

Effect of chain structure of polypropylenes on the melt flow behavior

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Abstract

Rheological Properties of polypropylenes having different molecular structures (linear polypropylene (PPL) and branched one (PPB)) were studied. Both the extensional flow and oscillatory shear flow properties were checked. Especially, the melt strength of polypropylenes having various shear history were investigated by using in-house-made Rheometer (called SMER). Compared to linear polypropylene, the branched polypropylene shows enhanced melt strength during extensional flow due to the retarded relaxation of molecules. When the slope of melt tension was plotted against take up speed of melt strand, the characteristic peak was observed in case of branched polypropylene, while the linear polypropylene shows only monotonously decreasing pattern. This entanglement was partially disrupted by physical forces such as shear during melt extrusion. However, the melt strength of PPB after multiple extrusion is still higher than PPL, implying the loss of elasticity during multiple extrusion is not so comprehensive. On dynamic experiments, PPB shows typical shear thinning behavior and the tangent delta of PPB is lower than PPL, reflecting high elasticity of PPB.

1. Introduction

Polypropylene has been increasingly used for many applications such as packaging films, injection molding, fiber, blow, sheet, covering virtually all application fields of thermoplastics (Kocsis, 1995; Maak, 2000). Behind the apparently far extending use of the polypropylene, there remains still drawbacks to be overcome by polypropylene manufactures. One of them is inferiority in melt strength, which denotes the resistance of polymer melt to the deformation or flow when exposed to the extensional flow. The poor melt strength causes too early rupture of gas bubble during foaming, interfering with reaching fine and homogeneous cell structure, one of crucial factors for getting low density foamed products. Another example of poor melt strength of PP is sagging of webs during the profile extrusion and sheet forming (Park et al., 1999). The sagging narrows the processing windows of materials and limits the thickness or specific weights of products because too heavy weight product profile leads to severe sagging of polymer melts during forming process (Bradley, 1990).

It is well understood that the low melt strength of polypropylene is due to its linear characteristics of molecules and relatively low glass transition temperature, around 0°C, compared to its conventional processing tem-

peratures, ranging from 200°C to 280°C. Many PP Manufacturers has been trying to enhance the melt strength of polypropylene by adding some source of knots or entanglements. Various methods are disclosed and discussed in literature (Phillips et al., 1992; Panzer, 1998; Shimomura, 1999). To mention just a few, the introduction of branching (or ladder structure) on the main backbone of polypropylene is one example. The method of branching can be through the free radical generation at low temperatures with electron beam radiation or chemical agent. Other method to be addressed is mixing an ultra-high molecular weight moiety with linear polypropylene during, so called, prepolymerization stage of polypropylene with Ziegler Natta Catalyst. The high molecular weight material plays a role as a tie molecule to retard the relaxation of polypropylene chains in the melt.

In this article, two types of polypropylenes were prepared for studying the effect of chain structures of polypropylene on the melt flow behavior. One has branch structure while the other one is linear polypropylene. Both extensional flow and shear flow was applied to the resin for better understanding the influences of molecular structure on the melt flow of polypropylene.

2. Experimental

2.1. Material preparation

For preparing the branched polypropylene (designated as

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Table 1. Material characterization results of polypropylenes

Material	Code	MFR dg/min	Mn g/mol	MWD	T_m/T_c °C	Die Swell
Linear PP	PPL	1.5	54,900	5.5	162.0/106.6	1.7
Branched PP	PPB	1.8	52,000	6.2	162.0/106.5	2.6

PPB), we used the in-reactor technology, it means, creating the branched site on the linear backbone during the polymerization stage of polymer in reactor. The reaction temperature is around 75°C in bulk state. For linear polypropylene (designated as PPL), a commercial grade from SGJ plant having the similar MI as PPB was chosen.

