공정 조건에 따른 polypropylene의 유변학적 거동에 관한 연구

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Rheological behavior of polypropylene with process condition

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Introduction

The shear deformation on crystallization of the semi-crystalline polymer was sensitively reflected by the rheological measurement. Due to the high sensitivity, rheological measurement is used as a tool to understand shear induced crystallization (Khanna, 1993; Boutahar et al., 1998). For example, Khanna (1993) has studied the crystallization by the rheometer.

In this study, polypropylene (PP) was extruded several times. It is expected that the chain scission of the PP occurred during extrusion. The shear induced crystallization of different number of extrusion PP were studied by advanced rheometric expansion system (ARES). Also, to better understand the crystallization behavior, the isothermal crystallization test was performed by different scanning calorimetry (DSC) and polarized microscopy (POM). The aim of this study is to detect the effects of extrusion on the PP sensitively.

Experimental

Preparations

PP was extruded using Prism twin screws extruder. PP used in this study was ethylene 6% block PP copolymer. PP copolymer is the largely used PP in automobile industry. PP was extruded as virgin, 1-time after extrusion, 2-times after extrusion and 3-times after extrusion. The virgin, 1-time after extrusion, 2-times after extrusion PP and 3-times after

extrusion were denoted virgin PP, 1st extrusion PP, 2nd extrusion PP, 3rd extrusion PP respectively.

Rheology

Dynamic oscillation measurements were carried out on ARES in linear viscoelastic region in the parallel-plate arrangement with 25 mm plate under dry nitrogen atmosphere. The frequency sweeps from 0.05 to 100 rad/sec were carried.

Crystallization

The isothermal crystallization of the PP were analyzed DSC. For the isothermal crystallization, samples were melted at 200°C for 5 minutes, and then rapidly cooled to the isothermal crystallization temperature. The spherulite morphology of the PP was analyzed with POM.

Results and discussion

Fig. 1 shows the storage modulus (G') with frequency for the virgin, 1st extrusion, 2nd extrusion, and 3rd extrusion PP at 190 °C. At 190 °C, the crystalline phase of the virgin, 1st extrusion, 2nd extrusion, and 3rd extrusion PP was expected to completely melt. For the virgin, 1st extrusion, 2nd extrusion, and 3rd extrusion PP, the storage modulus shows no pronounced differences among them.

Fig. 2 shows the storage modulus with frequency for the virgin, 1st extrusion, 2nd extrusion, and 3rd extrusion PP at 166.5 °C. At 166.5 °C, the melting process of PP did not completely terminated, and some crystalline phase was expected to remain. For the 2nd and 3rd extrusion PP, the storage modulus is decreased at all the frequency compared to the virgin and 1st extrusion PP. The decrease of the storage modulus of the 2nd extrusion and 3rd extrusion PP may be due to extrusion effect. To analyzed the dynamic rheology data, Winter and Chambon equation (Winter and Chambon, 1986; Chambon and Winter, 1987) was introduced:

$$G'(\omega) \sim G''(\omega) \sim \omega^n \qquad (1)$$

where, n is the relaxation exponent. According to eq. (1), the relaxation exponents from G' and G" show similar value as increasing crystallinity. Applying eq. (1) to the virgin and 1st extrusion PP, the relaxation exponents of the virgin and 1st extrusion PP show 0.818 for G' and 0.624 for G" (virgin PP) and 0.812 for G' and 0.624 for G" (1st extrusion PP), respectively. For the 2nd and 3rd extrusion PP, the relaxation exponents of 2nd and 3rd

extrusion PP show 0.977 for G' and 0.723 for G" (2nd extrusion PP) and 0.964 for G' and 0.713 for G" (3rd extrusion PP), respectively. The relaxation exponents results suggest that shear induced crystallization of PP is more predominantly shown in the virgin and 1st extrusion PP.

Fig. 3 shows the crystallization fraction (X_t) of the virgin, 1st extrusion, 2nd extrusion, and 3rd extrusion PP at 130°C. As increasing the increasing the number of extrusion time, the crystallization rate of the PP at 130 °C was decreased.

Fig. 4 (a) and (b) show the micrographs of the virgin and 3rd extrusion PP, respectively. The micrographs were obtained at 130 °C isothermal condition after 5 minutes. From Fig. 4 (a) and (b), the spherulite shape of each samples showed no pronounced difference. Also the growth rate of spherulite of each sample showed no pronounced difference. However the sperulite growth site was decreased as increasing the number of the extrusion time. Therefore, it is suggested that the decrease of the crystallization rate of PP with increasing the number of the extrusion time may come from the decrease of crystallization growth site with increasing the number of the extrusion time.

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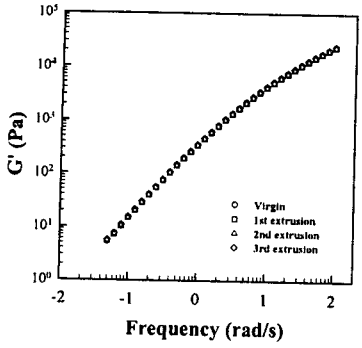


Fig. 1. Storage modulus of the virgin PP, 1st extrusion PP, 2nd extrusion PP and 3rd extrusion PP at 190°C.

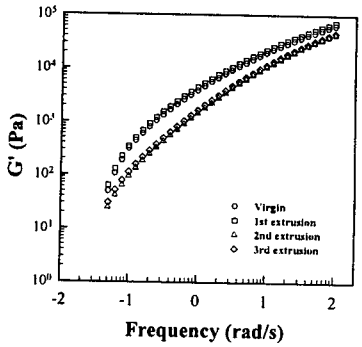


Fig. 2. Storage modulus of the virgin PP, 1st extrusion PP, 2nd extrusion PP and 3rd extrusion PP at 166.5 °C

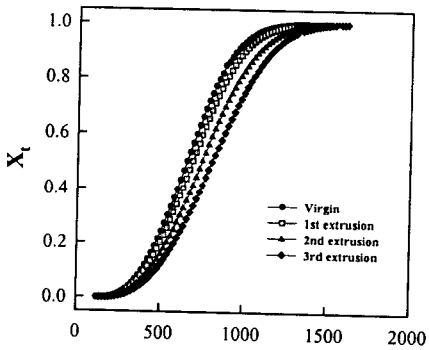
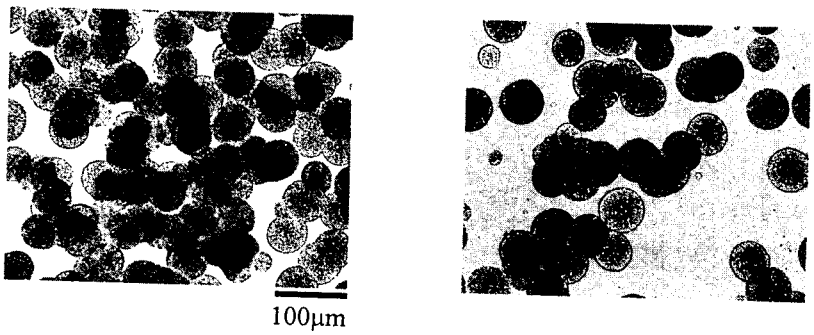


Fig. 3. Crystallization fraction (X_t) of the virgin, 1st , 2nd , and 3rd extrusion PP at 130 °C



(a) (b)

Fig. 4. Microscopy of the PP after 5 minutes isothermal test at 130 °C : (a) virgin PP, (b) 3rd extrusion PP