

EFFECT OF FINAL HEATING TEMPERATURE ON CRYSTALLIZATION OF ISOTACTIC POLYPROPYLENE NUCLEATED WITH AN ARYL AMIDE DERIVATIVE AS β -FORM NUCLEATING AGENT

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Abstract An aryl dicarboxylic acid amide compound TMB-5 is an efficient β -form nucleating agent for isotactic polypropylene (iPP). Because of the solubility of TMB-5, superstructure and morphology of iPP crystals changed with melting conditions. Effects of final heating temperature (T_f) on heterogeneous nucleation of iPP/TMB-5 were investigated. It was discovered that the crystallization temperature increased with decreasing T_f value. The optical microscopic images indicated that when TMB-5 partially dissolved in iPP melt, the remaining (non-dissolved) TMB-5 facilitated the recrystallization of dissolved nucleating agent from the melt, which promoted crystallization. Complete solubility of nucleating agent caused the decreasing efficiency. TMB-5 recrystallized in the form of tiny needles, whose aggregates induced dendritic iPP crystals.

Keywords: Isotactic polypropylene; Heterogeneous nucleation; Crystallization; Polymer processing; Melting temperature.

INTRODUCTION

Since polymer products affect everyday life, much attention has been directed toward property enhancement with lower cost and manufacturing cycles. Blending additives with polymers is a well-established method to improve their performance. Among the many additives in use with semi-crystalline polymers are nucleators, which raise the crystallization temperature and also shorten time required for crystallization, thus reducing the cycle time in injection molding processes. Nucleators increase the number of crystallization sites in a polymer thus reducing the spherulite size. They cause simultaneous crystal growth and thus evenly sized crystals. Smaller evenly sized crystals improve the physical properties of the polymers like transparency, surface gloss and impact strength.

Several possible candidates for nucleators of polyolefin have been studied for several decades. Metal aromatic carboxylates have been employed as nucleating agents for many years. Binsbergen investigated the physical and chemical nature of about 2000 nucleating agents and concluded that most agents are insoluble in the polymer and the soluble agents crystallize out of the polymer melt prior to polymer crystallization^[1]. According to the melting point, these soluble and insoluble nucleating agents are divided into two types: dissolution type and dispersion type^[2]. By dissolution type we mean that the nucleators dissolve in the polymer at the melting temperature of the polymer, whereas nucleators of dispersion type disperse in the polymer and remain in solid state at the melting temperature of the polymer^[3]. Usually the nucleating agents of dispersion type have higher melting points, with high thermal stability of the nucleating effect, while the thermal stability

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of nucleating effect of the dissolution type ones decreases with increasing the melting temperature^[4, 5].

In the processing of polypropylene (PP), the nucleating agent is usually used to reduce the size of the PP spherulites, improve the optical clarity, decrease the cycle time of the process and enhance the mechanical properties. So far, there have been a few reports dealt with the research on the relation between nucleators' stability and its nucleation efficiency, such as melting temperature and melting time's effect on the crystallization behaviors of polymers^[6–9]. It is usually accepted that high melting temperature would give rise to a better homogenization, which increases the efficiency of nucleating effect of nucleating agent. The increment of melting treatment temperature is expected to affect the concentration of athermal nuclei, which are preexisting crystalline domains in the melt with the same chemical structure as the molten polymer and extraordinarily sensitive to the melting temperature and the residence time in the molten phase^[10]. Higher heating temperature should result in slower crystallization rate^[11]. In some cases, the high melting temperature may be indispensable to the formation of special structure of nucleators in the molten *i*PP. Mohmeyer *et al.* studied trisamide derivatives in polypropylene melt and considered they are able to form intermolecular hydrogen bonds and tend to crystallize from the molten mixtures with *i*PP into tenuous three-dimensional structure^[12, 13]. The well-known dissolution type nucleators (traditional nucleator of α -form *i*PP), sorbitol derivative molecules, have been proved to self-associate in organic solvents and polymer melt to yield a fibrillar network that gels the matrix. Therefore, the processing and compounding of the *i*PP/sorbitol-based clarifier have to be performed beyond the melting point of the clarifier, which is higher than the processing temperature of a conventional *i*PP. As a result, the odor and discoloration due to the thermal degradation of the clarifier often become a severe problem and thus restrict the application. DBS has certain disadvantages such as evaporation during processing and bleeding out from the *i*PP film^[14–20].