2.2. Molecular characterization

The material characteristics of two polypropylenes are summarized in Table 1. The melt flow index (MI) was measured by using MI indexer according to the ASTM D 1238. The bore diameter is 2.095 mm (0.0825 inch) and its length is 8 mm (0.315 mm), with L/D of 3.82. The measuring temperature is 230°C. Die swell ratio (DSR value) was also calculated through dividing the diameter of the melt strand by the bore diameter. The diameter of the melt strand coming out from the die hole of MI indexer was measured for DSR value. The molecular weight (Mw) and molecular weight distribution (MWD) was measured with gel permeation chromatograph (GPC) at 135°C. Decaline was used as a carrier solvent. To observe thermal transition of polymers, DSC (Differential Scanning Calorimeter) was used. The heating and cooling rate was kept as 10°C/min. The samples were heated from room temperature to 220°C, then kept five minutes to get homogeneous melting, then cooled to room temperature. The exotherm of thermogram on cooling was recorded and the peak point of thermogram was taken as crystallization temperature (T_c). And then, the sample was heated again and the observed thermogram was also recorded. The peak point of melting endotherm was taken as melting temperature (T_m)

2.3. Melt Flow Behavior

For measuring the melt tension of polymer, we have devised an extensional rheometer (what Samsung calls, SMER Rheometer) as shown in Fig. 1. The basic units are composed of four parts: Capillary column for melting and extruding the resin through the die, take up wheel for stretching the melt strand after coming out from die, load cell detecting the level of forces imposed on the strand for keeping continuous spinning of the melt, DS (Data Processing System) A for converting the analogue signal to digitized value. A servo Motor (AC) was installed for controlling the acceleration rate of take-up speed. Additionally, A heating chamber was installed to prevent the rapid air quenching of the melt strand while measuring the melt vis-

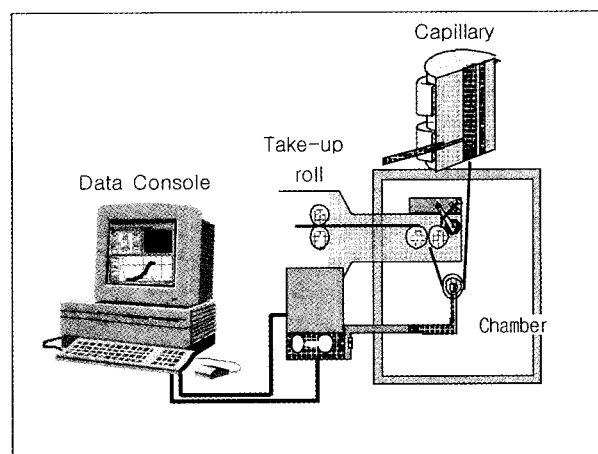


Fig. 1. The schematic drawing of SMER Rheometer for melt strength measurements.

cosity and tension so that the interference of temperature change during the data acquisition minimized.

Typical experiments conditions are as the followings.

Spinline : 300 mm, Chamber temperature : 130°C (PP), 80°C (PE)

Piston speed : 10 mm/sec

Wheel Acceleration rate: 1 mm/sec (PP), 2 mm/sec (PE)

Die geometry : Circular Die, L/D = 32/2

Melt temperatures : 200°C (PP), 180°C (PE)

To study the effect of shear history on the entanglements of polypropylenes, multiple pass extrusion was performed with a twin screw extruder (TSE) having kneading block segments on its screw configuration.

TSE : corrotating, intermeshing type, Diameter : 30 mm, L/D = 28.5

For understanding the melt flow behavior under oscillatory shear flow, RDS (Rheometrics Dynamic Spectrometer) was used. Before applying the oscillatory flow sweep, the Hookean linear viscoelastic regime was determined by measuring the shear modulus as a function of strain. The applied strain is from 5 to 15 units depending on the torque value of the data. The parallel plate (Dia 25 mm, Gap distance 2 mm) was used.

3. Results and Discussion

Due to low concentration of branched structure, it is very

difficult to get the clear picture of branch structure of polypropylene (PPB) by using conventional method. With NMR (Nuclear Magnetic Resonance), the branch frequency of PPB is estimated around 1 branch site per 1000 carbons assuming every tertiary carbon signal detected in NMR originates from branch point. However, one can postulate other possible structures of PPB such as ladder, partial network, et cetera. In other words, the structure of PPB may not be simple so that it contains certain complicated structures as well as branches.

Before getting into the polypropylene experiments, two exemplary PE samples having markedly different molecular structure chosen for control samples. One is low density polyethylene (LDPE, MI = 5.3 dg/min) having long branches and the other one is linear low density polyeth-

ylene (LLDPE, MI = 0.6 dg/min). The typical melt strength patterns of two PE samples having different structure are shown in Fig. 2. The similar results were published in literature (Ghijssels et al., 1992; Yan and co-workers, 1999; Panzer, 1998). As take-up speed of strand increases, the melt strength (or tension) also increases (Fig. 2-A). When compared the level of melt strength between two polymers, LDPE shows higher melt strength than the LLDPE. It should be pointed out that the MI value of LDPE is greater than LLDPE. Therefore, the observed difference between two PEs is of entanglement origin rather than molecular weight itself.

