

긴 결가지를 가진 폴리프로필렌 수지의 유변특성

유제현, 이재욱, 남기준*, 김정호*
서강대학교 화학공학과 유변공정연구센터
(주)효성 화학연구소*

Rheological characterization of the long chain branched polypropylene

J. H. Yoo, J. W. Lee, G. J. Nam*, J. H. Kim*
Applied Rheology Center, Dept. of Chem. Eng., Sogang University
R&D Center for Chemical Technology, Hyosung Corp.*

Introduction

Although Polypropylene(PP) has many useful properties, its melt strength is low and it exhibits no strain hardening behavior in the melt state. This is due to its linear chain structure, which is a direct result of the Ziegler-Natta polymerization method used for its production. Thus, its uses have been limited in applications requiring high melt strength, such as blow molding, extrusion coating and thermoforming. It is well known that the introduction of long-chain branching onto the PP backbone may be one of the alternatives to improve its melt strength shortcoming. Several possible methods have been introduced to branching PP and the most widely used methods are high-energy radiation and through the recombination reaction with a polyfunctional monomer in the presence of a peroxide[1-7].

We would like to present here the rheological property differences of the polypropylenes, which are due to the differences of molecular structure. Some characteristic behaviors, such as strain-hardening, are analyzed and the results will be discussed with regard to the molecular structure.

Experiment

Two PP samples of different molecular structure were characterized and their thermal and rheological behaviors have been investigated in shear and uniaxial extension. One is conventional homo PP(PP-1, $M_w=260000$, $MWD=8.2$) and the other is long chain branched PP(PP-2, $M_w=250000$, $MWD=8.5$), which were supplied by Hyosung Corporation. PP-2 has been made by a reactive extrusion process. Gel content was determined by Soxhlet extraction in boiling xylene for 24 hours and it was observed that no significant macrogel amount was formed in both PP.

Thermal characteristics of the polymers were measured using a Differential Scanning Calorimeter at a heating and cooling rate of $10^\circ\text{C}/\text{min}$. The melting and crystallization temperature were compared. Dynamic rheological measurements were carried out on a ARES (Rheometric scientific) using a parallel-plate geometry. Test temperature was 190°C , strain amplitude 10%, and the frequency ranges from 0.01 to 500. The tensile stress growth

coefficient(η_E') was measured in a silicone oil bath using a Meissner-type rheometer. Rod-like samples with diameter 3 mm and length of 180 mm were prepared by using a capillary rheometer(Toyoseiki, Capilograph). The measuring temperature was set to 190°C and the elongation rate was varied from 0.05 to 0.3.

Melt tension was measured by a Capilograph having orifice of 2.095 mm diameter at 230°C. Extrusion rate was 20 mm/min and take up velocity was 3.14 m/min. The melt tension value of PP-2 is 10.5 gf while that of PP-1 is 1.5 gf.

The sagging degree was compared to measure the thermoformability of both polymers. Test samples were prepared by compression molding and the dimensions of the sample strip were 1 x 20 x 200 mm(thickness x width x length). Tests were performed by clamping both side of the sample strip in an air circulating oven at various temperatures and the amount of sag at the center of the sheet was checked with time.

Results and Discussion

Figure 1 shows the result of melting behavior. Both PPs have similar T_m value but PP-2 shows somehow lower and broader T_m peak. This is maybe due to the introduction of chain defects and irregularity induced by the branching and grafting[5]. The level of crystallinity, which can be reflected by the heat of fusion is further reduced by the introduction of non-crystallizing structure in the chains. Crystallization peak is shown in Fig. 2. PP-2 has T_c of 124°C while that of PP-1 is 108°C. The introduction of branching or crosslinking unit considerably increases the nucleation density of polypropylene and it accelerates the crystallization[8].

Figure 3 and Fig. 4 represent the results of the complex viscosities and modulus from dynamic test. For the branched sample PP-2, there is a prominent yield behavior in complex viscosity at low frequency range. Also the connected structure increases the relaxation time of the branched PP-2 and it increases the dynamic modulus.

Figure 5 shows elongational viscosities with various strain rates at 190°C for both PP. The elongational viscosity of the PP-1 is substantially linear and slightly changed at different strain rates because it is straight chain, while for the PP-2, the elongational viscosity is nonlinear with time. As the strain rate increases(0.2, 0.3 s⁻¹), elongational viscosity increases more rapidly at an earlier stage. On the contrary, slower elongational rate such as 0.05 and 0.1 s⁻¹ give higher elongational viscosity at a later stage than the faster strain rate. Low density polyethylene has the same properties[9]. Some viscoelastic rheological models will be introduced to characterize the elongational deformation properties in the presentation.