However, there are few articles concerned with the thermal stability of the heterogeneous nucleation effect of β -nucleated PP. Chen *et al.* studied the thermal stability of the heterogeneous nucleation effect of PP nucleated with some nucleating agents^[5]. They reported that the crystallization temperature of PP nucleated with aliphatic diacids gradually decreased in multiscanning while no change for the PP nucleated with calcium carbonate, terephthalic acid, and sodium benzoate was observed. They presumed that the thermal stability of heterogeneous nucleation effect of PP nucleated with calcium carbonate, terephthalic acid, and sodium benzoate is better than that of PP nucleated with aliphatic diacids. Obviously, the thermal stability of the heterogeneous nucleation effect of nucleated PP depends on the type of nucleating agents.

TMB-5 is a commercialized β -form nucleating agent for *i*PP which has been proved highly efficient. In our previous studies, optical observations proved that TMB-5 dissolved partially or completely in the *i*PP melt and recrystallized during cooling^[21, 22]. The extent of dissolution, the size of the recrystallized nucleating agent and the supermolecular structure formed depend on the concentration of the nucleating agent and on the thermal conditions of crystallization. The dissolution promotes the homogeneous dispersion of nucleating agent in the matrix and results in the diverse supermolecular structure. Since the amount of dissolved and heterogeneous (non-dissolved) nucleating agent depends on T_f , it is inferred that the effect of melting condition on the crystallization and melting behavior of *i*PP becomes markedly more complicated in the presence of partially soluble nucleating agents. The relations between melting condition and polymer properties are complicated even more by the fact that the amount of non-dissolved, heterogeneous nucleating agent influences also the polymorphic composition of the sample. Thus it is significant to figure out the influence of melting condition on the crystallization behaviors of *i*PP nucleated with dissolution type nucleating agent. This paper is a more detailed study on how the solubility of TMB-5 affects the crystallization, polymorphic composition, and supermolecular structure of *i*PP. The conclusions are supported by calorimetry and optical measurements.

EXPERIMENTAL

Materials and Sample Preparation

The matrix polymer used in this work was a commercial grade *i*PP, 2401, with melt flow index of 2.5 g/10min,

$M_w = 4.4 \times 10^5$ and melting temperature of 165°C, produced by Yanshan Petroleum and Chemical Corp., China. The commercial β nucleating agent (TMB-5) is a kind of aryl dicarboxylic acid amide compound, provided by Shanxi Provincial Institute of Chemical Industry, with melting point of 197°C. Unfortunately, we are not aware of the corresponding work about chemical structure and crystal information of TMB-5 on basis of the relevant patent. As far as we know, it is an aromatic amide derivative with structure given in Fig. 1.

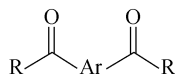


Fig. 1 Chemical structure of the β -nucleating agent TMB-5

Compounding of *i*PP with TMB-5 was produced using a co-rotating twin-screw extruder, operating at 210°C and 120 r/min. TMB-5 proportion in the blends was 0.3% by weight. The material obtained was compression molded with a hot press at 180°C and then cooled for subsequent POM and SEM observation.

Measurements

For optical microscopy observation, a Nikon type 104 optical microscope was used. The optical microscope was equipped with cross-polarizer, with a JVC color video camera incorporated and a programmable heating stage. The film sample (*ca.* 20 μm) was sandwiched between microscope cover lips, melting at a controlled temperature T_f for 5 min, and then cooled at 5 K/min to room temperature. The samples were not subjected to temperatures higher than 180°C before the systematic POM study, in order to minimize the influence of the partial dissolution of TMB-5 and avoid the thermo-oxidative degradation of the sample.

The thermal stability was studied by using a TA Instruments Q2900 differential scanning calorimeter (DSC) in a nitrogen atmosphere. The non-isothermal crystallization behaviors of these samples were investigated by conducting cooling scans at rate of 10 K/min from T_f (180, 190, 200, 210, 220, 230, 240, 250°C) to 80°C. At T_f , the time of heat treatment (t_f) was 5 min. The following heating scans were carried out at 10 K/min up to 200°C. For all pure and TMB-5 nucleated *i*PP samples, T_m and T_c were determined from the DSC curves as the maxima of the relevant peaks.

