Rheological properties and crystallization kinetics of polypropylene block copolymer with repeated extrusion

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Abstract

Rheological properties and crystallization kinetics of the polypropylene (PP) block copolymer and recycled PP block copolymer were studied by advanced rheometric expansion system (ARES), differential scanning calorimetry (DSC), and optical microscopy. In the study of the dynamic rheology, it is observed that the storage modulus and loss modulus for the PP block copolymer and recycled PP block copolymer did not change with frequency. In the study of the effect of the repeated extrusion on the crystallization rate, half crystallization time of the PP samples was increased with the number of repeated extrusion in isothermal crystallization temperature (T_c). From the isothermal crystallization kinetics study, the crystallization rate was decreased with the increase of the number of repeated extrusion. Also, from the result of Avrami plot, the overall crystallization rate constant (K) was decreased with the increase of the number of the repeated extrusion. From the study of the optical microscopy, the size of the spherulite of the PP samples did not change significantly with the number of repeated extrusion. However, it was clearly observed that the number of the spherulite growth sites was decreased with the number of repeated extrusion. From the results of the crystallization rate, isothermal crystallization kinetics, Avrami plots, and optical microscopy, it is suggested that the crystallization rate of the PP block copolymer is decreased with the increase of the number of repeated extrusion.

Keywords : polypropylene, crystallization kinetics, extrusion, rheology

1. Introduction

The properties of semi-crystalline polymer such as polypropylene (PP) are ultimately dependent on the structure of the polymer (Alamo and Mandelkern, 1991; Alamo et al., 2003; Chen et al., 1997; Chun et al., 2000; Kim et al., 1994; Mareau and Prud'homme, 2002; Marreau and Prud'homme, 2003; Schönherr et al., 2002). The structure of the semi-crystalline polymer is controlled by the mechanism of the crystallization and crystallization kinetics. The crystallization mechanism is influenced by several factors such as thermal treatment and geometrical factors (Mareau and Prud'homme, 2002; Marreau and Prud'homme, 2003; Schönherr et al., 2002). For example, Schönherr et al. (Schönherr et al., 2002) reported the effects of the thermal treatment on the crystallinity of the PP elastomer

and Mareau and Prud'homme (Mareau and Prud'homme, 2002) reported the dual growth rate mechanism in the crystallization of the poly(ε-caprolactone)/poly(vinyl chloride) blend which was caused by the geometric factor of the polymer sample. Also, the crystallization kinetics was extensively studied by several researchers (Alamo and Mandelkern, 1991; Alamo et al., 2003). Alamo and Mandelkern (Alamo and Mandelkern, 1991) studied the crystallization kinetics for the ethylene-hexane random copolymer by the overall crystallization. Alamo et al. (Alamo et al., 2003) reported the crystallization kinetics of the isotatic PP using the linear growth rate (G).

PP has been widely used in automobile industry. In some cases, the recycled PP are used as the automobile parts for environmental concern. For its industrial importance, many researches have studied the properties of the recycled PP (Aurrekoetxea et al., 2001a; Aurrekoetxea et al., 2001b). Aurrekoetxea et al. (Aurrekoetxea et al., 2001a) reported

the crystallization behavior and mechanical properties of the recycled PP and they also reported the fracture behavior of the recycled PP (Aurrekoetxea *et al.*, 2001b).

In this study, rheological properties and crystallization kinetics of the virgin PP copolymer and recycled PP copolymer were studied using the advanced rheometric expansion system (ARES) for the dynamic rheological properties and differential scanning calorimetry (DSC) for the overall crystallization rate, and the optical microscopy for the spherulite morphology.

2. Experimental

2.1. Polymers

The polymer used in this study was obtained from commercial source. PP (JI-360 grade) was provided by Honam Petroleum Corporation. The PP was synthesized using the $MgCl_2$-supported Ziegler Natta catalyst. The JI-360 grade is the 6 wt% ethylene containing PP block copolymer, which is widely used in the automobile industry. The PP contains phosphite antioxidant (3,000 ppm). The characteristics of the PP used in this study are shown in Table 1.

