POLYMER
TESTING

Material Properties

Synergistic toughening effect of β-nucleating agent and long chain branching on polypropylene random copolymer

CrossMark

Jing Cao, Yuying Zheng[*], Tengfei Lin

College of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, Fujian, People's Republic of China

ABSTRACT

β-nucleated long chain branched (LCB) polypropylene random copolymers (PPRs) were prepared via reactive extrusion by introducing β nucleating agent (NA), dicumyl peroxide (DCP) and various contents of 1, 6-Hexanediol diacrylate (HDDA) into PPR. Results of Fourier infrared spectroscopy (FTIR) and the rheological properties demonstrate the existence of LCB polypropylene. Mechanical properties including impact strength, tensile strength and elongation at break were studied. The crystal structure, morphology and crystallization behavior were investigated via wide-angle X-ray diffraction (WAXD), polarized light microscopy (PLM) and differential scanning calorimetry (DSC). Non-isothermal crystallization kinetics using the Jeziorny method was also studied. The results show an increased LCB degree with increasing HDDA amount. For the sample with a moderate LCB level, synergistic toughening effect of NA and LCB is achieved without deterioration of yield strength or elongation at break, partially because of its higher β-phase content and much smaller spherulite size. It exhibits the minimum values of T_c and Z_{c1}, and the maximum values of $t_{1/2}$ and n_1 in the primary stage of crystallization, regardless of the cooling rate, indicating a slower crystallization rate and more complicated nucleation and crystal growth model.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polypropylene random copolymer (PPR) is one type of commercial polypropylene (PP) which plays an important role in film, rigid packaging and pipe applications due to its desirable balance of clarity, flexibility and mechanical strength with respect to polypropylene homopolymer (PPH) [1–3]. However, commercial PPR produced with Ziegler-Natta or metallocene catalysts results in high linear chains, a narrow molecular weight distribution and relative low melt strength. Its rheological behavior is not fitting for processes where elongational flows are dominant, such as blowing, thermoforming or foaming. Thus, the preparation and research on high melt strength PP have drawn more and more attention recently [4–6].

High melt strength PP can be produced by introducing long chain branching (LCB) into linear PP [7,8]. A LCB structure can improve the processability of PP, including strain hardening and shear thinning under melt conditions. There are several methods to prepare branched PP including direct synthesis of LCB PP using metallocene catalysis [9,10], electron beam irradiation [11,12] and reactive extrusion processes [13–16], among which the reactive extrusion is mostly used in industry because of its many advantages such as simple operation, low cost and high productivity.

Rheological properties of a melt are strongly affected by the presence of LCB [5,9,10,13,14,17–20]. Thus, rheology has proven to be a reliable and easy to implement method for the verification of the existence of LCB on the polymeric chain [5,9,14]. Polymers with LCB on a molecular level can be characterized by comparative measurement of polymer hydrodynamic volume in a dilute solution, with the help of GPC coupled with on-line light scattering (LS), viscosity (CV) [20,21] and/or differential reflective index (DRI) detectors [22,23]. ^{13}C NMR measurements were also used to detect branching levels of 0.35 branches per 10,000 carbons in polyethylenes [24]. Compared to NMR, GPC and NMR, rheology is a more appropriate technique for verifying the existence of long branches, especially for low level LCB far below the detection limit of the above methods. Furthermore, the current research basically focusses on the rheological properties and chemical structure of LCB PP, while the crystallization behavior, morphology and the mechanical properties of the modified PP, which are very important in the practical applications, have been reported by very few

* Corresponding author.
  E-mail address: yyzheng@fzu.edu.cn (Y. Zheng).

authors [25]. Moreover, little research is based on the modification of PP copolymers [3], i.e. PPR, compared with those of PPH.

Considering the remarkable toughness of PP with β crystal form [26—29], it is speculated that transforming the crystalline form of LCB PPR from α to β may be an efficient way to improve its toughness and melt strength simultaneously. Therefore, it is possible to achieve products with both excellent toughness and processability by preparing β-nucleated LCB-PPR. However, to our knowledge, very few works in the open literature have addressed the combination of the β-nucleation with LCB PPR.

Therefore, in this paper, PPR was modified with β-nucleating agent, peroxide and polyfunctional monomer simultaneously by reactive extrusion to obtain β-nucleated LCB PPR. A synergistic toughening effect of β-nucleation and LCB was achieved in the studied PPR. Possible explanations for the improved toughness were studied from several aspects including rheological properties, crystal morphology, melting and crystallization behavior as well as the crystallization kinetics. Finally, this study provides an effective method to obtain product with both excellent toughness and processability.

2. Experimental

2.1. Materials

PPR with a melt flow rate of 2.2 g/10 min (230 °C/2.16 kg) and a density of 0.900 g/cm³ was supplied by LyondellBasell Industries (Netherlands). The PPR pellets were stabilized by the addition of 0.1% antioxidant Irganox 1010 (Jinhai Albemarle; China). DCP was purchased from China National Medicine Group (Shanghai Reagent Corp., China). HDDA was obtained from Beijing Eastern Acrylic Chemical Technology Co., Ltd. (China). The NA WBG-II was obtained from Guangdong Winner Technology Co., Ltd. (China).

