

THE VARIABLE ROLE OF CLAY ON THE CRYSTALLIZATION BEHAVIOR OF DMDBS-NUCLEATED POLYPROPYLENE*

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Abstract The effect of clay on the nucleating behavior of 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) in crystallization of isotactic polypropylene (*i*PP) was investigated by means of differential scanning calorimetry (DSC), dynamic rheology and polarized light microscopy (PLM). It is interesting to note that the incorporation of layered clay nanoparticles into DMDBS-nucleated *i*PP may induce a synergetic nucleation effect while the DMDBS content is below 0.1 wt%, otherwise it restricts the crystallization rate prominently as the DMDBS content increases up to 0.3 wt%, which has exceeded the content threshold to yield a nucleating agent (NA) network. As shown by dynamic rheological investigations, the clay nanoparticles demonstrate an obstructive effect of disturbing the consistency of DMDBS fibrils network. Moreover, to further demonstrate the importance of NA network formation in the crystallization of *i*PP, we used another NA named HPN-20e, which can not form network structure at all over the concentration studied, for comparison. In this case, the nucleated-crystallization rate is independent on the addition of clay nanoparticles, as the nucleating mechanism is an individual nuclei manner without NA network forming.

Keywords: DMDBS; Nucleating agent network; Clay nanoparticles; Nucleated-crystallization.

INTRODUCTION

Nucleating agent (NA) has been widely used for isotactic polypropylene (*i*PP) during processing to reduce the cycle time and improve the optical properties^[1, 2]. During heterogeneous nucleation, polymer nucleates at the sites on the surface of NA particles. Such a large specific surface area of NAs offers them excellent nucleation ability. 1,3:2,4-Bis(3,4-dimethylbenzylidene) sorbitol (DMDBS), considered as one kind of the most efficient NAs for nucleating polyolefin^[2, 3], has received considerable amount of interesting^[4–8]. Some previous studies have shown that the fibrillar morphology of DMDBS substance^[9] offers a large specific area for producing a dense nucleus density, and DMDBS fibrils nucleate polyolefin crystallization followed an epitaxial mechanism. However, specific area alone cannot explain the nucleation ability of DMDBS. Thierry *et al.*^[10] demonstrated that DMDBS was a good nucleating agent for *i*PP because of a good lattice matching between its crystals and the 3₁ helix of the polymer. These results have been confirmed by electron microscopy^[10] and AFM^[11] studies. Kristiansen *et al.*^[12] constructed experimentally a phase diagram for the binary polypropylene (PP)/DMDBS system. They demonstrated that the crystallization mode was dominated by DMDBS concentration. Furthermore, as approved experimentally by Shepard *et al.*^[2] and Thierry *et al.*^[10], the DMDBS fibrils will self-

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organize into a three-dimensional (3D) network, resulting in an obvious decrease in crystallization temperature when the DMDBS concentration reaches certain critical value. However, the critical value of DMDBS content required for the formation of NA network is very low (around 0.1 wt%) as suggested by Shepard *et al.*^[2]. The 3D network of DMDBS fibrils provides a good consistency for melt systems and may facilitate the subsequent nucleation and crystallization growth extremely significant.

The mechanism of *i*PP crystallization with the presence of DMDBS is very complicated, and still remains unclear. Kristiansen *et al.*^[12] investigated the phase diagrams of *i*PP and DMDBS mixtures during cooling and heating. They observed that, DMDBS crystallized/phase separated at T_c^{DMDBS} during cooling, and DMDBS melts restored to homogeneous mixture during heating, at a temperature T_m^{DMDBS} which was sensibly higher than T_c^{DMDBS} . Both T_c^{DMDBS} and T_m^{DMDBS} are dependent on the composition of these two components. The rheological studies presented by Kristiansen *et al.* suggest that, the network of DMDBS fibrils is retained for $T_c^{\text{DMDBS}} < T < T_m^{\text{DMDBS}}$ during heating. However, this network can be destroyed by shearing which aligns the fibrils^[13, 14]. Except for temperature and DMDBS content, the effect of exogenic action (such as the presence of layered filler) on the formation of the physical network of DMDBS fibrils have not been explored. On the other hand, although the nucleated crystallization behaviors of *i*PP with DMDBS alone have been widely studied with many techniques, including calorimetry, optical microscopy and X-ray scattering, *etc.*, the composite (bicomponent) nucleating agent based on DMDBS has been rarely investigated in literature^[15]. In our present study, a kind of layered clay nanoparticle, montmorillonite (MMT), is incorporated into the DMDBS-nucleated *i*PP. The nanoparticles of MMT can serve as a heterogeneous NA for semi-crystalline polymers^[16, 17], as well as a reinforcement element to offer good mechanical strength, rigidity, thermal stability and low permeability^[18, 19]. Therefore, the development of complex nucleating system containing inorganic nanoparticle and organic compound NA, *i.e.* MMT/DMDBS, has a huge potential in industrial applications to provide products based on *i*PP with good comprehensive performance and process-ability. At the current research stage, the research is focused on the crystallization behavior of MMT/DMDBS/*i*PP system. The effect of additional MMT on the self-organized supermolecular structure of DMDBS component and its subsequent impact on the nucleated crystallization of *i*PP will be elucidated clearly. Moreover, DMDBS is substituted with another NA (HPN-20e) to nucleate *i*PP crystallization originally from an individual spot-like nuclei manner for comparison purpose.

