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Morphology of polypropylene/poly(ethylene-*co*-propylene) in-reactor alloys prepared by multi-stage sequential polymerization and two-stage polymerization

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ABSTRACT

The morphology of two polypropylene/poly(ethylene-*co*-propylene) (PP/EPR) in-reactor alloys prepared by multi-stage sequential polymerization (MSSP) and two-stage polymerization (TSP) processes, respectively, was investigated. It is observed that the alloy prepared by MSSP (sample 1) exhibits lower phase separation temperature than the alloy prepared by TSP (sample 2), probably due to the higher content of PP segments in the blocky copolymer fractions of sample 1. Two thermal treatments were applied to the samples: (1) The samples were directly quenched from 230 °C to 132 °C for isothermal crystallization; (2) The samples were firstly held at 160 °C for 60 min for phase separation and then cooled to 132 °C for crystallization. It is found that both microstructure and thermal treatment affect the morphology of the alloys, and the differences in morphology are interpreted in terms of phase diagram. For sample 1 and for the samples subjected to phase separation prior to crystallization, the EPR-rich phase contains more PP and thus is more viscous, which leads to more inclusion of the EPR-rich phase into the spherulites. A coarse spherulitic structure is formed due to crystallization of PP in the included EPR-rich phase. More included EPR-rich phase and its stronger crystallizability can further lead to the narrower boundaries and formation of connections between the adjacent spherulites.

1. Introduction

As is well-known, in-reactor blending, which involves homopolymerization of propylene followed by copolymerization of ethylene and propylene, can significantly improve the poor low temperature impact properties of polypropylene (PP) [1–3]. The so-called polypropylene/poly(ethylene-*co*-propylene) (PP/EPR) in-reactor alloy is now mainly produced by a two-stage polymerization (TSP) process. In the first stage, propylene homopolymerization is performed in the presence of a spherical $TiCl_4/MgCl_2$-based catalyst and porous PP particles were produced. In the second stage, ethylene–propylene copolymerization occurs and a rubbery EPR phase was prepared and incorporated into the pre-formed PP matrix [4–7]. It has been demonstrated that the PP/EPR alloy possesses excellent impact strength, in comparison to mechanical blends of PP/EPR, benefited from its unique morphology [8–16] and special components such as ethylene–propylene blocky copolymer [17–19]. Recently a new process for producing PP in-reactor alloy based on multi-zone circulating reactor (MZCR) was reported [20–23]. In this process, the polymer granules are rapidly circulated between a reaction zone containing pure propylene and a reaction zone where a mixture of ethylene and propylene is fed. This means that the retention time of the polymer granules in each homopolymerization and copolymerization stage is very short, while the whole polymerization time is still long enough to reach a high polymer yield. The switch frequency between homopolymerization and copolymerization stages can be regulated by changing the retention time in these two reaction zones. We simulated such a polymerization process and prepared two PP/EPR alloys by multi-stage sequential gas-phase homopolymerization of propylene and gas-phase ethylene–propylene copolymerization in a circular mode [24]. The switch times between homopolymerization and copolymerization stages is 8 and 1 for sample 1 and sample 2, respectively, and the total time for homopolymerization and copolymerization maintains the same for both samples. It should be noticed that sample 2 could be well representative of in-reactor alloy produced by conventional two-step process (TSP). We found that, when the switch frequency between homopolymerization and copolymerization increased, the dimension of EPR phase decreased and the size distribution of the dispersed EPR phase became more uniform, but

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the total EPR content in the in-reactor alloys was hardly influenced [24]. The PP/EPR in-reactor alloy prepared by MSSP exhibits better mechanical properties in both impact strength and flexural modulus tests than PP/EPR alloy produced by conventional two-stage polymerization process. So far most reports focused on the relationship between structure and properties of PP/EPR alloys prepared by two-stage polymerization [25–28], but very few on PP/EPR alloys prepared by MSSP or MCZR.

On the other hand, the PP/EPR alloy is a mixture, which contains crystalline PP homopolymer, amorphous EPR, blocky and/or segmented ethylene–propylene copolymers [29–31]. For a blend containing both crystalline and amorphous components, the ultimate morphology and mechanical properties strongly depend on thermal treatment due to the interplay of phase separation and crystallization. It has been demonstrated that crystallization kinetic and morphology of crystalline/amorphous polymer blends are affected by the rates of crystallization and phase separation, size of the phase-separated domains, crystallization temperature, temperature and time for phase separation and other factors [32–47].

In the present work, we compared the morphologies of two PP/EPR alloys prepared by TSP and MSSP, respectively, under different thermal treatments, and the differences were interpreted in terms of structure and phase diagram. The aim of this preliminary study work is to reveal how the morphology of PP/EPR in-situ alloys can be controlled by regulation of polymerization process (or microstructure of the alloys) and interplay of phase separation and crystallization.