2.2. Preparations

The recycled PP samples were prepared by extrusion of the virgin PP using Prism twin screw extruder. The 1-time extrusion of the virgin PP, 2-times repeated extrusion of the virgin PP, and 3-times repeated extrusion of the virgin PP were designated as PP-A, PP-B, and PP-C, respectively. The PP samples were dried under vacuum (< 1 mmHg) at 90°C for 12 hrs before use. The temperatures of the extruder were set at 180 and 220°C in feeding and barrel zones, respectively.

2.3. Rheology

Dynamic measurements were carried out on advanced rheometric expansion system (ARES) in oscillatory shear at 10% strain in the parallel-plate arrangement with 25 mm plate under dry nitrogen atmosphere. The PP samples were fabricated in a disk with 2 mm in thickness. The frequency sweeps from 0.05 to 100 rad/s were carried out at 190°C. For all measurements, it has been verified that the behavior of the PP samples were linear viscoelastic.

Table 1. Characteristics of the ethylene containing polypropylene block copolymer used in this study

Sample	$\overline{M_n}$	$\overline{M_w}$	MWD	T_m (°C) [a]	Ethylene content (wt%)
PP[b]	4.4×10^4	2.2×10^5	5.0	164	6

[a]Measured in our laboratory by DSC.
[b]Supplied by Honam Petroleum Corp.

2.4. Differential scanning calorimetry

The isothermal crystallization of the PP samples was analyzed by a Perkin-Elmer DSC-7. Temperature calibration was performed using indium ($T_m = 156.6°C$, $\Delta H_f = 28.5$ J/g). For the isothermal crystallization of the PP samples, the samples were melted at 200°C for 5 min, and then rapidly cooled to the isothermal crystallization temperature (115, 120, 125, 130°C). During isothermal crystallization of the PP samples, the heat flow was recorded until the heat flow is not changed.

2.5. Optical microscopy

The microscopy tests were carried out with optical microscopy (Olympus BX-60F) for the spherulite growth. For the microscopy test of the isothermal crystallization of the PP samples, the PP samples were melted on a hot stage (Mettler FP-90) at 200°C for 5 min, and then cooled 130°C by 5°C/min.

3. Results and discussion

Fig. 1 shows the storage modulus (G') and loss modulus (G") with frequency for the virgin PP, PP-A, PP-B, and PP-C at 190°C. It is observed that the storage modulus and loss modulus for the virgin PP, PP-A, PP-B, and PP-C do not change with frequency. From Fig. 1, it is also observed that the relaxation time of the virgin PP, PP-A, PP-B, and PP-C from the cross-over point of the storage modulus and loss modulus does not change. It is known that the dynamic rheological properties such as storage modulus, loss modulus, and relaxation time reflect on the molecular structure such as molecular weight, molecular weight distribution, and branching degree (Peón *et al.*, 2001; Shroff
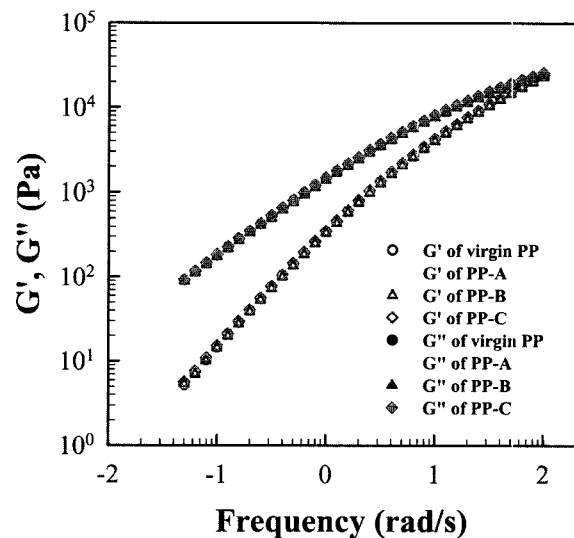

