Thermochimica Acta 604 (2015) 67–76

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Influence of melt structure on the crystallization behavior and polymorphic composition of polypropylene random copolymer

Bin Wang [a,b], Zhengfang Chen [a], Jian Kang [a,*], Feng Yang [a], Jinyao Chen [a], Ya Cao [a], Ming Xiang [a]

[a] State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China
[b] Ecole Normale Supérieure, CNRS-ENS-UPMC UMR 8640, 24 Rue Lhomond, Paris 75005, France

ARTICLE INFO

Article history:
Received 10 December 2014
Received in revised form 13 January 2015
Accepted 20 January 2015
Available online 23 January 2015

Keywords:
Polypropylene random copolymer
Ordered structures
β-Nucleation agent
Polymorphic composition

ABSTRACT

Polypropylene random copolymer (PPR) is one of important polypropylene types for the application fields. However, due to the random copolymer chain configuration, it is difficult to obtain high proportion of β-phase even under the influence of β-nucleating agent (β-NA). In this study, the melt structure (namely, the content of ordered structures in the melt) of β-nucleated ethylene-copolymerized PPR (β-PPR) was controlled by tuning the fusion temperature (T_f), and its impact on the crystallization and polymorphic behavior of β-PPR was investigated by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), polarized optical microscopy (PLM) and scanning electronic microscopy (SEM). The result revealed that compared with the β-nucleated iPP homo-polymer, it is more difficult for β-PPR to form β-crystals; interestingly, when T_f is in the temperature range of 162–173 °C, the ordered structures survived in melt exhibit high β-nucleation efficiency under the influence of β-NA, resulting in significant increase of β-phase proportion and evident variation of crystalline morphology, which is called the Ordered Structure Effect (OSE). Moreover, through investigating the self-nucleation behavior and equilibrium melting temperature of pure PPR (non-nucleated PPR), the physical nature of the lower and upper limiting T_f temperatures for the occurrence of OSE in β-PPR was explored; the role of ethylene co-monomer in the occurrence of OSE was discussed.

1. Introduction

Isotactic polypropylene (iPP) is one of the most widely used semicrystalline polymers, which has a fairly stimulating polymorphic behavior with three common crystal forms including the monoclinic α-form [1–6], the trigonal β-form [7–10] and the triclinic γ-form [11,12]. It is well known that the β-form usually shows some superior properties such as excellent toughness and ductility [13,14]. To achieve better toughness, the enhancement of β-form content is an efficient way. However, the β-form can be obtained in large amount only under several specific conditions such as shearing [15–19], using specific β-nucleating agents (β-NA) [20–23] and directional crystallization in temperature gradient [24].

Polypropylene random copolymer (PPR) is one of the important PP types, obtained by copolymerization of propylene with olefins (e.g. ethylene and 1-butene) [25,26]. In such copolymer, the co-monomers randomly distribute into the long propylene sequences, resulting in the decrease of crystallization ability of homo-propylene sequences and thus the decline of total crystallinity and finally leading to an excellent balance of stiffness and toughness. It should be noted that the polymorphic behavior of PPR is somewhat different from that of the iPP homo-polymer: it is even more difficult for PPR to increase the β-crystallization ability by the common methods mentioned above [27–31]. Therefore, it is very important to explore useful and effective way to enhance the crystallization ability and β-phase content of PPR.

On the other hand, an increasing number of experimental results indicate that some kind of ordered structures might exist in supercooled polymer melt before the beginning of real crystallization and affect the crystallization behavior [32–39]. When the fusion temperature (T_f) is not high enough for the polymer to achieve complete melting, an amount of ordered structures may survive in the melt [40–43]. The ordered structures can serve as self-nucleation agents during the subsequent cooling, resulting in notably increase of nucleation density, elevated crystallization temperature and accelerated crystal growth rate. Therefore, tuning the melt structure (i.e., the content of ordered structures in the

---

* Corresponding author. Tel.: +86 2885406333.
E-mail address: jiankang@scu.edu.cn (J. Kang).

http://dx.doi.org/10.1016/j.tca.2015.01.015
0040-6031/

melt) is an efficient way to control the crystallization behavior of the polymer.

Recently, researchers also pointed out interesting phenomenon that the ordered structures are crucial to β-crystallization of PP under specific conditions. Zhang et al. [18,19] investigated effects of ordered structures and shear flow on polymorphic nature of β-cylindrites of iPP and found that the survived ordered structures may remain in the melt which can act as shear-precursor during recooling, initiate the shear-induced crystallization and encourage the formation of β-cylindrites. Liu et al. [15,44,45] introduced partly melting iPP fiber to homogeneous supercooled iPP melt, and systematically investigated the β-crystallization of iPP/iPP single fiber composite. They claimed that partly melting of orientated crystal structure plays very important role in the β-phase formation. Alfonso and coworkers [46,47] studied the formation and relaxation of shear-induced nucleation and found that shear flow and partially molten fiber have similar effect on the formation of β-phase.

From the above outstanding works, two factors that are crucial to the β-crystallization of PP in above cases can be summarized: one is the ordered structure survived within the partial polymer melt; the other is external dynamic stimuli (shearing and orientation). Considering the reported dynamic stimuli, it is logical to ask if the quiescent conditions can be used to achieve this kind of polymorphic behavior and significant increase of β-phase content.