Field emission scanning electron microscopy (FESEM) was performed on a JEOL model JSM-7401 apparatus with an operating voltage of 1.0 kV to investigate the morphology of the film. For the purpose of contrasting the crystalline morphology, permanganic etching was adopted. The samples were coated with gold by using an ETD-200 SEM coating system (Beijing Elaborate Technology Development Ltd.) operating at 5 mA for 5 min.

RESULTS AND DISCUSSION

Influence of T_f on the Crystallization and Polymorphic Composition in *i*PP

Abundant experimental information is available in the open literature about the effect of the final heating temperature (T_f) on the crystallization of *i*PP^[11, 23–28]. These results suggest that a smaller or larger number of self-nuclei remain in the melt above the melting point of the polymer. These self-nuclei considerably influence the rate of recrystallization after melting and the characteristics of the resulting super-molecular structure. However, a critical temperature T_s^* exists, above which an “empty” melt free of self-nuclei is present. Further increase of the final heating temperature above this threshold does not influence the recrystallization of the polymer. We must note here that T_s^* depends also on the time of heating and on the super-molecular structure of the initial sample.

The exothermic curves obtained under dynamic conditions after melting at various T_f are shown in Fig. 2. It has been observed that the exothermic curves of pure *i*PP do not change much with various T_f . Therefore, the lowest T_f in our experiments (180°C) is above T_s^* and the self-nucleation can be excluded in this case. The cooling curves of *i*PP are rather blunt with a shoulder at high temperatures. This shoulder could be attributed to a mechanism similar but opposite to melt reorganization observed during melting which was discussed before.

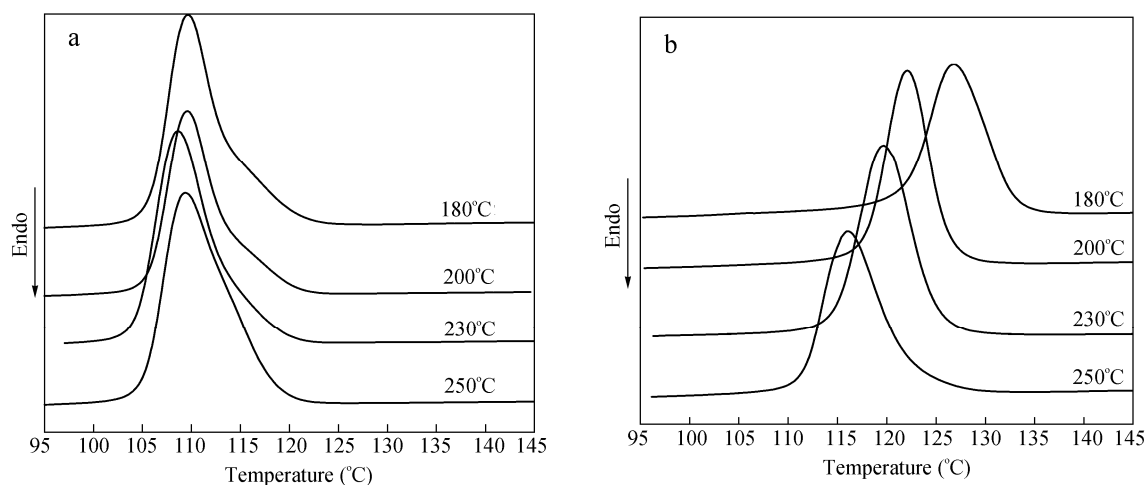


Fig. 2 Effect of the final temperature of heating on the crystallization behaviors of pure *i*PP (a) and β -nucleated *i*PP (b)

Seen from Fig. 2(b), the addition of TMB-5 increases the crystallization temperature of *i*PP by 5–20°C. The peak temperature as well as the temperature range of crystallization shifts toward lower values with increasing T_f . The evolution of the crystallization temperature is shown in Fig. 3. The crystallization temperature of pure *i*PP keeps almost constant around 110°C, while the crystallization temperature of β -nucleated *i*PP increases with lowering T_f . This dependence on T_f indicates that the nucleating agent is responsible for the observed increasing T_c with decreasing T_f . Though higher T_c values of *i*PP/TMB-5 samples than pure *i*PP are displayed, the decreasing values at higher T_f proved its decreasing efficiency of inducing heterogeneous nucleation.

