Polypropylene random copolymer in pipe application: Performance improvement with controlled molecular weight distribution

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ABSTRACT

The performance of polypropylene random copolymer (PP-R) for pipe applications, including their processability and final mechanical properties, can be balanced by finely controlling the molecular weight distribution (MWD). In this study, two representative samples chosen from a material optimization design procedure were analyzed. Rheology tests showed that broadening MWD will improve the processability of PP-R. The samples were then fractionated according to molecular weight and studied by isothermal and non-isothermal crystallization kinetics as well as self-nucleation and annealing (SSA) technique. The results indicated that the ultra high molar mass component resulting from a broader MWD can act as nucleation agent, which might decrease the spherulite size and increase the tie-chain content of PP-R. Finally, polarized optical microscope (POM) and tensile tests were carried out to ascertain these speculations. It appears that finely controlling the MWD has a synergetic effect on the processability and mechanical properties of PP-R.

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1. Introduction

Polypropylene has experienced a huge growth in consumption over the last few decades because of its good mechanical and thermal properties [1]. As one type of modified PP, polypropylene random copolymer (PP-R) has received a great deal of attention from academics and industry [2–4]. By copolymerizing propylene with ethylene comonomer, the crystallization of propylene sequences is disrupted by the occasionally embedded ethylene units, leading to a decrease in total the crystallinity, rigidity, and melting point of PP. As a result, PP-R has shown to have attractive properties such as thermal stability, aging resistance, and mechanical properties, making it suitable for piping systems for both domestic and industrial applications [5–7]. The above achievement has benefited a lot from the significant contributions from the development of new catalyst systems and the increased understanding of structure-property relationships of PP [8].

The mechanical properties of semicrystalline polymers have often been related to crystallinity, crystalline structure and morphology [9–14], amorphous chain orientation, as well as distribution and concentration of tie chains in the interlamellar amorphous region [15–23]. It is generally recognized that the tie chains, linking two adjacent crystallites, not only determine the conventional short-term properties, such as the stiffness and strength, but also the long-term properties of semicrystalline polymers [24,25]. Zuo et al. [26] hypothesized that the formation of tie chains, which is directly influenced by the entanglement network of amorphous chains in the interlamellar region, can play a vital role to affect the overall mechanical behavior and deformation-induced structure/morphology changes.

In the peculiar case of PE, intensive research has been focused for the last 30 years on understanding the role of the molecular architecture in the concentration of tie-chains. The aspects of molecular architecture that have been specifically addressed are the molecular weight distribution and the co-unit content and distribution [22]. It is well accepted that the chain entanglements and co-units, brought by high molecular weight chains and copolymerization respectively, would be excluded from the crystalline phase and lead to the formation of tie-chains [27]. We can expect that the more concentrated co-units along the high molar mass component of the polymer would greatly improve the formation of tie-chains. But this might be contradictory to the fact that the co-units in PP copolymers are preferentially concentrated in low molecular weight chains when Ziegler–Natta catalyst is used in polymerization process [28]. However, the seemingly theoretically impossible limit can be overcome owing to the opportunity to incorporate the co-units in the high molecular weight chains by means of cascade polymerization process. Preferred incorporation of the co-units in long chains was indeed suspected to provide a synergetic effect on lifetime [29–34]. Nevertheless, the materialization through forementioned methods will give PP-R a broad

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molecular weight distribution (MWD). As a result, the rheological properties and crystallization behaviors of PP-R can be greatly affected.

Industrially, processability of polymeric materials is of great importance. Commercially PP-R pipe resin must be melt processable at reasonable rates during extrusion formation. The linear molecular structure of PP-R can result in low melt strength which is undesirable for pipe fabrication [35]. Broadening MWD can improve the melt strength of a polymer [36,37], however might have impact on its processing properties because of the increased melt viscosity. Still, for the procedure of pipe extrusion formation, there are mainly three stages the polymer melt will undergo: screw flow, die transition and calibration after the die. During screw flow, the shear rate is usually high. But during the pipe calibration stage, the employed shear rate is substantially low. Consequently, high flowability at screw flow stage and high melt strength at calibration stage is desired for the pipe material. It appears that appropriately broadening MWD might be beneficial to the both stages. MWD can greatly influence the rheological behavior of a polymer. Hence, the processability of PP-R can be evaluated by carrying out theoretical analysis of the polymer melt flow. A better understanding of the rheological characteristics of PP-R can solve the existing problems and reliably secure a successful processing.