LDPE contains long branches while LLDPE has only short branches so that the long branches of LDPE induce more chain entanglements in melt state, contributing to enhancing the melt strength over LLDPE. Apart from the difference of melt strength level, the melt growth pattern of two polymers is also totally different. The melt strength curve of LDPE shows strain hardening as manifested by

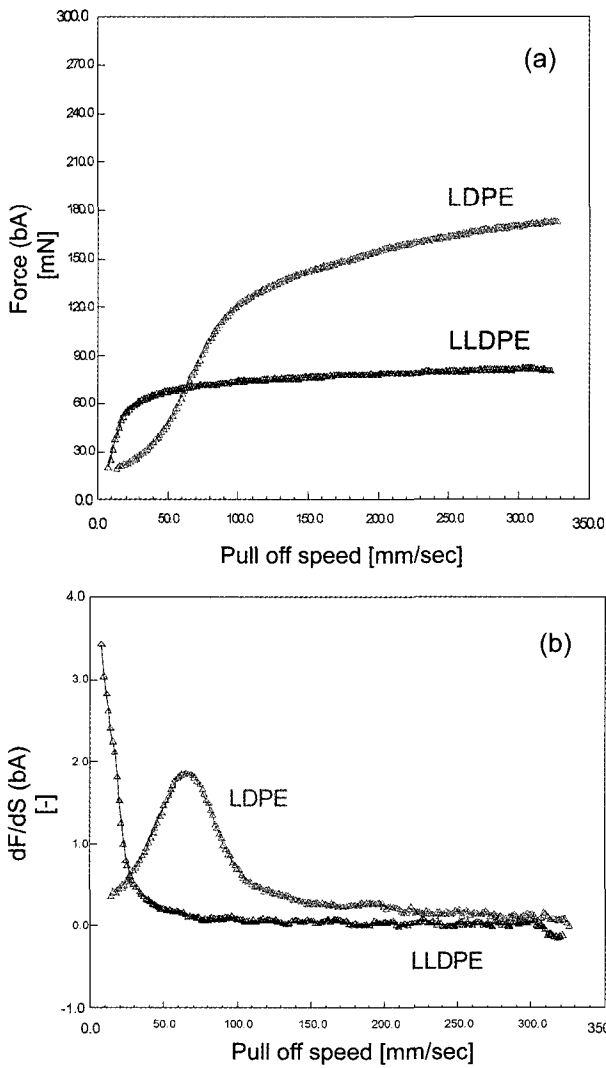


Fig. 2. (a) Melt tension versus take up speed for LDPE (MI = 5.3 dg/min) and LLDPE (MI = 0.6 dg/min), (b) The derivative of melt tension versus take up speed for LDPE (MI = 5.3 dg/min) and LLDPE (MI = 0.6 dg/min).