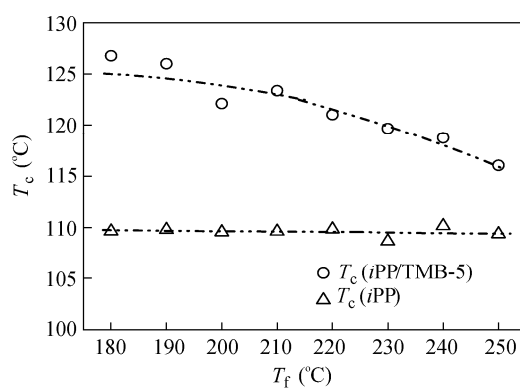


Fig. 3 Crystallization temperature (T_c) characterizing the efficiency of the nucleating agent plotted against the final temperature of heating (T_f)

Compared with single α -phase endotherm in the melting curves of pure *i*PP (Fig. 4a), dominant β -phase of *i*PP forms for *i*PP/TMB-5 samples at all T_f values we studied between 180–250°C (Fig. 4b). The α -phase melting area shows a splitting of the endotherm associated with the α and α' phase at 164°C and 170°C (arrows α and α' in Fig. 4b), respectively. The new monoclinic crystals that form during the $\beta \rightarrow \alpha$ transition are α' and melt at a higher temperature than α monoclinic crystals formed during cooling from the melt. The tendency for $\beta \rightarrow \alpha$ recrystallization in *i*PP was attributed to the formation of monoclinic crystals within the β spherulites because of secondary crystallization in the cooling process below $T_{\alpha\beta}$ (low transition temperature). These finely distributed monoclinic crystals act as α precursors during the partial melting of the β phase and generate the

monoclinic α' phase. When the β crystals are less perfect (i.e., low T_c , higher supercooling degree), the $\beta \rightarrow \alpha$ transition becomes more remarkable. At $T_f = 250^\circ\text{C}$, the proportion of α phase increases as well as $\beta \rightarrow \beta'$ recrystallization becomes more remarkable, showing that β phase proportion and the perfect degree of β crystals both decreased.

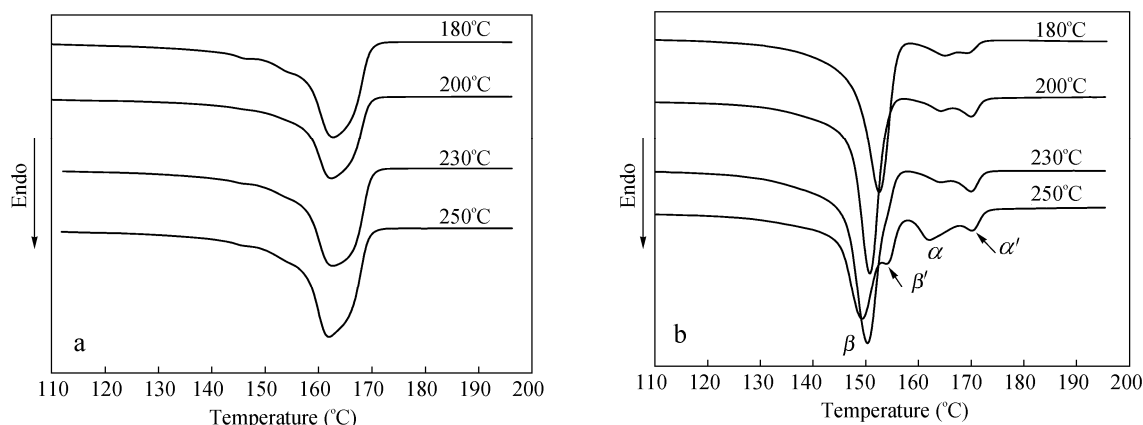


Fig. 4 Effect of the final temperature (T_f) of heating on the melting behaviors of pure *i*PP (a) and β -nucleated *i*PP (b)
 T_f value was indicated in each curve.