EXPERIMENTAL

Materials

A commercially available isotactic polypropylene (trade marked as T30S, Yan Shan Petroleum China) with $M_w = 29.2 \times 10^3$ and a density of 0.91 g/m^3 , was used as the basal polymer. DMDBS (Millad 3988) and HPN-20e were obtained in powder form from Milliken Chemicals (Gent, Belgium) and used as received. Sodium montmorillonite with a cation exchange capacity (CEC) of 68.8 mmol/100g (RenShou, Sichuan, China) was organically modified through ion-exchange reaction with dioctadecyl dimethylammonium bromide, and the detailed procedure could be found in the previous publication^[20]. The d-spacing of intergallery has been prominently improved from 1.4 nm for raw MMT to 3.2 nm after ion-exchanging, indicating a good availability of such MMT for organic modification. Thereafter, the organically modified MMT was abbreviated as OMMT.

Preparation of the Composites

First a batch of pellets with the blends of PP/DMDBS and PP/HPN-20e (95/5 wt%) and another batch of pellets with the composite of PP/OMMT (90/10 wt%) were melt-blended in a TSSJ-2S co-rotating twin-screw extruder. The temperatures of the extruder were maintained at 165°C, 190°C, 195°C, 200°C, 200°C and 195°C from hopper to die, and the screw speed used was 110 r/min. Then a series of nanocomposites were obtained through adding *i*PP to dilute the as-prepared master-batch in the extruder. The resulted nanocomposites are hereafter abbreviated as PPDM(HP)xOMy (wt%, $x = 0, 0.01, 0.1, 0.3$; $y = 0, 1, 3$). After being pelletized and dried, the extruded specimens were compression molded upon 200°C and 15 MPa for 3 min, and then the compressed specimens were used to perform various crystalline characterizations.

Measurements and Characterization

X-ray diffraction (XRD)

The XRD experiments were carried out with a Rigaku (Japan) D/max 2400 diffractometer. The X-ray beam was derived from nickel-filtered Cu K α ($\lambda = 0.154$ nm) radiation in a sealed tube operated at 40 kV and 200 mA. The test samples were prepared by compression molding, and the experiments were performed in the 2θ range of 2° – 10° at a scanning rate of 0.02 ($^\circ$)/s.

Rheological measurements

All rheological measurements were performed on a Gemini 200 dynamic rheometer (Malvern Instruments Ltd., UK). Disk samples with the thickness of 1.2 mm and diameter of 25 mm were prepared by compression molding of the extruded pellets at 200°C for 3 min. Testing samples were first heated to 230°C for 5 min to eliminate the pristine crystalline structures and then cooled to the desired temperature at a rate of -2 K/min. All dynamic rheological experiments were performed upon a single angular frequency of 0.3 rad/s and constant strain of 1%.

Differential scanning calorimetry (DSC)

The calorimetric analysis of the as-prepared samples was conducted using a Perkin-Elmer pyris-I DSC calibrated by indium. The slices, about 5 mg, were cut from the compression molded samples. The slices were heated to a preset temperature (230°C) at a rate of 100 K/min and held at such temperature for 5 min to eliminate the initial thermal history. Then, they were cooled down to 50°C under a constant rate of -10 K/min for nonisothermal crystallization measurements.