From this point, our group [48–50] prepared iPP homo-polymer nucleated by 0.03 wt% β-NA (the β-NA has dual-selectivity, such as the rare earth based β-NA with tradename WBG-II, and the widely used *N*,*N*′-dicyclohexyl-2, 6-naphthalenedicarboxamide, DCNDCA). By tuning the fusion temperature (T_f), the melt structure (i.e., the content of ordered structures in the melt) of the sample was controlled, and the crystallization behavior of the sample with different melt structures was studied. We reported for the first time that in quiescent melt without orientation or shearing, the variation of melt structures greatly influences the crystallization and polymorphic behavior of the β-nucleated iPP. When T_f was in the temperature range of 168–189 °C, mass of ordered structures survived in the melt and exhibited high β-nucleation efficiency under the influence of the β-NA, resulting in significant enhancement of β-phase content, which was called “Ordered Structure Effect” (OSE). Since it is well recognized that in the classical self-nucleation behavior of the pure iPP without β-NA, the ordered structures can only elevate crystallization temperature, increase α-nucleation sites and decrease α-crystallite sizes [40,43], the presence of certain amount of the β-NA should be a key factor in OSE. A possible mechanism depicting a two-step β-nucleation behavior of iPP was also proposed there.

Considering PPR and PP homo-polymer have quite different chemical compositions and polymorphic behaviors, it is still not known if the OSE could take place in β-nucleated PPR; if the OSE could take place, the role of ethylene copolymer in the occurrence of OSE is still not known neither. The aim of this work is to further investigate the crystallization behavior and polymorphic composition of β-nucleated ethylene-type PPR with different melt structures, so as to explore the role of ethylene co-monomer during the crystallization process, as well as the physical nature of OSE.

2. Experimental

2.1. Materials

Polypropylene random copolymer (PPR), with the tradename 4220, melt flow rate of 2.2 g/10 min (230 °C/2.16 kg), M_w of 48.2×10^4 g/mol, polydispersity index = 5.20 and ethylene content of 3.4 wt%, was supplied by Yanshan Petrochemical Corp., SINOPEC (Beijing, China). The PP homo-polymer, tradename T38F (Lanzhou OilChem Corp., China) with average isotacticity 97.6%, M_w 34.7×10^4, polydispersity index = 3.63, was used.

The β-NA (tradename WBG-II) was supplied by Guangdong Winner Functional Materials Corp., China. WBG-II is a high efficient β-NA with dual-selectivity, namely, it can encourage both β- and α-nucleating depending on the crystallization conditions [23,27]. It is heteronuclear dimetal complex of lanthanum and calcium with some specific ligands, which is a kind of irregular block-like crystal whose single crystal diameters is about tens of nanometers. WBG-II has a general formula of $Ca_xLa_{1-x}(LIG1)_m(LIG2)_n$, where x and $1-x$ is the proportion of Ca^{2+} and La^{3+} ion in the complex, while LIG1 and LIG2 are respectively a dicarboxylic acid and amide-type ligand with coordination numbers of m and n.

2.2. Sample preparation

The β-nucleated iPP and β-nucleated PPR were prepared using a corotating twin-screw extruder (SHJ-20, Nanjing Giant Machinery Corp., Ltd.) at 200 °C. To achieve desired loading and good dispersion of small amount of nucleating agent (0.03 wt%) in polymer matrix, a master batch of 1 wt% β-NA in polymer matrix was firstly prepared and then, the master batch and the raw material were melt-blended again to obtain the final samples. For convenience, the obtained specimens were abbreviated as β-PPR or β-iPP, where β indicates that the sample was nucleated with 0.03 wt% β-NA of WBG-II.

To create β-PPR with different melt structures for WAXD and SEM characterizations, the hot-molding procedure was used: after drying at 60 °C for 12 h, the pelletized granules were compression-molded. All the samples were firstly melted with platen vulcanizing press at 200 °C for 5 min and molded for another 10 min, then cooled down to room temperature still under press (10 MPa) to create 1 mm flat sheets with “standard” thermal history and to ensure the miscibility. After that, they were melted again in the platen vulcanizing press at different fusion temperatures (168, 172 and 200 °C, respectively) and 10 MPa for 5 min, and then molded at that T_f for another 5 min. After that, they were cooled down to room temperature under press in another platen vulcanizing press whose temperature was set as room temperature. Finally, flat sheets (about 1 mm) with smooth surface were obtained for further measurements.

2.3. Differential scanning calorimetry (DSC)

All the calorimetric experiments were performed with Mettler Toledo DSC1 (Mettler Corp., Switzerland) differential scanning calorimeter (DSC) under nitrogen atmosphere (50 mL/min). The temperature scale calibration was performed using indium as a standard to ensure reliability of the data obtained [51–54]. 5 mg round samples were used. All the heating curves were fitted into several separated peaks using Peakfit 4.12 software according to literatures [9,55,56], and their areas were calculated. In this way, the relative percentage crystallinities of α-crystal (α_c) and β-crystal (β_c) were estimated by the following expressions:

$$\beta_c = \frac{X_\beta}{(X_\beta + X_\alpha)} \tag{1}$$

where the degree of crystallinities X_α and X_β associated with α-phase and β-phase, respectively.

To investigate the crystallization and melting behavior of β-PPR with different melt structures, the thermal protocol proposed in Scheme 1 was applied. The sample was: firstly held at 200 °C to erase any thermal history, and cooled to 50 °C to create the