



Analysis of crystalline structure and morphology of isotactic polypropylene under the coexistence of organic montmorillonite particles and shear flow

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ABSTRACT

In this work, the different effects of organic montmorillonite (OMMT) particles and shear flow on the crystallization behavior of isotactic polypropylene (iPP) were discussed. While neat iPP and OMMT filled iPP were treated using the multistage stretching extrusion technology, changing the number of laminating-multiplying elements (LMEs) can obtain samples with different dispersion degree of OMMT particles and different orientation degree of molecular chains. With the increase of LME number, the content of β -crystal in neat iPP increased. But for OMMT/iPP composites, decreasing LME number caused the increase of content of β -crystal. The experimental results showed that the shear flow and large OMMT aggregations were essential factors for the formation of β -crystal in composites, and the crystalline morphology strongly depended on the size of OMMT particles. The scanning electron microscope (SEM) images of sample with 3 wt% of OMMT particles and without LME illustrated that β -trans-crystallinity, fan-shaped β -crystal and α -spherulite were induced by different size of OMMT particles, respectively. A schematic was proposed to describe the formation mechanism of α -crystal and β -crystal under the coexistence of OMMT particles and shear flow.

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1. Introduction

A considerable amount of attentions have been devoted to polymer/layered silicate (PLS) nanocomposites in both academic and industrial research over past few decades [1–6]. PLS nanocomposites exhibited superior thermo-oxidative stability and flame retardancy, along with increased barrier and mechanical properties when compared to their neat counterparts [7–12].

Additionally, the incorporation of nanoscale layered-silicates into various semi-crystalline polymers, such as polypropylene (PP), syndiotactic polystyrene (sPS), polyamide (PA), or polylactide (PLA), can remarkably influence the crystalline behavior of the polymers including crystallization kinetics, crystalline structure, and crystallinity, all of which significantly determined the final performance of a PLS nanocomposite. It has been well demonstrated that these silicate nanoplatelets were prone to attract polymer chains and act as a template for the growth of polymer

crystals [10]. The contact between the polymer lamella and the substrate surface can lead to develop new crystalline morphology by appropriate lattice matching [10,13]. Meanwhile, some researchers have reported that the dispersion degree of the nanoclay in the matrix also played a vital role in the final crystal morphology. For instance, Ghosh et al. [14] suggested that when nanoscale organo-clay were well dispersed in syndiotactic polystyrene (sPS), it could promote the rapid formation of α -crystals while β -crystals were more likely to form on clay aggregations. Moreover, the crystalline morphology of PA-6 has also been reported to be closely related to the dispersion degree of the nanoclay [15]. Consequently, it was rational to hypothesize that both the addition of nanoclays and ameliorating the dispersion of nanoclays in polymer matrix can effectively influence the molecular arrangement of polymer in its crystallite structures.

Apparently, it was a great practical challenge to prepare excellent dispersion of PLS nanocomposites due to the strong attraction interaction between the nanoplatelets, especially through melt blending, which were considered as the most commercially attractive approach [16]. To overcome this restriction, strong shear

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force was inevitably provided to attain better dispersion of PLS nanocomposites in melt extrusion, especially based on the polyolefin matrix. It has been well documented that the shear force not only can reduce the initial aspect ratio of clay particles by breaking the particles but also result in the orientation of particles, which were both responsible for the good dispersion of nanoclays [17,18]. In addition, the orientation of polymer molecular chain induced by shear flow during processing can deeply enhance the crystallization kinetics and influence final crystal morphology like distinctive “shish-kebab” crystal [19–24]. The effect can be attributed to the formation of oriented molecular chains, which can make shish nucleation sites and then form kebab crystal structure along the shish nucleation sites. Therefore, it can be concluded that the shear force could not only greatly improve the dispersion of nanoplatelets but also promote the generation of new crystal morphology in PLS nanocomposites.

As stated above, both the layered-silicates and shear force can greatly affect the crystallization behavior of semi-crystalline polymers. Nevertheless, the collaboration or competition of these two factors on semi-crystalline polymers was still rarely studied and not fully understood in the present articles [21,25–28]. This issue was especially important for polyolefin/montmorillonite composites, because they were frequently prepared through the melt blending under a shear field [29,30]. As one of semi-crystalline polymers, polyolefin were able to exhibit various crystal structure and morphology under different conditions, which had a great influence on the final performance of products [27,31–33]. Consequently, it is of great academic and reality significance to investigate the combined influence of the dispersed degree of MMT particles and the shear flow on the crystallization behavior of PLS nanocomposites.

Zhongming Li et al. have investigated combined effects of graphene nanosheets (GNSs) and shear flow on the crystallization behavior of isotactic polypropylene (iPP) under a relatively weak shear flow (at a rate of 20 s^{-1}) and a low degree of supercooling (at $145 \text{ }^\circ\text{C}$) [21]. They found that GNSs induced a network structure hindering the mobility of iPP chains and allowing the survival of oriented row nuclei for a long period of time. Therefore, iPP exhibited an isotropic structure with β -crystals. But in their work, the content of β -crystals was very low, and the size of GNSs, the strength of shear force and the morphology of β -crystals weren't considered.