Fig. 1. Storage modulus (G') and loss modulus (G") vs. frequency for the virgin PP, PP–A, PP-B, and PP-C at 190 °C.
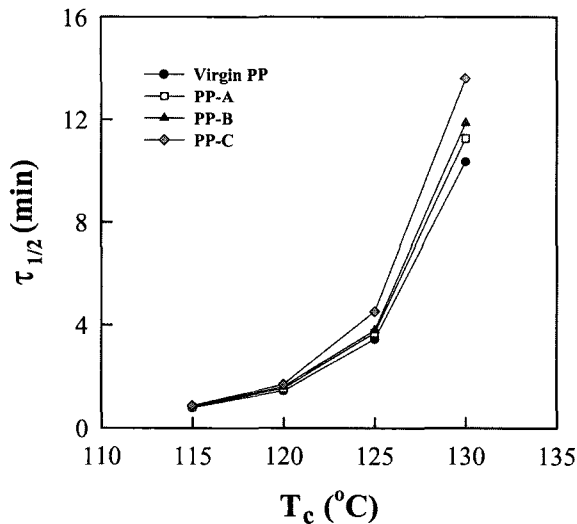
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Fig. 2. Half crystallization time $(\tau_{1/2})$ of the virgin PP, PP-A, PP-B, and PP-C with isothermal crystallization temperature (T_c).

Table 2. Half crystallization time $(\tau_{1/2})$ of the virgin PP, PP-A, PP-B, and PP-C with isothermal crystallization temperature (T_c)

Sample	$\tau_{1/2}^{a}$ (min)	$\tau_{1/2}^{b}$ (min)	$\tau_{1/2}^{c}$ (min)	$\tau_{1/2}^{d}$ (min)
Virgin PP	0.8	1.5	3.5	10.4
PP-A	0.8	1.5	3.7	11.3
PP-B	0.8	1.6	3.8	11.9
PP-C	0.9	1.7	4.5	13.6

[a] $\tau_{1/2}$ was measured by DSC at 115°C.
[b] $\tau_{1/2}$ was measured by DSC at 120°C
[c] $\tau_{1/2}$ was measured by DSC at 125°C
[d] $\tau_{1/2}$ was measured by DSC at 130°C

and Mavridis, 1999; Vega et al., 1998). Therefore, it is thought that the molecular weight and molecular weight distribution among the PP samples do not change significantly with repeated extrusion.

Fig. 2 shows the half crystallization time $(\tau_{1/2})$ of the virgin PP, PP-A, PP-B, and PP-C with isothermal crystallization temperature (T_c). The half crystallization time of the PP samples is increased with increasing the number of the extrusion in the crystallization temperature range (115~130°C). The increase of the half crystallization time of the PP samples is clearly observed at the slow crystallization temperature (130°C). At 130°C, the half crystallization time is increased from 10.3 to 13.6 min for the virgin PP and PP-C, respectively. In Table 2, the half crystallization time $(\tau_{1/2})$ of the virgin PP, PP-A, PP-B, and PP-C with isothermal crystallization temperature (T_c) is represented.

Fig. 3 shows the crystallization fraction (X_t) of the virgin PP, PP-A, PP-B, and PP-C at 130°C, which obtained form the thermal analysis results of the differential scanning cal-
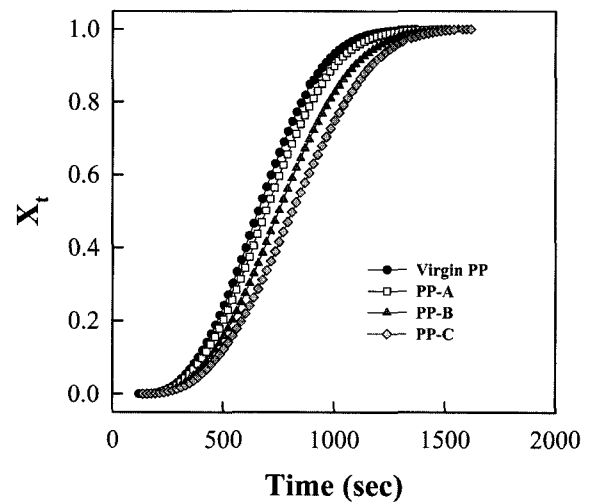