In Fig. 5 we show the dependence of the melting peak temperature on the final temperature of heating. The peak temperatures monotonously increased with decreasing T_f in β -nucleated *i*PP, while peak temperatures of pure *i*PP kept almost unchanged. The tendency is similar to the curves of Fig. 3. It is reasonable that at lower T_f the crystallization of β -nucleated *i*PP occurred at higher temperatures, thus forming more stable crystals which melt at high temperature. The melting temperatures of α -phase in β -nucleated *i*PP samples are higher than those of pure *i*PP, which might be also attributed to higher crystallization temperature in β -nucleated *i*PP samples.

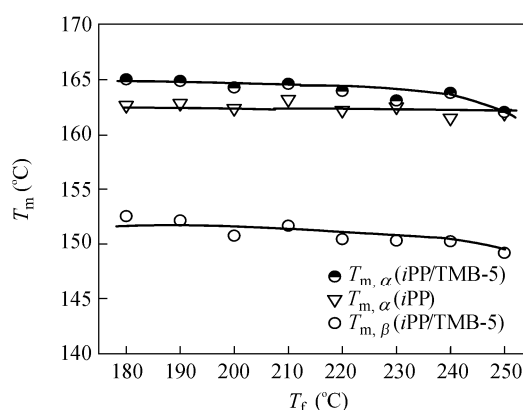


Fig. 5 Melting temperature of pure and nucleated *i*PP versus T_f

Morphological Evolvement of β -Nucleated Samples with Changing T_f

The melting and crystallization behavior of the *i*PP/TMB-5 system was investigated also by polarized microscopy. Figs. 6–7 present micrographs of *i*PP/TMB-5 after cooling from the different temperatures (T_f) to room temperature at a rate of 5 K/min. As can be clearly seen, the resulting morphology strongly depends on the final melting temperature.

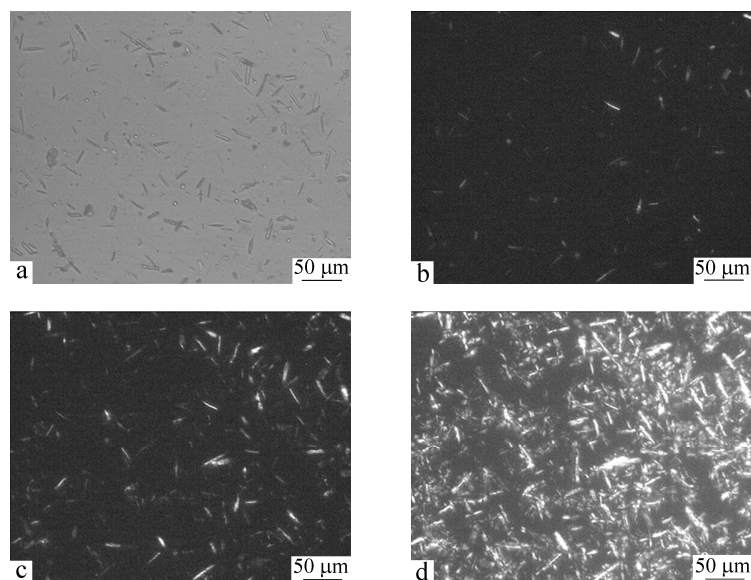


Fig. 6 Growth of the crystallization structure of the β -*i*PP at a cooling rate of 5 K/min ($T_f = 180^\circ\text{C}$)
The POM photographs were taken at different temperatures: (a) 179.8°C ; (b) 121.0°C ; (c) 117.2°C ; (d) 114.9°C

