm") and a less relatively medium and low-isotacticity component ("rr" and "rr"), indicating that the distribution of stereo-defects of PP-B is more uniform.

Other raw materials are obtained through direct purchase. Guangdong Winner Functional Material Co., Ltd. (China) provided β-NA named WBG-II, which is composed of heterocyclic double metal (lanthanum and calcium) complexes; Chengdu Changzheng Chemical Glass Apparatus Co., Ltd. (China) provided octadecylamine (ODA), ethanol, and xylene; Guangzhou Angstron Graphene Technology Co., Ltd. (China) provided graphene oxide (GO).

#### 2.2. Sample Preparation

For the purpose of grafting ODA onto GO, ODA (0.9 g) and GO (0.5 g) were added into 200 mL of ethanol and the mixture was stirred under reflux for 20 h at 90 °C, then vacuum filtration was carried on. The reaction product was dissolved again in 200 mL of ethanol and then ultrasonically dispersed for 5 min, followed by vacuum filtration. Cycle the rinse–filter process four times, the physically adsorbed and excess ODA would be cleared away. The GO grafted with ODA was dried under vacuum at 60 °C for 24 h. The dried powder was dissolved in 200 mL of xylene solution and then ultrasonically dispersed for 30 min. A certain amount of iPP was added into the above solution to keep the mass fraction of GO at 5% and stir the mixture at 130 °C for 2 h. Finally, the solution was vacuum filtered and dried for 24 h to obtain the iPP/GO masterbatch. On the other hand, to obtain fine dispersion of β-NA in the matrix, the β-NA masterbatch was also prepared via a twin extruder (SHJ-20, Nanjing Giant Machinery Co., Ltd., China), the screw speed was 20 rpm, and the temperature of each part

| Table 1. Molecular Structural Parameters of PP-A and PP-B |
|---------------------------------|------------------|------------------|
| sample | XS/% | isotacticity/% | $M_a$ (g/mol) | mm | mm | mm + rr | rr | rr |
| PP-A | 3.8 | 96.6 | 365050 | 95.07 | 1.59 | 0.41 | 2.12 | 0.57 | 0.30 | 0.61 | 0.45 | 0.88 |
| PP-B | 3.9 | 96.4 | 347150 | 94.78 | 1.47 | 0.53 | 2.17 | 0.71 | 0.31 | 0.65 | 0.48 | 0.90 |

"Xylene soluble fraction at room temperature according to ASTM D5492. Isotacticity were obtained from high temperature 13C NMR at 120 °C. Molecular mass and distribution were performed by GPC at 130 °C. Samples were extracted in n-heptane for 24 h at desired temperatures and then the insoluble fraction was collected and dried for high-resolution 13C NMR measurement to exclude the influence of the atactic fraction.

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was 185, 195, 200, and 200 °C, respectively) and pelletized to obtain a masterbatch, and the β-NA concentration was 1 wt %.

After that, the iPP/GO masterbatch, β-NA masterbatch, and iPP pellets were mixed using the twin extruder again to obtain the β-iPP/GO composites with a GO concentration of 1 wt % and a WBG-II concentration of 0.135 wt %. After mixing, the sample was pressed by a pressure molding machine for further measurement. To benefit discussion, two iPP (PP-A and PP-B) with GO (1 wt %) and WBG-II (0.135 wt %) were denoted as NPP-A and NPP-B, respectively.

2.3. Characterization. 2.3.1. Differential Scanning Calorimetry (DSC). All the calorimetric experiments were performed with a Mettler Toledo DSC1 (Mettler Toledo Corp., Switzerland) differential scanning calorimeter (DSC) under a nitrogen atmosphere (50 mL/min). 3–5 mg of samples were used. All the melting curves were fitted using the Peakfit 4.12 software according to the literature.43 The relative percentages of the β-crystal (βf) were estimated by the following expression

\[ \beta_f = \frac{X_f}{X_i + X_f} \]  

(1)

where the degree of crystallinities \( X_i \) and \( X_f \) associated with α- and β-phases, respectively.

The crystallization and melting behavior of two samples were investigated by the DSC thermal treatment program as shown in Scheme 1. First, all samples were heated to 200 °C at 10 °C/min and kept for 5 min to erase any previous thermal histories. Then they were cooled down to \( T_{\text{end}} = 50 \) °C or \( T_{\text{end}} = 100 \) °C at a cooling rate of 2, 5, 10, 20, and 40 °C/min respectively. Finally, they were heated to 200 °C at 10 °C/min.