Fig. 3. Crystallization fraction (X_t) of the virgin PP, PP-A, PP-B, and PP-C at 130°C.

orimetry. The crystallization fraction (X_t) was determined as follows:

$$X_t = \frac{\int_0^t (dH/dt)dt}{\int_0^\infty (dH/dt)dt} \tag{1}$$

where X_t is the crystallization fraction after time t. A numerator is the heat generated after time t and a denominator is the heat generated after time goes infinite.

From Fig. 3, it is observed that the crystallization fraction shifts to longer crystallization time with the increase of the number of repeated extrusion, indicating that the PP samples crystallize slowly with the increase of the number of repeated extrusion. For the heat of fusion (ΔH_f) of the virgin PP, PP-A, PP-B, and PP-C, however, does not change significantly, which shows 88 ± 5 J/g.

The crystallization kinetics of the PP samples under isothermal crystallization were analyzed by the following Avrami equation (Avrami, 1940):

$$\log[-\ln(1 - X_t)] = \log K + n\log t \tag{2}$$

where n is the Avrami exponent and K is the overall crystallization rate constant, respectively.

Fig. 4 shows the Avrami plots of the virgin PP, PP-A, PP-B, and PP-C at 130°C. From Fig. 4, the overall crystallization rate constant (K) is decreased from 9.55×10^{-11} to 3.98×10^{-11} for the virgin PP and PP-C, respectively (Table 3). The Avrami exponent (n) of the PP samples, however, do not change with the number of repeated extrusion (Table 3). In general, the Avrami exponent (n) is related to the type and geometry of the nucleation and growth.

Fig. 5 (a) and (b) show the optical micrographs of the virgin PP and PP-C under the isothermal crystallization at 130°C, respectively. The micrographs were taken after 5 min isothermal condition at 130°C. From Fig. 5, it is observed that the virgin PP and PP-C show the spherulite
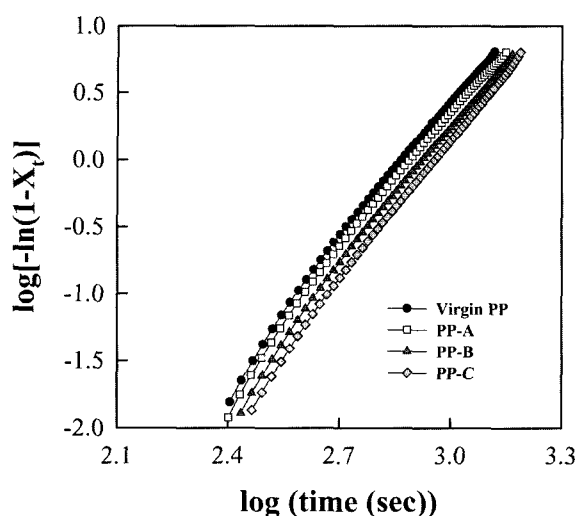
Fig. 4. Avrami plots of the virgin PP, PP-A, PP-B, and PP-C at 130°C.

Table 3. Overall crystallization rate constant (K) and Avrami constant (n) of the virgin PP, PP-A, PP-B and PP-C at 130°C

Sample	K^a	n^a
Virgin PP	9.55×10^{-11}	3.48
PP-A	8.32×10^{-11}	3.48
PP-B	6.31×10^{-11}	3.48
PP-C	3.98×10^{-11}	3.51

$^a K$ and n were calculated from the Avrami equation (Avrami, 1940).