In our previous study, we reported that the strong force provided by multistage stretching extrusion can destruct the Van der Waals interaction between the laminate OMMT particles, resulting in the exfoliation and orientation of OMMT particles in isotactic polypropylene (iPP) matrix free of compatilizer [34]. With increasing number of laminating-multiplying elements (LMEs), the dispersion degree of OMMT particles became better due to the stronger shear force.

This study aimed at elucidating the interrelation between the dispersed degree of OMMT particles and shear flow on the crystallization behavior of iPP. Here, different dispersed degree of OMMT/iPP composites and various shear force was obtained by multistage stretching extrusion, which enabled us to extensively and systematically investigate the combined effects of the dispersion of OMMT particles and shear flow on the crystallization behavior of iPP.

2. Experimental section

2.1. Materials

A commercially available isotactic polypropylene (T30S, Lanzhou Petroleum China) with a density of 0.899 g/cm^3 and a melt

index of 3.8 g/10 min ($230 \text{ }^\circ\text{C}$, 21.6N) was used as the basal polymer. The montmorillonite (Fenghong, Zhejiang, China) was organically modified through ion-exchanged reaction with hexadecyl trimethyl ammonium bromide. To avoid hydrolysis, OMMT was dried in a vacuum oven at $110 \text{ }^\circ\text{C}$ for at least 12 h prior to processing.

2.2. Specimen preparation

A master-batch consisted of OMMT/iPP (97/3 wt.%) was melt-mixed in a co-rotating twin-screw extruder (TSSJ-23, $d = 25 \text{ mm}$, $L/d = 33$) and the mixing temperatures were 145 , 190 , 200 and $195 \text{ }^\circ\text{C}$ from the hopper to the die. The pelletized granules were subsequently molded from the multistage stretching extruder that contained a single-screw extruder, a connector and some LMEs, and finally formed a 1.0 mm thick and 65 mm wide sheet after cooling. The multistage stretching extrusion with an assembly of LMEs is illustrated in Fig. 1. The processing parameters, the characteristics and detailed experimental procedure of multistage stretching extruder were described in Ref. [34]. It should be emphasized that the connector was a rectangular channel which can also provide some shear force to the melts. For comparison, neat iPP specimen was also prepared under the same processing procedure as mentioned above. For clarity, the samples prepared through the multistage stretching extruder were marked as A–B listed in Table 1, where A and B denoted the content of OMMT particles and number of LMEs, respectively.

2.3. Characterization

2.3.1. X-ray diffraction

The X-ray diffraction (XRD) was conducted on a Philips X'Pert PRO diffractometer (Holland) with $\text{Cu-K}\alpha$ radiation of wavelength 0.154 nm to determine the crystal structure of OMMT/iPP composites. The scanning 2θ angle ranged between 1.5° and 35° with a step scanning rate of $2^\circ/\text{min}$. The samples were placed with the melt flow direction perpendicular to the scanning beams. The relative amount of the β -crystal, K_β , was evaluated by the method of Turner-Jones et al. [35,36]:

$$K_\beta = \frac{I_{\beta(300)}}{I_{\alpha(110)} + I_{\alpha(040)} + I_{\alpha(130)} + I_{\beta(300)}} \quad (1)$$

Where $I_{\beta(300)}$ is the intensity of the 300 lattice plane, and $I_{\alpha(110)}$, $I_{\alpha(040)}$ and $I_{\alpha(130)}$ are the intensities of the 110, 040 and 130 planes respectively. The crystallinity (X_{c-XRD}) of all samples obtained by an interactive peak-fit procedure can be estimated by the following equation:

$$X_{c-XRD} = \frac{\Sigma A_{cryst}}{\Sigma A_{cryst} + \Sigma A_{amorp}} \quad (2)$$

where A_{cryst} and A_{amorp} are the fitted areas of crystalline and amorphous phases respectively.

2.3.2. Differential scanning calorimetry

The melting behavior of the samples was carried out on a differential scanning calorimetry (DSC-204, TA instruments, USA). Firstly, the sample was heated from $40 \text{ }^\circ\text{C}$ to $210 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ and then isothermal for 10 min at $210 \text{ }^\circ\text{C}$ to erase the influence of thermal history. After cooling down to $40 \text{ }^\circ\text{C}$ from $210 \text{ }^\circ\text{C}$ at a cooling rate of $10 \text{ }^\circ\text{C}/\text{min}$, the sample was repeatedly heated to $210 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ to observe the melting behaviors. Both of two heating scan curves of each sample were adopted to account for the melting behaviors. The crystallinity (X_{c-DSC}) of all samples can be calculated as follows:

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