2.3.2. Wide-Angle X-ray Diffraction (WAXD). A DX-1000 (China) diffractometer was used to record the wide-angle X-ray diffraction (WAXD) behavior of the samples. The basic parameters of the diffractometer are as follows, the wavelength of Cu Kα is \( \lambda = 0.154 \) nm, the 2θ test range is 5–35°, the scanning step is 0.02°, and the scanning rate is 2°/min. A standard method for determining the content of the β-crystal is recorded in the references, and the formula used is as follows

\[ k_\beta = \frac{H_\beta(110)}{H_\alpha(110) + H_\alpha(110) + H_\alpha(040) + H_\alpha(130)} \]  

(2)

where \( k_\beta \) denotes the relative content of the β-crystal form (WAXD), \( H_\beta(110), H_\alpha(040), \) and \( H_\alpha(130) \) are the intensities of the strongest peaks of the α-form attributed to the (110), (040), and (130) planes of monoclinic cell, respectively. \( H_\alpha(110) \) is the intensity of the strongest (110) diffraction peak of the trigonal β-form.

2.3.3. Scanning Electron Microscopy (SEM). A JSM-5900 LV environmental scanning electron microscope (JEOL, Corp. Ltd., Japan) was used at an accelerating voltage of 20 kV to observe the morphology of the samples (scanning electronic microscopy, SEM). According to the standard procedure in the literature, all the samples must be etched for 4 h in a solution constituting 65.8 wt % concentrated phosphoric acid (H₃PO₄), 1.3 wt % potassium permanganate (KMnO₄), and 32.9 wt % concentrated sulfuric acid (H₂SO₄), and then coated with a thin layer of gold by ion sputtering prior to SEM characterization.

3. RESULTS AND DISCUSSION

3.1. Nonisothermal Crystallization Behavior. 3.1.1. Cooling Curves. The crystallization curves of NPP-A and NPP-B at different cooling rates (curve 1 in Scheme 1) are shown in Figure 1. The variations of the peak, onset, and endset crystallization temperatures (\( T_\beta, T_{\text{onset}} \) and \( T_{\text{endset}} \)) of the samples are plotted as a function of the cooling rate in Figure 2.

As shown in Figures 1 and 2, for the samples, the crystallization temperature and the crystallization peak width (\( T_{\text{onset}} - T_{\text{endset}} \)) become bigger with the increase of the cooling rate. At the same cooling rate, the \( T_\beta \) of NPP-A is slightly larger than that of NPP-B by about 1 °C, indicating that NPP-B prefers to crystallize at a lower temperature. The trend of two samples is basically the same, and there is no significant difference in crystallization. Therefore, it is difficult to distinguish the difference in crystallization ability between the two samples from the crystallization curve.

3.1.2. Nonisothermal Crystallization Kinetics. The semi-crystallization time (\( t_{0.5} \)) of the samples at different cooling rates was calculated using the following equation

\[ X_t = \frac{\int_0^t \left( \frac{dH}{dt} \right) dt}{\int_0^\infty \left( \frac{dH}{dt} \right) dt} \]  

(3)

A plot of relative crystallinity \( X_t \) versus crystallization time is plotted and a crystallization time of 50% relative crystallinity is recorded as \( t_{0.5} \), which is used to measure the crystallization rate. The larger the \( t_{0.5} \), the slower the crystallization rate of the sample. Then the Kissinger method is used to calculate the crystallization activation energy \( (E_c) \) by the following expression

\[ \ln \left( \frac{D}{T_c^2} \right) = -\frac{E_c}{RT_c} + \text{const} \]  

(4)