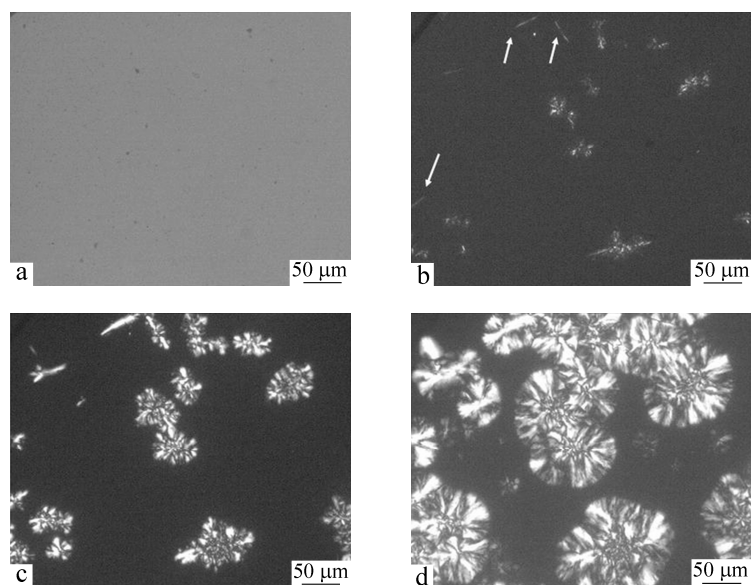


Fig. 7 Dendritic crystallization of the β -*i*PP on the surface of recrystallized TMB-5
at a cooling rate of 5 K/min ($T_f = 250^\circ\text{C}$)
The POM photographs were taken at different temperatures during cooling process:
(a) 179.6°C ; (b) 118.9°C ; (c) 112.8°C ; (d) 108.4°C .

Polarized optical microscopy was also employed to determine melting and crystallization transitions in *i*PP/TMB-5 systems. The melting point of *i*PP reported here refer to those temperatures at which no more birefringence arising from the characteristic polymer spherulites could be detected under crossed polarizers. It was found that the melting point of α - and β -phases was *ca.* 162°C and *ca.* 140°C , respectively. Without crossed polarizers, more clear morphology could be observed that most of nucleating agents were insoluble in the form of needles and dispersed particles (Fig. 6a). Upon cooling to a temperature, the number of birefringent structures

increased under optical microscope with crossed polarizers (Fig. 6b), indicating the initial of crystallization. The TMB-5 needles induced nucleation quickly (Figs. 6b–6d). The nucleating density was so high that individual crystal shape could not be recognized. According to Fig. 4(b), these tiny crystals belong to β crystals.

When the sample was heated to 250°C, TMB-5 almost completely dissolved in the molten *i*PP. The particles of the dispersed nucleating agent could hardly be detected by POM in the molten film (Fig. 7a). Upon cooling, the nucleating agent crystallized in the form of very fine needle crystals (shown by arrow in Fig. 7b). These needles linked and formed dendritic structure. As the crystallization proceeded, β crystals grew on the lateral surface of the needles. Compared with Fig. 6, the crystals grew slower under this condition.

Figure 8 shows how crystal morphology changes from transcrystalline to dendritic with increasing the final heating temperature. When nucleating agent partially dissolved in the molten polymer, the remaining TMB-5 (nondissolved) served as “nucleators” for the dissolved nucleating agent and thus accelerated the recrystallization of TMB-5 from the matrix. Once TMB-5 recrystallized from the matrix, they induced β nucleation quickly. The nuclei were so dense that they contacted with each other very soon and small transcrystalline structures were obtained.

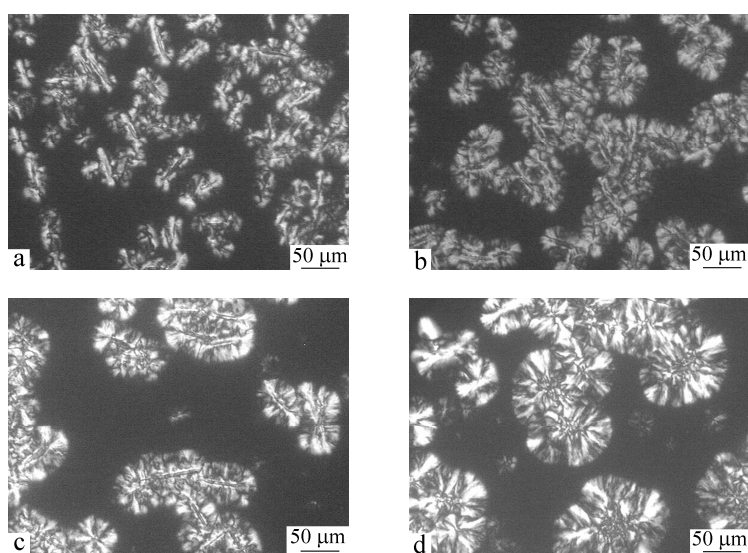


Fig. 8 Crystalline evolutions with T_f : (a) 200°C, (b) 220°C, (c) 240°C and (d) 250°C