Finally, sagging test results are plotted in Fig. 6. Test temperature was 170°C. PP-2 shows far less sagging length than PP-1.

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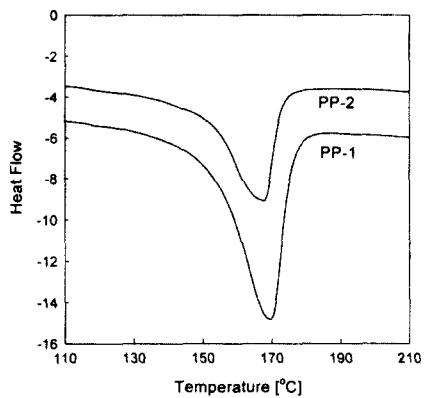


Fig. 1. DSC melting behavior of the two PPs.

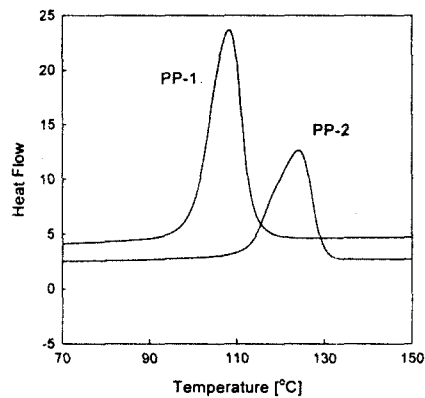


Fig. 2. DSC cooling behavior of the two PPs.

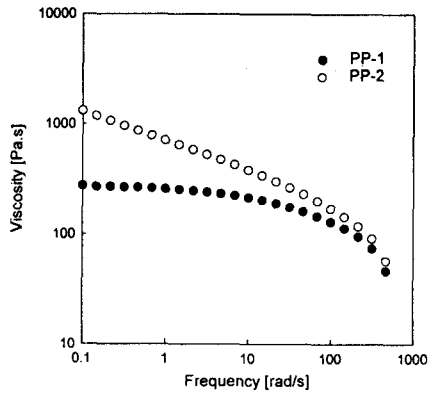


Fig. 3. Complex viscosities of the two PPs.

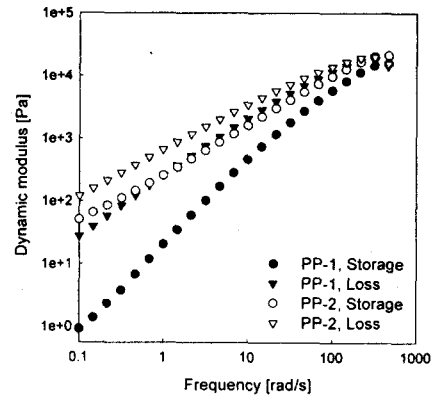


Fig. 4. Dynamic modulus of the two PPs.

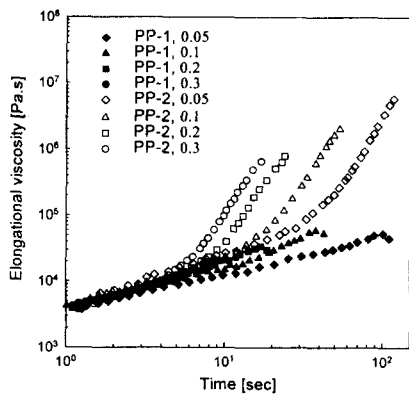


Fig. 5. Elongational viscosity of two PPs at different elongational rates.

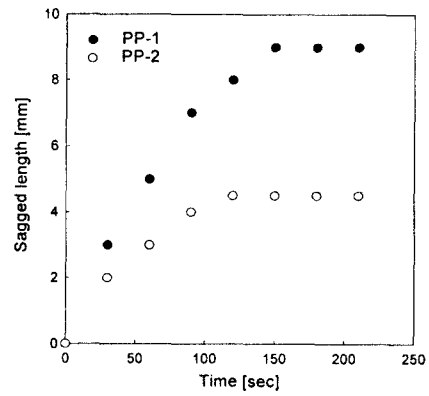


Fig. 6. Comparison of sagged length