where \( R \) is the gas constant, \( D = \text{d}T/\text{d}t \) is the cooling rate, and \( T_c \) is the crystallization temperature corresponding to the maximum crystallization rate on the cooling crystallization curve. Plot 1/\( T_c \) with \( \ln(D/T_c^2) \), the crystallization activation energy \( (E_c) \) can be obtained from the slope. \( E_c \) represents the energy barrier that needs to be overcome for the crystallization of the sample. The larger the \( E_c \), the more difficult the sample is to crystallize, and the worse the crystallization ability of the sample. According to eqs 3 and 4, and the crystallization activation energy \( E_c \) are calculated and the data are listed in Table 2. Relative crystallinity as a function of crystallization time of (a) NPP-A and (b) NPP-B are shown in...
The results in Figure 4 and Table 2 show that the $E_c$ of NPP-B ($-247.9$ KJ/mol) is smaller than the $E_c$ of NPP-A ($-232.2$ KJ/mol), indicating that the crystallizability of NPP-B has been greatly improved, which has exceeded its counterpart of NPP-A. On the other hand, the $t_{0.5}$ of NPP-A and NPP-B has the same changing trend with the variation of the cooling rate, that is, the faster the cooling rate, the shorter the $t_{0.5}$. However, at the same cooling rate, $t_{0.5}$ of NPP-B is always smaller than NPP-A. As displayed in Figure 3 and Table 2, NPP-B has the shortest $t_{0.5}$ (0.21 min) when the cooling rate is 40 °C/min and NPP-A has the longest $t_{0.5}$ (0.75 min) when the cooling rate is 2 °C/min. In general, the crystallization rate of NPP-B is faster than that of NPP-A, which is in accordance with the result of activation energy.

It should be emphasized that in the previous study, it was found that for pure iPP, the $t_{0.5}$ and $E_c$ of PP-A are all higher than that of PP-B. Therefore, the finding in this section suggests that under the influence of β-NA and GO, PP-B with more uniform stereo-defect distribution exhibits stronger crystallizability compared with PP-A whose stereo-defect distribution is less uniform.

### 3.2. Melting and Polymorphic Behavior

It is reported that the unstable β-crystals will convert into the α-phase and affect the polymorphic behavior of PP when the end temperature of cooling ($T_{end}$) is below 100 °C in the cooling process. Therefore, by comparing the melting curves of the samples when $T_{end} = 100$ °C and $T_{end} = 50$ °C, results...
concerning the thermal stability of the β-phase can be obtained. To further study the effect of stereo-defect distribution on the polymorphic behavior of the β-iPP/GO and thermal stability of the formed β-phase, the melting behavior of NPP-A and NPP-B was observed after holding at 200 °C for 5 min and then cooling to $T_{\text{end}} = 100$ °C and $T_{\text{end}} = 50$ °C, respectively, at different cooling rates.

The melting curves (curve 2 in Scheme 1) of NPP-A and NPP-B when $T_{\text{end}} = 100$ °C and $T_{\text{end}} = 50$ °C are shown in Figures 5 and 6, respectively, whereas the relative content of β-crystals is shown in Figure 7a. Moreover, the difference between the β-phase content when $T_{\text{end}} = 50$ °C and $T_{\text{end}} = 100$ °C, $\beta_c (T_{\text{end}} = 100$ °C) − $\beta_c (T_{\text{end}} = 50$ °C), is calculated as shown in Figure 7b. The larger the $\beta_c (T_{\text{end}} = 100$ °C) − $\beta_c (T_{\text{end}} = 50$ °C), the higher the amount of β-phase that takes part in $\beta \rightarrow \alpha$ recrystallization when $T_{\text{end}} = 50$ °C, and the lower the thermal stability of the β-phase.

As can be seen from Figures 5–7, for NPP-A, the melting temperatures of α-phase and β-phase become lower with the increase of the cooling rate, indicating that NPP-A prefers to form α- and β-phase with lower lamellar thickness at a higher

Figure 3. Relative crystallinity as a function of crystallization time of (a) NPP-A and (b) NPP-B.

Figure 4. Kissinger plots for evaluating nonisothermal crystallization activation energies of NPP-A and NPP-B.

Figure 5. Heating curves of (a) NPP-A and (b) NPP-B at different cooling rates (after being held at 200 °C for 5 min and then cooled under different rates to $T_{\text{end}} = 50$ °C).
cooling rate. This rule also applies to NPP-B. Moreover, two α-melting points appear on the curve of NPP-B when the cooling rate is over 5 °C/min, since the unstable β-phase changes into α-crystal nucleus during the melting process, which then induces α-recrystallization and results in the recrystallized α-phase with a higher melting temperature.

On the other hand, it can be seen that both NPP-A and NPP-B form more amounts of β-crystals at a low cooling rate and the relative content of β-crystals formed by NPP-B is much higher than that of NPP-A, indicating that for β-iPP/GO composites, the iPP matrix with more uniform stereo-defect distribution is more favorable for the formation of a higher amount of β-phase.