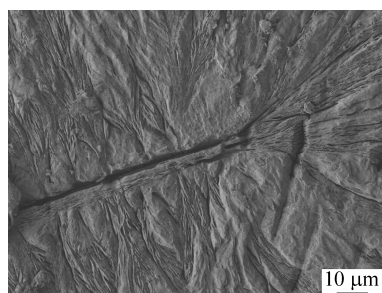


Fig. 9 SEM micrographs taken from the etched surface of the *i*PP/TMB-5 film cooled at 5 K/min ($T_f = 230^\circ\text{C}$)

SEM micrograph taken from the etched surface of needle induced transcrystalline structure indicates that mixed polymorphic structure forms on the lateral surface of the needle crystal, while a structure richer in the β -*i*PP appears around the tip of the needle (Fig. 9). The morphology was very similar to the α/β transcrystalline growth model provided by Varga^[9]. These structures can be unambiguously identified by the analysis of the

structure left behind by the separate melting of the β -phase (Fig. 10b). In Fig. 10(b) locations A, B, C and D mark the remaining α -*i*PP on the lateral surface of the needle crystal after β -*i*PP has already melt around 147°C.

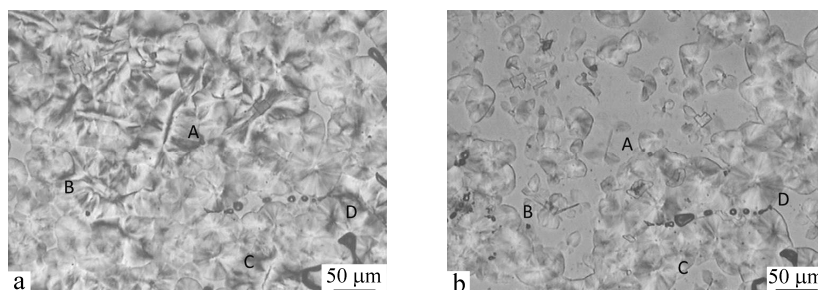


Fig. 10 PLM micrographs demonstrating the crystallization of *i*PP on the surface of TMB-5 needle crystals: (a) structure formed at 111.7°C when cooled from 230°C, (b) structure left behind after the separate melting of the β -phase at 147°C

The compatibility of TMB-5 and *i*PP was improved at higher T_f value. They recrystallized from the melt in the form of dispersed fine needles. These needles aggregated into dendritic structure and the dendritic surface provided the nucleating sites for *i*PP. Both the crystallization rate of TMB-5 and *i*PP were slower than those of partially dissolved samples. The crystals growing on the lateral surface of TMB-5 can develop fully. Thus the length to diameter ratio of transcrystalline reduced until dendritic structure forms.

Generally speaking, complete solubility of the nucleating agent in molten polymer matrix at the employed processing temperature is very important for homogeneous distribution of the additive and efficient nucleation. In our experiments, the dendritic structure is not achieved until the nucleating agent is completely dissolved in the molten *i*PP. As long as the nucleating agent partially dissolved in molten matrix, the recrystallized nucleating agents tended to assemble around the needle tip of the nondissolved nucleating agent due to the interaction between nucleating agent themselves, and thus larger nucleating agent needles formed.

It should be interestingly noted that from the DSC curves, the sample that was initially melted at 180°C has fully crystallized by 120°C, yet the appropriate micrograph (Fig. 6b) showed negligible crystallinity. The same inconsistency can be identified by comparing Figs. 2(b) and 7. The contradiction between DSC results and POM observations can be explained that the atmosphere in these two measurements were not totally equal. The former was in a vacuum. The latter was a hot air space sealed from the outside by high-temperature resisted glass cover. The sample might inevitably oxidative degrade a little and the flow in the lab might disturb the temperature of the sealed hot stage.

Thermal Stability of the Heterogeneous Nucleation Effect of *i*PP Nucleated with TMB-5

In order to investigate further the influence of complete solution of nucleating agent, we carried out DSC multi-scanning. In this experiment, T_f was changed in a systematic way. First we heated the sample to a lower temperature ($T_f = 180^\circ\text{C}$), and then repeated the process twice with different T_f values 250°C and 180°C respectively.