Polarized Light Microscopy

The morphological observations of *i*PP crystallites were conducted on a Leica DMIP polarizing light microscope (PLM) equipped with a Linkam THMS 600 hot stage under crossed polarizers. The thin slices were cut from the compression-molded specimens, inserted between two microscopic cover glasses, melted at 200°C and squeezed to obtain thin films. The slices were held at 230°C for 5 min to achieve thermal equilibrium. Subsequently, the molten slices were rapidly cooled to a desired crystallization temperature (134°C) and then the *in situ* morphological observation of crystallization was implemented under isothermal condition.

RESULTS

Dispersion of Clay Nanoparticles in *i*PP Matrix

The X-ray diffraction patterns of OMMT, PPDM0.01OM3, PPDM0.1OM3, and PPDM0.3OM3 are shown in Fig. 1 and the interlayer distances of the four samples are listed in Table 1. The average interlayer distance of

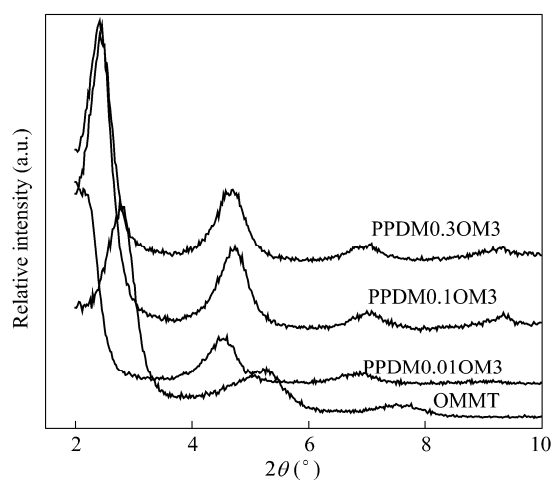


Fig. 1 Intensity versus 2θ patterns for the specimens of OMMT and PP/DMDBS/OMMT composites with the fixed content of 3 wt% OMMT

neat OMMT is about 3.2 nm, which is deduced from the (010) diffraction peak located at $2\theta = 2.8^\circ$. In the samples of PPDMxOMy, the interlayer distance is enlarged substantially to about 4 nm. This means that the polymer chains did intercalate into the organoclay intergalleries after blending. However, the interlayer distance of PPDM0.01OM3 is larger than that of the other two samples. It is because that the supermolecular network of DMDBS nanofibrils can prevent more PP chains to enter the interlayer of OMMT. The obvious increment in the interlayer distance demonstrates good dispersion state of OMMT attained *via* melt compounding strategy.

Table 1. Interlayer spacing of hybrid materials derived from XRD

Sample	Interlayer spacing (nm)
PPDM0.01OM3	4.0
PPDM0.1OM3	3.8
PPDM0.3OM3	3.8
OMMT	3.2

Nonisothermal Crystallization Evaluated by DSC

The crystallization behaviors of *i*PP nucleated by different amounts of OMMT are first estimated by a traditional calorimetric approach, DSC. A simple estimation of the effect of OMMT content on the nucleation efficiency is obtained through nonisothermal cooling crystallization approach, as shown in Fig. 2. The improvement in crystallization temperature (T_c) indicates that OMMT nanoparticles can indeed promote the crystallization rate of *i*PP. The T_c is increased from 113°C to 117°C while the OMMT content is below 1 wt%. It is almost kept constant within a relatively high content range (3 wt% to 5 wt%), except for a slight increase of 2 K achieved at the highest OMMT content (5 wt%).

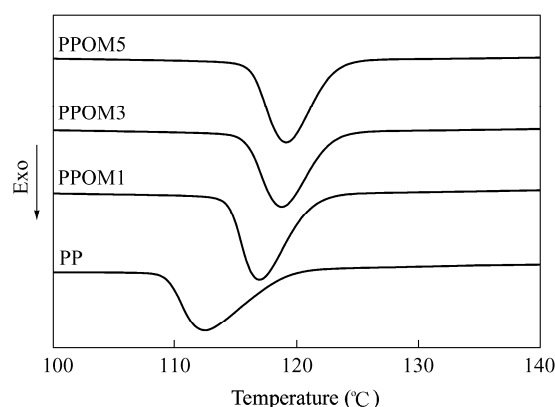


Fig. 2 Nonisothermal crystallization DSC thermograms of *i*PP with different contents of OMMT