Comparing the results of Figure 5 (T_{end} = 50 °C) and Figure 6 (T_{end} = 100 °C), it can be seen that when T_{end} = 100 °C, the relative contents of the β-phase of both NPP-A and NPP-B are obviously enhanced and the α-double peak formed by β→α recrystallization on the melting curve of NPP-B disappears, indicating that the influence of β→α phase transition during the melting process is eliminated.

Moreover, the difference between the β-phase content when T_{end} = 50 °C and T_{end} = 100 °C, \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \), can be regarded as an indicator of the thermal stability of the β-phase during the melting process. It can be seen that the higher the cooling rate, the larger the \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \) for both NPP-A and NPP-B, indicating that the composites of both NPP-A and NPP-B prefer to form more β-crystals with less thermal stability at a higher cooling rate. Meanwhile, the \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \) value of NPP-B is always higher than its counterpart of NPP-A, suggesting that NPP-B is more preferred to form the β-phase with less thermal stability, which should be attributed to its more uniform stereo-defect distribution.

3.3. WAXD. To understand fully, the WAXD test is carried out in this section. The samples are disposed as follows. First, put the molded sheet specimens in the drying oven at 200 °C for 20 min to erase any previous thermal history. Then, the specimens were cooled under three different conditions, that is, (1) taking out the specimens from the oven immediately and placing them into cold water for fast cooling (named A-F and B-F, cooling rate of about 200 °C/min), (2) taking out the sheets and placing them at room temperature for medium speed cooling (named A-M and B-M, cooling rate of about 50 °C/min), and (3) leaving the specimens in the oven for slow cooling (named A-S and B-S, cooling rate. This rule also applies to NPP-B. Moreover, two α-melting points appear on the curve of NPP-B when the cooling rate is over 5 °C/min, since the unstable β-phase changes into α-crystal nucleus during the melting process, which then induces α-recrystallization and results in the recrystallized α-phase with a higher melting temperature.

On the other hand, it can be seen that both NPP-A and NPP-B form more amounts of β-crystals at a low cooling rate and the relative content of β-crystals formed by NPP-B is much higher than that of NPP-A, indicating that for β-iPP/GO composites, the iPP matrix with more uniform stereo-defect distribution is more favorable for the formation of a higher amount of β-phase.

Comparing the results of Figure 5 (T_{end} = 50 °C) and Figure 6 (T_{end} = 100 °C), it can be seen that when T_{end} = 100 °C, the relative contents of the β-phase of both NPP-A and NPP-B are obviously enhanced and the α-double peak formed by β→α recrystallization on the melting curve of NPP-B disappears, indicating that the influence of β→α phase transition during the melting process is eliminated.

Moreover, the difference between the β-phase content when T_{end} = 50 °C and T_{end} = 100 °C, \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \), can be regarded as an indicator of the thermal stability of the β-phase during the melting process. It can be seen that the higher the cooling rate, the larger the \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \) for both NPP-A and NPP-B, indicating that the composites of both NPP-A and NPP-B prefer to form more β-crystals with less thermal stability at a higher cooling rate. Meanwhile, the \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \) value of NPP-B is always higher than its counterpart of NPP-A, suggesting that NPP-B is more preferred to form the β-phase with less thermal stability, which should be attributed to its more uniform stereo-defect distribution.

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On the other hand, it can be seen that both NPP-A and NPP-B form more amounts of β-crystals at a low cooling rate and the relative content of β-crystals formed by NPP-B is much higher than that of NPP-A, indicating that for β-iPP/GO composites, the iPP matrix with more uniform stereo-defect distribution is more favorable for the formation of a higher amount of β-phase.

Comparing the results of Figure 5 (T_{end} = 50 °C) and Figure 6 (T_{end} = 100 °C), it can be seen that when T_{end} = 100 °C, the relative contents of the β-phase of both NPP-A and NPP-B are obviously enhanced and the α-double peak formed by β→α recrystallization on the melting curve of NPP-B disappears, indicating that the influence of β→α phase transition during the melting process is eliminated.

Moreover, the difference between the β-phase content when T_{end} = 50 °C and T_{end} = 100 °C, \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \), can be regarded as an indicator of the thermal stability of the β-phase during the melting process. It can be seen that the higher the cooling rate, the larger the \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \) for both NPP-A and NPP-B, indicating that the composites of both NPP-A and NPP-B prefer to form more β-crystals with less thermal stability at a higher cooling rate. Meanwhile, the \( \beta_c (T_{end} = 100 °C) - \beta_c (T_{end} = 50 °C) \) value of NPP-B is always higher than its counterpart of NPP-A, suggesting that NPP-B is more preferred to form the β-phase with less thermal stability, which should be attributed to its more uniform stereo-defect distribution.