2. Experimental

2.1. Preparation of PP/EPR in-reactor alloys

Details for preparation of PP/EPR in-reactor alloys were described in reference [24]. A multi-stage sequential polymerization process was conducted using a high yield spherical Ziegler-Natta catalyst, $TiCl_4/MgCl_2 \cdot ID$ (where ID is an internal donor), kindly donated by BRICI, SINOPEC (Beijing, China). In the first stage, propylene homopolymerization was carried out for 60 min after the prepolymerization conducted in a well-stirred glass reactor. Next is a circular reaction mode including ethylene–propylene copolymerization, in which an ethylene–propylene mixture of a constant composition (propylene/ethylene = 1.5) was continuously supplied to the autoclave under constant pressure (0.4 MPa), and propylene homopolymerization under constant pressure (0.6 MPa). That is to say, after ethylene–propylene copolymerization for a designed time, the polymerization was switched to propylene homopolymerization and subsequently ethylene–propylene copolymerization at the same conditions as above. The circular reaction mode was carried out for 80 min at 60 °C. In the circular reaction, sample 2 was prepared by ethylene–propylene copolymerization for 20 min and then propylene homopolymerization for 60 min, namely, the switch times of sample 2 was 1. Analogically, sample 1 was synthesized by ethylene–propylene copolymerization for 2.5 min and then propylene homopolymerization for 7.5 min in a circle and its switch times was 8. It is noteworthy that compared to sample 1 prepared by MSSP process, sample 2 is actually prepared by the conventional TSP process. The polymerization parameters and mechanical properties of both samples are given in Table 1.

2.2. Thermal fractionation

About 5 mg of each sample was sealed in an aluminum pan and subjected to stepwise isothermal crystallization according to the following procedure: The samples were first heated to 200 °C under nitrogen atmosphere and held for 100 min to erase the thermal history. Then the samples were cooled down to the first isothermal crystallization temperature ($T_{c1} = 130$ °C) and held at this temperature for 12 h, and then successively cooled down to a series of isothermal crystallization temperatures (T_c) set at 125, 120, 115, 110, 105, 100, 95, 90, 85, 80, 75, 70, 65, and 60 °C, respectively, and held at each temperature for 12 h. This temperature difference (5 °C) is defined as the "fractionation window". The melting endotherms of the samples after step crystallization were recorded on a Perkin-Elmer Pyris-1 calorimeter at a heating rate of 10 °C/min from 30 to 200 °C. In the other procedure, a "fractionation window" of 10 °C and holding time of 24 h at each T_c were employed as well.

2.3. Optical microscopy

Polarized optical microscopy (POM) observations were carried out on an Olympus BX-51 polarized optical microscope (Tokyo, Japan) equipped with a hot-stage and a digital camera. A small piece of sample placed between two cover glasses was first melted at 230 °C for 10 min on the hot-stage and the thermal history of the sample was erased, and then morphology during isothermal crystallization was observed. Two different thermal treatments were applied to the samples prior to isothermal crystallization. In the first thermal treatment, the samples were cooled directly from 230 °C to 132 °C at a rate of 30 °C/min to complete isothermal crystallization. In the second thermal treatment, the samples were firstly quenched from 230 °C to 160 °C and held for 60 min to facilitate phase separation, and then cooled to 132 °C at a rate of 30 °C/min for isothermal crystallization. The samples in POM experiments were also used for phase contrast optical microscopy (PCOM) observations, which were carried out on phase contrast microscope (XSZ-HX, Chongqing, China) equipped with a JVC color video camera (TK-C921EC).

2.4. Scanning electron microscopy (SEM)

The morphology of spherulites was investigated using a scanning electron microscope (FEI-SIRION). The SEM samples were prepared as follows: films of sample 1 and sample 2 were placed between two cover glasses on the hot-stage of the above-mentioned Olympus BX-51 optical microscope (Tokyo, Japan), and first melted at 230 °C for 10 min to erase the thermal history of samples. Then two different thermal treatments as described in Section 2.3 were applied to the films before isothermal crystallization at 132 °C. The film was then etched by xylene for 24 h at room temperature to remove non-crystalline ethylene–propylene random copolymer and then coated with gold before observation.

Table 1
Polymerization conditions and mechanical properties of two PP/EPR in-reactor alloys.

Sample	Retention time in each polymerization cycle (min)		Switch number (times)	Impact strength (KJ/m^2)	Flexural modulus (MPa)
	Propylene homopolymerization	Ethylene–propylene copolymerization			
Sample 1	2.5	7.5	8	13.6	915.7
Sample 2	20	60	1	3.9	770.7