The non-isothermal crystallization behaviors of PPDMxOMy samples are shown in Fig. 3. One can note from Fig. 3(a) that, T_c is increased from 113°C to 115°C with additional 0.01 wt% DMDBS. It is interesting to observe that the T_c of PPDMxOMy is increased up to 119°C, which is substantially higher than that of PP/OMMT and PP/DMDBS. This indicates the presence of a synergistic nucleating effect between DMDBS and OMMT on the crystallization of *i*PP. Such a synergistic effect provides the complex NA system with higher nucleating efficiency than single NA system. As shown in Fig. 3(b), T_c is enhanced to 118°C for PP/DMDBS blend with additional 0.1 wt% DMDBS, and it is kept almost constant when the OMMT is added to form PPDMxOMy samples. As shown in Fig. 3(c), T_c is increased prominently to 130°C for the PP/DMDBS blend containing 0.3 wt% DMDBS. However, T_c of PPDMxOMy is abnormally decreased to 119°C as the OMMT nanoparticles are added. This indicates that the nucleating effect of DMDBS for *i*PP crystallization is restricted by OMMT nanoparticles. Summarizing from the above mentioned, the role of OMMT nanoparticles on the crystallization behavior of DMDBS-nucleated *i*PP is variable with increasing DMDBS content: the higher the DMDBS content, the lower the heterogeneous nucleating efficiency. For comparison purposes, Fig. 4 shows the

nonisothermal crystallization curves of PPHP x OM y samples (with HPN-20e). It can be noted that the T_c does not change obviously with increasing OMMT content. This approves that OMMT almost has no effect on the nucleation of HPN-20e.

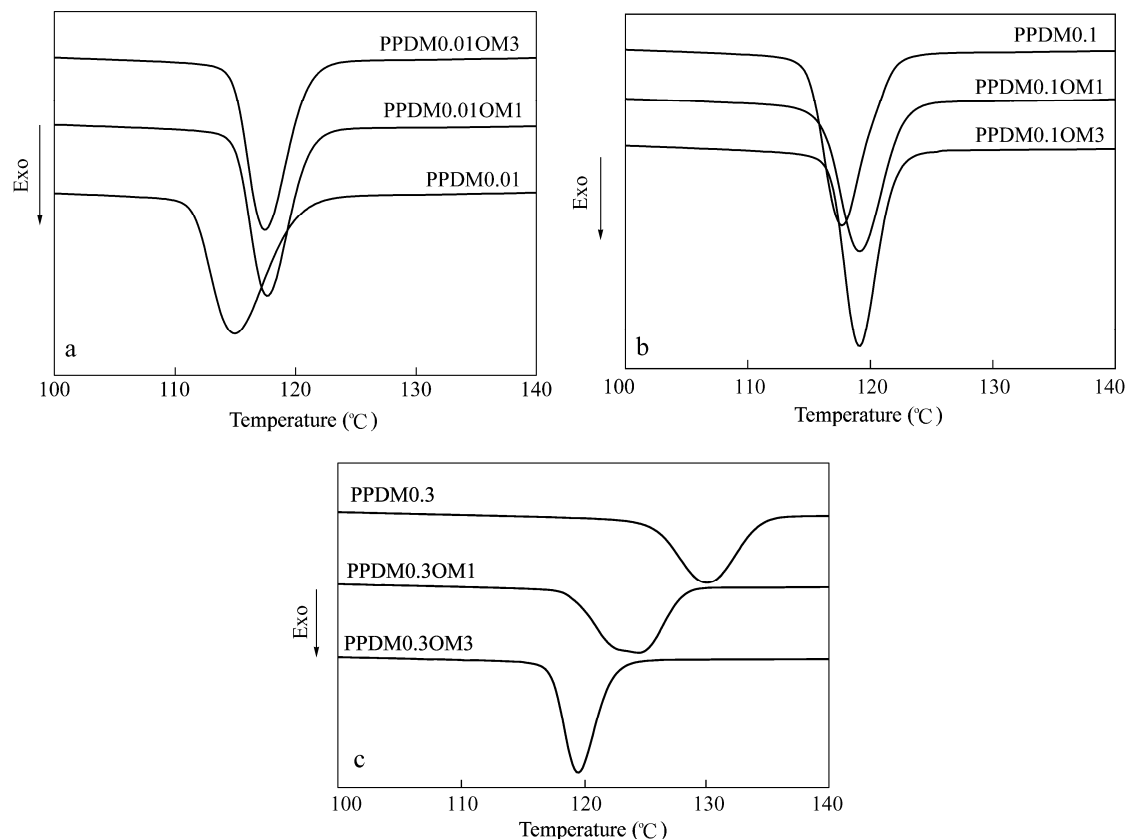


Fig. 3 Nonisothermal crystallization DSC thermograms of PP/DMDBS/OMMT composites with fixed DMDBS content of (a) 0.01 wt%, (b) 0.1 wt% and (c) 0.3 wt%