A product rich in β -form *i*PP with high crystallization temperature (126.78°C) forms at low $T_f = 180^\circ\text{C}$ (Fig. 11). When the sample was heated subsequently to $T_f = 250^\circ\text{C}$, the α -modification endotherm proportion increased and in the meanwhile β -form endotherm split into double peaks (Fig. 11b, curve 2). The experimental results, which are in accordance with POM observations, indicate that nucleating agent dissolves completely in the melt, leading to a big decrease in T_c (Fig. 11a, curve 2). When the sample was heated to 180°C again, the high nucleating efficiency appeared at $T_f = 180^\circ\text{C}$ could not be reproduced, although the crystallization temperature was several degrees higher than that at $T_f = 250^\circ\text{C}$. Figure 11(b) curve 3 indicates the β -form proportion as well as crystal stability both increased compared with those of crystals formed when $T_f = 250^\circ\text{C}$.

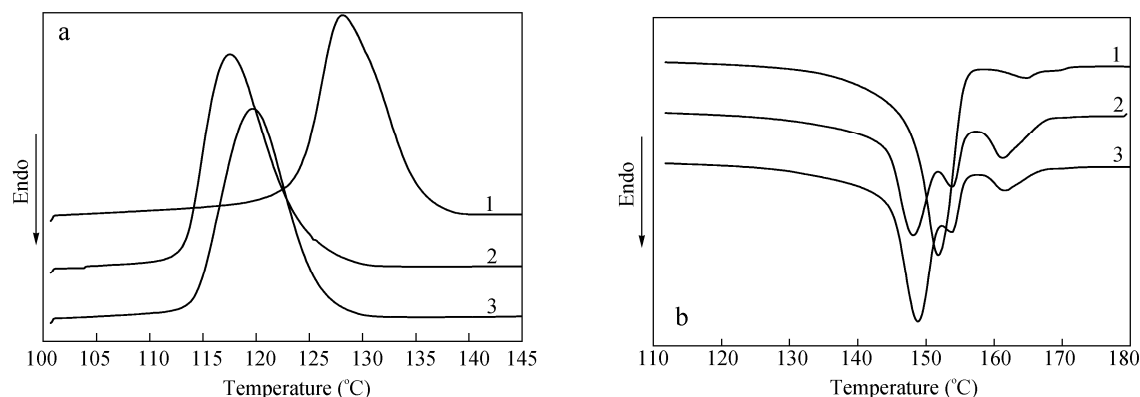


Fig. 11 Crystallization (a) and melting (b) traces recorded on samples with different thermal history

T_f , curve 1 = 180°C; T_f , curve 2 = 250°C; T_f , curve 3 = 180°C

The DSC multi-scanning experiments show that the value of T_f governs the polymorphic composition of the sample and the crystallization process. It is reasonable because T_f , as well as melting point of nucleating agent, contributes to the dispersion state of nucleator in the molten matrix. It is generally considered that the β -nucleating agents work only if their crystallites are present in the *i*PP melt. However, according to Garbarczyk *et al.*^[3], phenanthrene with a melting point 77°C lower than the melting point of *i*PP leads to the significant formation of β -form (β -form content is 30%). So the melting point of the additive, above the melting point of *i*PP, is not a determinant factor for the β -form to appear during crystallization from the melt. The trigonal form occurs only when the structure of additives is quasiplanar, which suggests the formation of complexes of an additive and a polymer. In our work, once the nucleating agent dissolves in *i*PP melt, the changed morphology of recrystallized nucleating agent may influence lattice matching (or complex relation) between polymer and nucleating agent, thus changing the β nucleating mechanism. The recrystallized nucleating agent is not effective as the primary ones though it is still efficient as β -form nucleating agent of *i*PP. When TMB-5 totally dissolves in melt *i*PP, a distinct dendritic superstructure forms, which is quite different from the transcrystalline structure formed in partially dissolved systems.

CONCLUSIONS

POM and DSC studies showed the partial and complete dissolution and β nucleating effect of TMB-5. The amount of not dissolved nucleating agent and heterogeneous nucleation behaviors were heavily influenced by the final temperature of heating. The nucleating efficiency of nucleating agent was increased with lowering the T_f value. In partially dissolved samples, the primary and recrystallized TMB-5 induced fast transcrystalline growth on the surface of nucleating agent at higher temperatures. Complete dissolution promoted the compatibility between TMB-5 and *i*PP. The recrystallized nucleating agents presented tiny needles and aggregated into dendritic structure. This structure developed slowly and induced crystallization at lower temperatures.

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