The MWD will also have intensive influence on the crystallization behaviors of semicrystalline polymers and therefore plays an important part in the final mechanical properties of this kind of materials. In recent years, a lot of researchers have been devoted to studying the effect of molecular characteristics, preferentially the type and content of comonomer as well as its distribution, on crystallization behaviors of PP-R [38–48]. Paukkeri [49] found that in the main part of the molecular weight range studied (weight-average molecular weight between 2200 and 94,700 g/mol), molecular weight had no or only a small influence on crystallization behavior. Wang et al. [50] found that for the case of a binary polymer blend, broadening MWD would decrease the energy barrier of nucleation and theoretically the high molar mass component has the capability of inducing nucleation. It has been claimed that the crystallization behaviors would be greatly influenced when isotactic polypropylene contains a high molar mass component [37,51–53]. PP-R will actually contain an ultra high molar mass component if its MWD is broad enough. Whether this component will have a special crystallization behaviors has not been well understood till now, although some investigations have paid attention to the effect of molecular weight on the crystallization behavior of PP-R under shear [54–56].

The increased understanding of structure-property relationships of PP-R prompts us to pre-design the corresponding chain structures of this polymeric material in the hope of seeking a balance between the processability and service properties of PP-R. In the present study, tailoring of PP-R pipe materials was realized by employing a cascade process, where the pre-designed chain structures including ethylene content and its distribution as well as MWD were achieved by finely adjusting the catalytic polymerization process in different reactors. For the case of optimizing the final properties as well as the processing properties of PP-R, finely controlling its WMD will be particularly taken into account. Our work is to emphasize the effect of MWD on the processing property and crystallization behaviors of PP-R, as this could on the contrary allow us to better design the preferred MWD for pipe application. For this purpose, two representative samples were chosen from the above procedure of optimal design, one of which has a particularly broad MWD and would accordingly result in more content of ultra high molar mass component. The chain structures, rheological property, crystallization behaviors and mechanical properties of the two samples were subsequently analyzed.

Table 1
Molar mass and molecular weight distribution of PP-Rs and their fractions.

Samples	Relative content (%)	M_n (kg/mol)	M_w (kg/mol)	MWD (M_n/M_w)
PP-R1	–	145.3	714.8	4.92
PP-R1-F1	56.0	224.2	470.3	2.10
PP-R1-F2	43.5	52.3	150.1	2.87
PP-R2	–	158.6	1036	6.53
PP-R2-F1	64.4	250.4	486.8	1.94
PP-R2-F2	34.8	60.3	145.5	2.41

2. Experimental

2.1. Materials

PP-Rs designated as PP-R1 and PP-R2 were chosen from the procedure of performance optimization. They were kindly supplied by Daqing Refinery Co. (Heilongjiang, China) and had a melt flow rate (MFR) of 0.31 and 0.23 g/10 min (230 °C/2.16 kg) respectively. PP-R2 was obtained with broadened MWD by slightly increasing the molar mass of the polymer in the second reactor during polymerization process. The degree of crystallinity of both samples was about 36% (DSC, compression molded). In particular, it should be pointed out that they were produced under finely changed polymerization conditions and had the approximate ethylene content of about 3.5 wt% (NMR).

2.2. Fractionation by precipitation

Fractionation of the sample according to molecular weight was conducted with the following method: 0.5 g PP-R was dissolved at 130 °C in 50 ml xylene containing Irganox 1010 using a heatable magnetic stirrer, after the dissolution was completed, 70 ml ethylene glycol monoethyl ether was dropwisely added to the homogeneous solution at 130 °C till equilibrium was achieved. The insoluble fraction, designated as F1, was collected by filtration of the solution through a metal screen (mesh number of about 400) at 130 °C. The filtrated solution was cooled to room temperature and allowed to be furtherly precipitated by excess acetone. The precipitate was collected using filter paper and designated as F2. After drying of the collected samples, the mass percent of each fraction was calculated and the results were shown in Table 1.

2.3. Characterization

2.3.1. High temperature gel permeation chromatography (HT-GPC)

Molar mass and molecular weight distributions were determined using a PL-220 high temperature chromatograph (Polymer Laboratories Ltd., USA) equipped with a differential refractive index and viscosity detector. The equipment responses were calibrated using polystyrene standard EasiCal PS-1 (PL Ltd) before testing. Samples were dissolved at 140 °C for 6 h to achieve equilibrium. The solvent used was 1,2,4-trichlorobenzene, stabilized with moderate Irganox 1010. The measurements were performed at 140 °C at a flow rate of 1 ml/min. The operation time for each sample was 35 min.

2.3.2. Rheological properties

The test for determination of extrusion flow behavior was conducted using a high-pressure capillary rheometer (Rosand RH7) supplied by Malvern company, England. The applied temperatures are 220 °C, 230 °C, 240 °C, 250 °C, 260 °C respectively and the shear rate fell in the range from 10 to 3000 s^{-1}, The capillary diameter (D) was 1 mm, while the ratio of die length (L) to D was 16. The