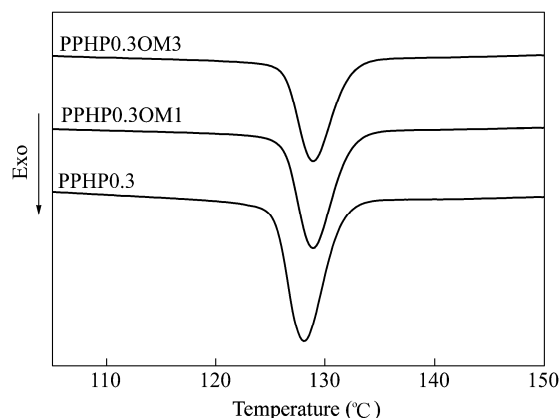


Fig. 4 Nonisothermal crystallization DSC thermograms of PP/HPN-20e/OMMT composites with the fixed content of 0.3 wt% HPN-20e

Nonisothermal Crystallization Followed by Rheometry

Subsequently, the nonisothermal crystallization behavior will be characterized through the measurement of rheological viscoelasticity. The evolutions of G' with decreasing temperature obtained *via* single frequency

sweep for the specimens containing 0.3 wt% DMDBS or HPN-20e are plotted in Fig. 5. For the specimens of PPDM0.3OM3, PPHP0.3 and PPHP0.3OM3, the G' increases gradually and monotonically with decreasing temperature until a critical temperature, where a sudden jump is observed. This sudden increase in G' indicates the onset of *i*PP nucleation/crystallization, thus this temperature is designated as the beginning crystallization temperature ($T_{c, beg}$). The G' versus temperature curve for PPDM0.3 with an additional increment in G' appearing before the onset of *i*PP nucleation/crystallization, is obviously different from that for others. A similar phenomenon has been often observed in DMDBS-nucleated polymer systems^[10, 21, 22]. It is reported to be caused by the formation of a physical network consisting of DMDBS nanofibrils. Obviously, this physical network can be regarded as a supermolecular structure originated from the self-organization of DMDBS substance prior to the occurrence of nucleated crystallization of *i*PP. Moreover, it can be concluded that the formation of NA network is restricted in the following two cases: (1) OMMT nanoparticle is added into the system, (2) the nucleating mechanism is changed to individual spot-like nucleus manner.

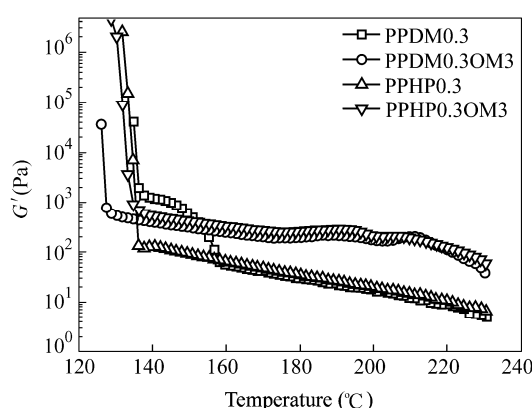


Fig. 5 Evolutions of elastic modulus as a function of cooling temperature for *i*PP's composites

Crystal Morphology Observed with PLM

As shown in Fig. 6, the isothermal crystallization morphologies of samples were characterized with PLM. For *i*PP with 0.01 wt% DMDBS, perfect and large spherulites are observed and the average diameter is around 300 μm . The presence of OMMT (1 wt% and 3 wt%) in PPDMxOMy samples increases the nucleation density and decreases the diameter of *i*PP spherulites. For *i*PP with 0.3 wt% DMDBS, one can observe that much smaller *i*PP spherulites with average diameter from 1 μm to 5 μm are obtained. They are difficult to be identified (see Fig. 6d) due to the excellent nucleation efficiency of DMDBS. As shown in Fig. 6(e) and Fig. 6(f), the spherulite diameter is increased significantly with the addition of OMMT in PPDM0.3, and the average spherulite diameter is around 50 μm . For *i*PP with 0.3 wt% HPN-20e, the spherulite morphology is similar with that of PPDM0.3, and it does not change with the addition of OMMT as shown in Figs. 6(g) to 6(i).