3.3. WAXD. To understand fully, the WAXD test is carried out in this section. The samples are disposed as follows. First, put the molded sheet specimens in the drying oven at 200 °C for 20 min to erase any previous thermal history. Then, the specimens were cooled under three different conditions, that is, (1) taking out the specimens from the oven immediately and placing them into cold water for fast cooling (named A-F and B-F, cooling rate of about 200 °C/min), (2) taking out the sheets and placing them at room temperature for medium speed cooling (named A-M and B-M, cooling rate of about 50 °C/min), and (3) leaving the specimens in the oven for slow cooling (named A-S and B-S,
Figure 8. WAXD profiles of (a) NPP-A and (b) NPP-B after being held at 200 °C for 5 min and then cooled under three kinds of cooling rates to room temperature.

Figure 9. SEM images (after etching) of (a) A-S, (b) B-S, (c) A-M, (d) B-M, (e) A-F, and (f) B-F after being held at 200 °C for 5 min and then cooled under different cooling rates to room temperature.
cooling rate about 1 °C/min). The WAXD results are shown in Figure 8.

It should be noted that since WAXD is measured at room temperature, the obtained β-phase content (kβ) from WAXD is not confused by the thermal stability of the β-phase. Figure 8 reveals that for both NPP-A and NPP-B, the kβ value is obviously enhanced at the fast cooling rate, indicating that the fast cooling rate is more favorable for the formation of a high content of β-phase no matter the stereo-defect distribution of the iPP matrix. Meanwhile, the β-phase of NPP-B is evidently higher than its counterpart of NPP-A, which is in line with the DSC results above.

3.4. SEM Observation. To directly study the polymorphic morphologies of the samples, the temperature-treated sheets described above were etched and then subjected to SEM measurement.

At a slow cooling rate (Figure 9a,b), NPP-A (A-S) forms a large amount of highly stable α-crystals (relatively dark areas in the image), which are quite difficult to be etched. Meanwhile, a small amount of β-crystals (loosely stacked lamellae structures in the relatively bright area in the image) randomly distributed in the image. In clear contrast, for NPP-B (B-S), a high amount of large-sized β-crystals can be observed, indicating that NPP-B with more uniform stereo-defect distribution has a stronger ability to form a large amount of β-crystals even during slow cooling. At a medium cooling rate (Figure 9c,d), a small amount of β-crystals can be observed in NPP-A (A-M), whereas large amounts of β-crystals with relatively small size exist in NPP-B. At a fast cooling rate (Figure 9e,f), the crystalline sizes of both NPP-A and NPP-B decrease evidently, whereas their β-phase content further increases. In general, the results of SEM more intuitively reflect the crystalline structure and polymorphic behavior of the composites, which are in accordance with the results of DSC and WAXD. For β-iPP/GO composites, although the crystallization conditions (cooling rate) greatly influence the polymorphic behavior and crystalline structures of the composites, the uniformity of the stereo-defect distribution is found to be the first factor determining the formation of the β-phase.

4. CONCLUSIONS

In this study, using two iPP with similar average isotacticity and molecular weight, but different uniformities of stereo-defect distribution, the β-iPP/GO composites (NPP-A and NPP-B) were prepared to investigate the effect of stereo-defect distribution on the nonisothermal crystallization kinetics and polymorphic melting behavior. The results revealed that in the case of β-iPP/GO composites, in the aspect of crystallization, more uniform stereo-defect distribution leads to a slight increase of the crystallization rate and decrease of the crystallization activation energy Eα. Meanwhile, for melting behavior, NPP-B with more uniform stereo-defect is more favorable for the formation of a large amount of β-phase. Moreover, the role of the cooling rate was also discussed. The higher the cooling rate, the higher the β-phase content and the smaller the crystalline sizes, meanwhile, the higher the amount of β-phase with relatively lower thermal stability that will take part in β→α recrystallization during the subsequent melting process. It should be noted that for β-iPP/GO composites, although the cooling rate greatly influences the polymorphic behavior and crystalline structures of the composites, the uniformity of stereo-defect distribution is found to be the first factor determining the formation of β-phase.
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