type crystallization morphology. From Fig. 5(a) and (b), the size of the spherulite of the virgin PP and PP-C does not change significantly between the samples. However, it is clearly observed that the number of the spherulite growth sites is decreased for the sample of PP-C, which suggests that the crystallization rate of the PP-C is slow compared to the virgin PP. The decrease of the spherulite growth sites may be due to the increase of impurities caused by the increase of number of repeated extrusion. This result is consistent with the results of the isothermal crystallization and Avrami plot of the PP samples at 130°C, which suggests that the crystallization rate is slow with the increase of the number of repeated extrusion. From the above isothermal crystallization, Avrami plot, and the optical microscopy studies, it is suggested that the crystallization rate of the PP is decreased with the increase of the number of repeated extrusion time, which caused by the decrease of the number of the spherulite growth sites.

4. Conclusions

Rheological properties and crystallization kinetics of the
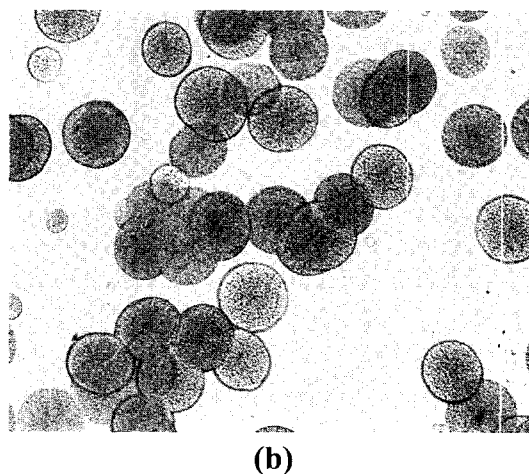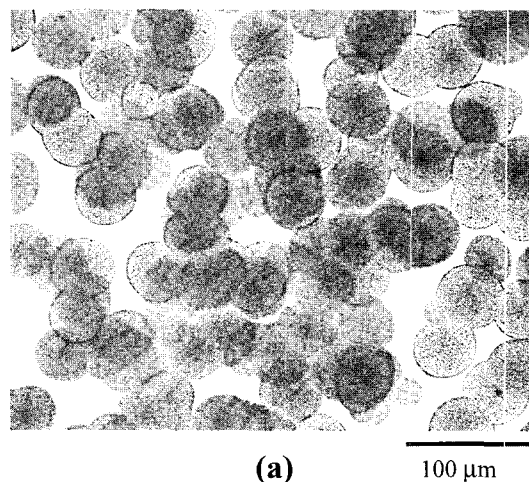

(a) 100 μm

(b)

Fig. 5. Optical microscopy of the spherulite of the virgin PP and PP-C at 130°C: (a) virgin PP; (b) PP-C.

ethylene containing polypropylene (PP) block copolymer and recycled PP block copolymer were investigated. In the study of the dynamic rheology, it is observed that the storage modulus and loss modulus for the PP block copolymer and recycled PP block copolymer did not change with frequency.

In the study of the effect of the repeated extrusion on the crystallization rate, half crystallization time of the PP samples was increased with the increase of the number of repeated extrusion in the crystallization temperature range (115~130°C).

In the study of the isothermal kinetics of the PP samples at 130°C, the crystallization rate of the PP samples was decreased with the number of repeated extrusion. Also, from the Avrami plots results, the overall crystallization rate constant (K) of the PP samples was decreased with the increase of the number of the repeated extrusion. From the above results of the isothermal crystallization and Avrami plots, it is concluded that the crystallization rate is decreased with the increase of the number of repeated extrusion.

From the result of the optical microscopy study, the spherulite size of the PP samples did not change significantly between the PP samples. However, it is clearly observed that the number of the spherulite growth sites was decreased with the increase of the number of repeated extrusion time. This result is consistent with the results of the isothermal crystallization and Avrami plots of the PP samples at 130°C.

From the results of the half crystallization time, isothermal crystallization, Avrami plots, and optical microscopy studies, it can be concluded that the crystallization rate of the PP block copolymer is decreased with the increasing the number of repeated extrusion.

Acknowledgement

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