DISCUSSION

As demonstrated in the former section of calorimetric measurements, a positive influence of OMMT on facilitating *i*PP nucleation and crystallization has been unambiguously approved at the relatively low DMDBS content of around 0.01 wt% (as shown in Fig. 3a). This indicates the presence of synergistic effect between DMDBS and OMMT on the *i*PP crystallization. It is due to the unsaturated DMDBS concentration and the well dispersed OMMT (which has been confirmed with XRD) can act as heterogeneous nucleation agent. Therefore, T_c of *i*PP is further increased and the average spherulite diameter is decreased with additional OMMT in *i*PP/DMDBS. It is also noted that the T_c of PPDM0.01OMy does not change with the increasing content of OMMT, indicating that the complex NA system with 0.01 wt% DMDBS and 1 wt% OMMT has reached the saturation nucleating concentration for *i*PP crystallization^[23, 24].

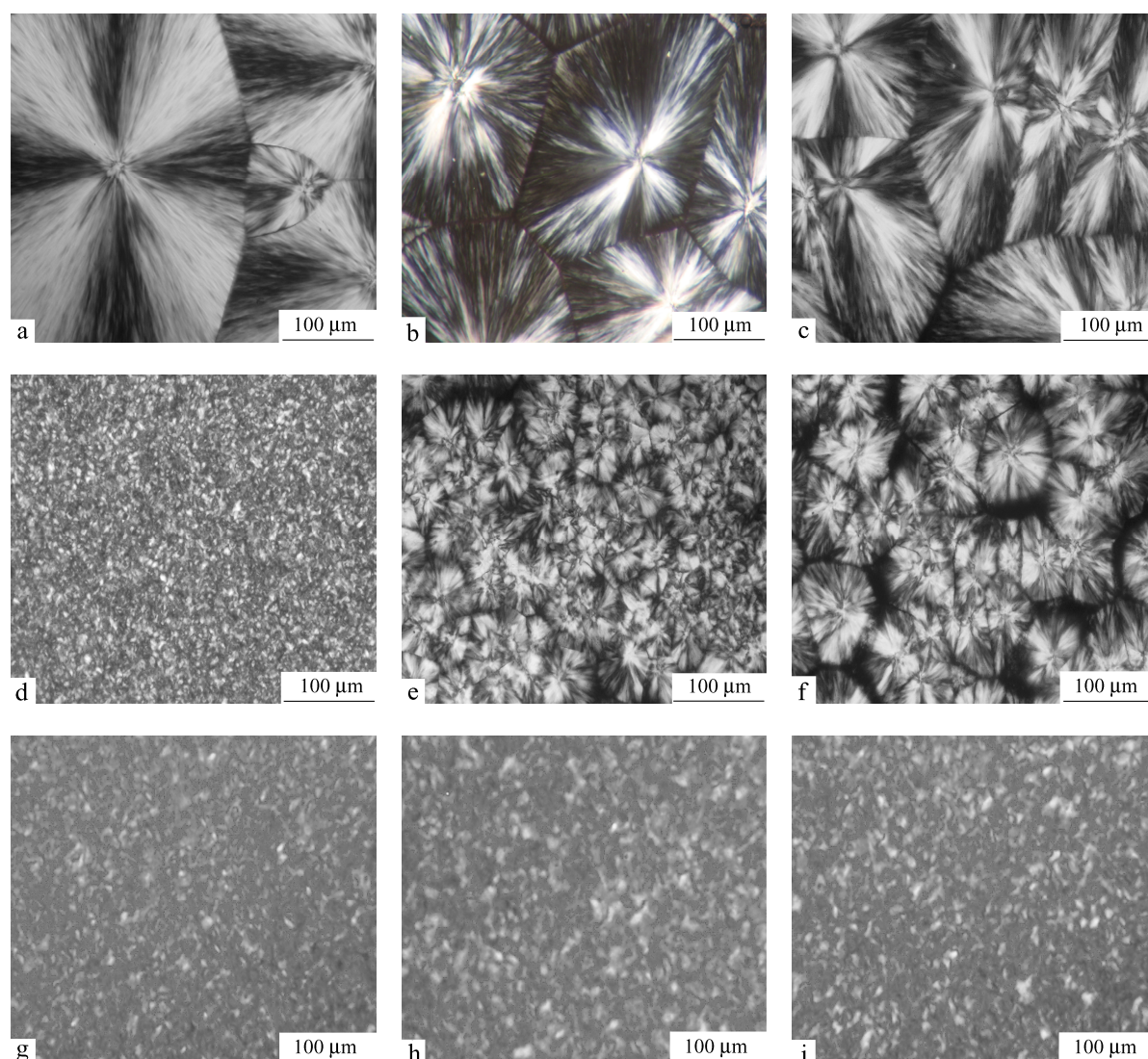


Fig. 6 Optical micrographs of spherulite morphology obtained at 134°C: (a) PPDM0.01, (b) PPDM0.01OM1, (c) PPDM0.01OM3, (d) PPDM0.3, (e) PPDM0.3OM1, (f) PPDM0.3OM3, (g) PPHP0.3, (h) PPHP0.3OM1 and (i) PPHP0.3OM3

It has been reported by Shepard *et al.*^[2] that the critical value of DMDBS content required for the formation of DMDBS fibrils network is very low (around 0.1 wt%). OMMT nanoparticles are added into the system at the critical point, and the T_c s are almost identical between PP/DMDBS and PP/DMDBS/OMMT. It indicates that the content of 0.1 wt% is indeed the critical point for the formation of DMDBS fibrils network as well as the saturation nucleation point for nucleating crystallization of *i*PP. Therefore, the OMMT nanoparticles have no apparent effect on the crystallization of *i*PP.

While the DMDBS concentration exceeds the critical value and reaches 0.3%, it is observed in rheological measurements (see Fig. 5) that the DMDBS fibrils self-organize into a physical network prior to the occurrence of nucleated-crystallization of *i*PP. The DMDBS fibrils network offers good consistency throughout melt system and large specific area for producing high nuclei density, therefore the T_c is promoted dramatically from 113°C to 130°C, as shown in Fig. 3(c). It is interesting to note that T_c is abnormally decreased with the addition of OMMT, and the average spherulite diameter increases dramatically as shown by PLM. By considering the

