Polypropylene의 Thermorheological 거동에 관한 연구

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Thermorheological Behavior of Polypropylene

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Introduction

Rheological behavior of polymer is very sensitively on several factors such as molecular structure, molecular weight, and molecular weight distribution (MWD). Due to the high sensitivity, rheological method is used as a tool to detect the molecular structure. For example, several studies were successfully underdone to using rheological method to detect the long chain branch (LCB) of Polyethylene. (Vega et al., 1998; Shroff and Mavridis, 1999; Wood-Adams and Costeux, 2001; Lohse et al., 2002). In some cases the effects of molecular structure on rheological behavior were described by the presence of additional relaxation processes (Shroff and Mavridis., 1999; Wood-Adams and Costeux., 2001) and thermorheologically complex behavior (Lohse et al., 2002).

In this study, the Polypropylene (PP) was extruded several times. It is expected that the chain scission of PP was occurred during extrusion. The aim of this study is to detect the effects of extrusion by rheological methods quantitatively and qualitatively.

Experimental

Preparations

PP was extruded using Prism twin screws extruder. PP used in this study contains 20 weight percent of talc. The talc-containing PP is the largely used PP in automobile industry. PP was extruded as virgin, 1-time after extrusion, and 2-times after extrusion. The virgin, 1-

time after extrusion, and 2-times after extrusion PP were denoted virgin PP, 1^{st} extrusion PP, and 2^{nd} 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 out at 200, 220 and 240 °C.

Results and discussion

Fig. 1 shows the storage modulus (G') of the virgin PP, 1^{st} extrusion PP and 2^{nd} extrusion PP at 200°C. For the virgin PP and 1^{st} extrusion PP, the storage modulus of each other is superimposed so well. For the 2^{nd} extrusion the storage modulus shows higher values compared to virgin PP and 1^{st} extrusion PP at low frequency. Fig. 2 shows the Cole-Cole plots of the virgin PP, 1^{st} extrusion PP, and 2^{nd} extrusion PP. For the virgin PP and 1^{st} extrusion PP, it can be shown the single relaxation process. For the 2^{nd} extrusion PP, another relaxation process at low frequency is observed. The second relaxation at low frequency for 2^{nd} extrusion PP is thought to correspond to the increase of storage modulus at low frequency. This elastic properties and long time relaxation process at low frequency might be come from the chain-scission of PP during the extrusion.

Fig. 3 shows the Cole-Cole plots of the virgin PP, 1^{st} extrusion PP and 2^{nd} extrusion PP at 220 °C. It is observed that the single relaxation process for virgin PP and 1^{st} extrusion PP and another second relaxation process at low frequency for 2^{nd} extrusion PP. Fig. 4 shows the Cole-Cole plots of the virgin PP, 1^{st} extrusion PP and 2^{nd} extrusion PP at 240 °C. Compared to Fig. 2 and Fig.3, the unexpected rheological behaviors is observed of 1^{st} extrusion PP. The 1^{st} extrusion shows another relaxation process at the low frequency. This unexpected second relaxation process might be come from annealing effects of PP chain scission during the dynamic oscillation test. To get the activation energy (E_a), the Arrhenius relation is introduced :

$$a_T = \exp[\frac{E_a}{R}(\frac{1}{T} - \frac{1}{T_0})] \qquad (1)$$

where, a_T is the shift factor, R is the gas constant, and T_o is the reference temperature (In this study, T_o is 200°C).

For the virgin PP, the activation energy calculated from 220 and 240°C shows 36.0 and

35.0KJ/mol, respectively. It is thought that the activation energy calculated from different temperature is the same value in the experimental error extent. For the virgin PP, the time-temperature superposition is also valid (This result is omitted). This result is consistent with the single relaxation process of the virgin PP for 200, 220 and 240°C and the virgin PP shows the "thermorheologically simple behavior". For the 1^{st} extrusion and 2^{nd} extrusion PP, the activation energy calculated from 220 and 240°C are 34.6, 16.6 KJ/mol (1^{st} extrusion), 27.9 and 18.7 KJ/mol (2^{nd} extrusion), respectively. From this result, the 1^{st} extrusion and 2^{nd} extrusion PP shows "thermorheologically complex behavior".