2.2. Sample preparation

To obtain even dispersion of NA in PPR, firstly, β-PPR master-batch with 4 wt% NA was prepared by mixing PPR and NA in a twin-screw extruder. The temperatures of the extruder zones were maintained at 170—205 °C from hopper to die. DCP and HDDA were dissolved in 50 mL of acetone, then the solution was added to 800 g of PPR pellets and mixed for 10 min in a high-speed mixer. After the volatilization of solvent, the as-obtained mixtures and β-PPR masterbatch were mixed in a twin-screw extruder. For comparison, samples without NA were also prepared by the same method, except that no masterbatch was added. The constituents of the samples are listed in Table 1.

The pellets were then injection molded with an injection machine (SZ-550NB, Ningbo Plastic Machine Co., China) with a screw temperature profile of 180—225 °C. The injection molded samples were dumbbell-shaped samples for tensile tests and rectangular samples for impact tests. For rheological measurements, the blended pellets were compression molded at 170 °C and 5 MPa for 3 min to obtain disk-shaped samples with a thickness of 2.0 mm and a diameter of 25 mm.

Table 1
Constituents of various samples.

Samples	A0	AH1	AH2	AH3	AH4	B0	BH1	BH2	BH3	BH4
PPR (g)	800	800	800	800	800	800	800	800	800	800
DCP (ppm)	0	300	300	300	300	0	0	300	300	300
HDDA (phr)	0	1	1.5	2	2.5	0	0	1	1.5	2
WBG-II(phr)	0	0	0	0	0	0.3	0.3	0.3	0.3	0.3

2.3. Gel determination

The original and modified PPR samples obtained from extruder were packed with filter paper, and then extracted in a Soxhlet apparatus with xylene for 24 h at 140 °C. No gel was observed for all samples.

2.4. Fourier transformation infrared spectroscope (FTIR)

FTIR spectra of all samples were measured using a Nicolet 5700 FTIR. The modified PPRs were dissolved in hot xylene at 140 °C, and then the solutions were charged into acetone at room temperature. Unreacted HDDA monomer and copolymerized HDDA remained soluble, while PPR and PPR-g-HDDA precipitated out. PPR and PPR-g-HDDA were separated by filtration and dried at 80 °C under vacuum for 48 h. The purified samples were pressed into films for FTIR analysis.

2.5. Oscillatory shear rheology

The small-amplitude oscillatory shear rheology measurements were conducted with a Bohlin Gemini 200 rheometer (England) equipped with a parallel-plate fixture (25-mm diameter). The gap between the two parallel plates was maintained at 1.75 mm for all these rheological measurements. The measurements were performed as a function of angular frequency (ω) ranging from 0.03 to 100 rad/s at 190 °C. A fixed maximum strain of 1% was used to ensure that the measurements were carried out within the linear viscoelastic range of the materials.

2.6. Mechanical characterization

Charpy impact tests were performed following ISO 179—1:2000. Injection-molded rectangular samples with dimensions of 80 mm × 10 mm × 4 mm and a single-edge 45° notch were tested using a Charpy impact tester (XJJ-50, Chengde Jiande Testing Equipments Co., Ltd, China).

Tensile tests were carried out following ISO 527-2: 1997. Dumbbell-shaped specimens of dimensions 115 mm × 10 mm × 4 mm in the narrow section were tested using an electromechanical testing machine (CMT6104, Shenzhen Skyan Power Equipment Co., Ltd, China) at a crosshead speed of 50 mm/min.

2.7. Wide angle X-ray diffraction (WAXD)

The WAXD tests of the samples were carried out on an Ultima III instrument. A conventional CuKα X-ray tube at a voltage of 40 kV and a filament current of 40 mA was used to obtain the WAXD spectra. The scanning 2θ range was 5°—40° with a scanning rate of 4°/min. The analysis method of WAXD spectra was described elsewhere by Huo et al. [30]. The overall crystallinity was determined by the following equation

$$X_c = A_c/(A_c + A_a) \times 100\% \tag{1}$$

where A_c and A_a are the areas under the crystalline peaks and amorphous halo, respectively. The content of β-form crystal was calculated by the Turner-Jones equation [31].

$$K_\beta = I_{\beta(300)} \Big/ I_{\beta(300)} + I_{\alpha(110)} + I_{\alpha(040)} + I_{\alpha(130)} \tag{2}$$

where K_β is the relative content of β-form, and $I_{\beta(300)}$, $I_{\alpha(040)}$, $I_{\alpha(110)}$, and $I_{\alpha(130)}$ are the diffraction peak intensity of (300) crystal plane of β-form, the peak intensities of (110), (040) and (130) crystal planes