layered structure of OMMT, such a phenomenon is attributed to the obstruction effect of OMMT on the DMDBS fibrils network: the connection between NA fibrils is destroyed by the presence of layered OMMT nanoparticles. For comparison, the calorimetric measurement results of HPN-20e (0.3 wt%) systems are shown in Fig. 4. It is further confirmed by Fig. 5 that HPN-20e substance can not self-organize into a physical network; consequently, OMMT has no apparent effect on the nucleated crystallization behavior.

Moreover, it is observed that the crystallization temperature (T_c) of nucleated *i*PP is about 119°C at the saturation of nucleation. For example, T_c is increased from 113°C for the pure *i*PP to 119°C for the PP/OMMT (3 wt%) composite. And this remains unchanged with further increasing OMMT content up to 5 wt%. It indicates that the saturated OMMT content for nucleation is 3 wt% and the corresponding T_c is 119°C. Interestingly, the concentration of nucleation sites in complex NA system is also saturated at a T_c of 119°C (for PPDM0.3OM3, see Fig. 3c), where the DMDBS fibrils network is destroyed by the additional 3 wt% OMMT (see Fig. 5).

CONCLUSIONS

The role of OMMT nanoparticles in the crystallization behavior of DMDBS-nucleated *i*PP has been demonstrated in detail with increasing DMDBS content. A synergic nucleating effect between DMDBS and OMMT is identified at an extremely low DMDBS content of 0.01 wt%, as T_c of the sample containing complex NA system is higher than that of the sample nucleated with single NA. Whereas, the incorporation of OMMT plays a negative role on facilitating the nucleated crystallization of *i*PP as the DMDBS content reaches 0.1 wt%. An obvious reduction in T_c is observed at a DMDBS content of 0.3 wt% comparing to the sample nucleated merely by DMDBS. This negative effect of OMMT on the crystallization behavior of DMDBS-nucleated *i*PP is due to the restriction of physical network of DMDBS nanofibrils by OMMT nanoparticles, and thus the consistency between NA fibrillar entities is reduced. However, the nucleated crystallization behavior is independent on the addition of inorganic nanoparticles if the nucleating mechanism of NA is changed from a self-organized supermolecular network to an individual spot-like nucleus manner.

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