To better understand of the unexpected relaxation process of 1^{st} extrusion PP at 240°C, the annealing experiment was underdone. Fig 5 shows the Cole-Cole plot of non-annealing 1^{st} extrusion PP and annealing for 5 minutes at 240°C 1^{st} extrusion PP at 220 °C. For the annealing 1^{st} extrusion PP shows another relaxation process at low frequency and this results consistent with the assumption that chain-scission is occurred during the dynamic oscillation test at 240 °C.

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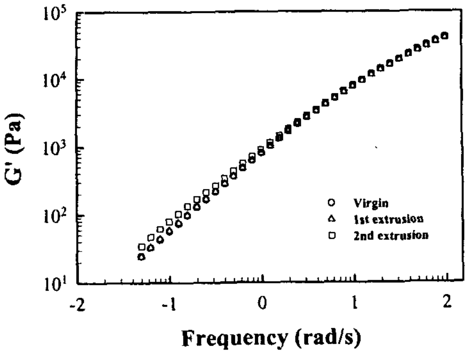

Fig. 1. Storage modulus of the virgin PP, 1st extrusion PP, and 2nd extrusion PP at 200°C.

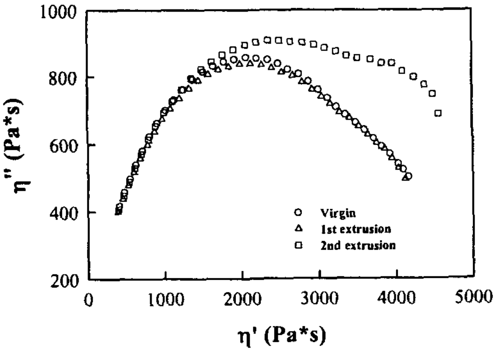

Fig. 2. Cole-Cole plots of the virgin PP, 1st extrusion PP, and 2nd extrusion PP at 200°C

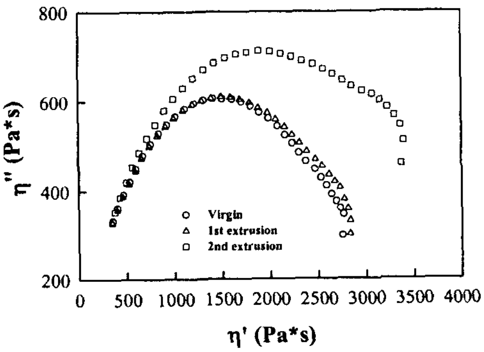

Fig. 3. Cole-Cole plots of the virgin PP, 1st extrusion PP, and 2nd extrusion PP at 220°C.

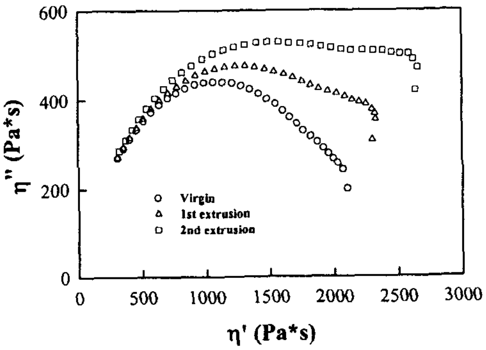

Fig. 4. Cole-Cole plots of the virgin PP, 1st extrusion PP, and 2nd extrusion PP at 240°C.

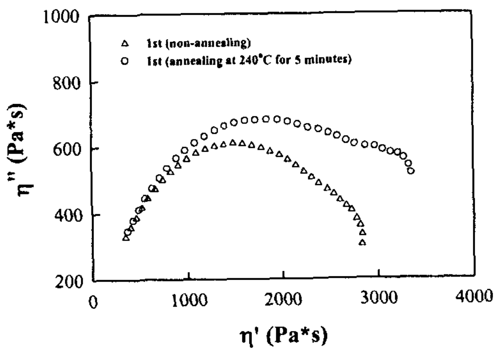

Fig. 5. Cole-Cole plots of the non-annealing and annealing for 5 minutes at 240°C 1st extrusion PP at 220°C.