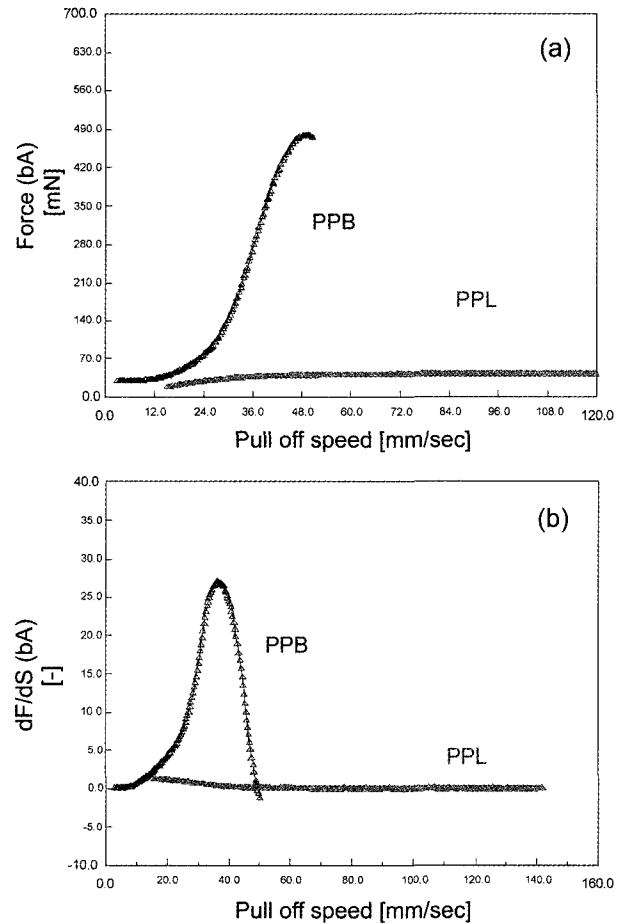


Fig. 3. (a) Melt tension versus take up speed for Polypropylenes PPB (MI = 1.8 dg/min) and PPL (MI = 1.5 dg/min), (b) The derivative of melt tension versus take up speed for Polypropylenes PPB (MI = 1.8 dg/min) and PPL (MI = 1.5 dg/min).

the increasing slope of the curve while LLDPE shows monotonous decrease of slope (Fig. 2-B). Upon passing the certain level of take up speed, however, the slope of LDPE curve in Fig. 2-B shows monotonously decreasing patterns like LLDPE.

Fig. 3-A shows the melt strength profile of two polypropylenes (designated as PPL and PPB). As in the case of PE experiments, PPL and PPB shows very different patterns depending on the molecular structures of each polymer. Compared to PPL (linear polypropylene), PPB (branched polypropylene) shows higher melt strength over all take up speed. Also, when the derivative of melt tension over take up speed is plotted (Fig. 3-B), the slope initially increases as the speed increases, then reaching a maximum, and then decreases, similar pattern as LDPE having long branches. Prior to interpreting the different melt tension patterns of each polymer, the basic principles of spinning of melt strand will be briefly reviewed (Han 1976; Wagner 1996). The measured tension, F depends on several variables such as polymer properties, the geometry of die, die land, spin line as well as the processing conditions (e.g. melt temperature (T), pressure (P), draw ratio (V) etc). Under the steady state conditions, this can be expressed as

$$F = F(De, V) \quad (1)$$

where De (Deborah Number) means the ratio of the characteristic material response time scale to the characteristic processing time scale. The material time scale can be identified as the relaxation time of polymer melt. The characteristic processing time (t_{pz}) may be taken as a time for a polymer melt to flow through the spinline (L_0) with velocity (v_0). Then the Deborah number can be expressed as

$$De_i(P, T) = \frac{t_i}{t_{pz}} = \frac{\lambda_i(T)}{(L_0/v_0(P, T))} \quad (2)$$

In the viewpoint of Equation 2, as the relaxation of the molecules retards, the De number decreases, leading to increased tension in the melt strand. In case of LDPE, the relaxation time is longer than the LLDPE having no long branch due to the entanglement effect of long-branch. The similar interpretation may be possible for the results of polypropylenes. The branched polypropylene (PPB) having more entanglement sites in molecules gives longer relaxation time than the linear polypropylene (PPL). The maximum point in Fig. 3-B may be understood as the point where the difference between the stress build up rate in polymer melt and the deformation rate reaches its peak. Fig. 4 shows the shear viscosity profile of polypropylenes under oscillatory flow. Compared to the linear polypropylene (PPL), branched PP (PPB) shows clearly shear thinning pattern. This can be understood in two aspects. First, MWD (molecular weight distribution) value of PPB is

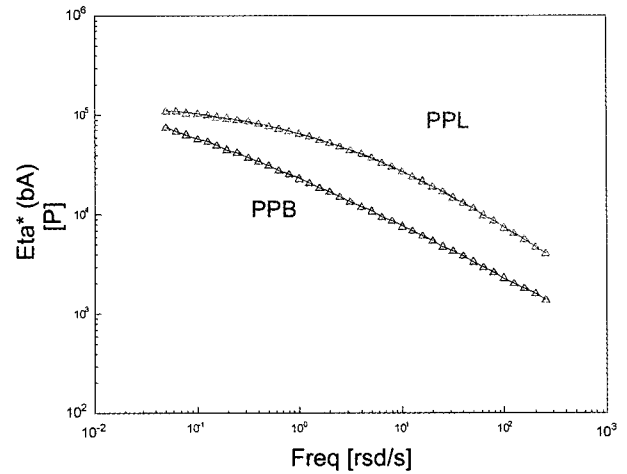


Fig. 4. The complex viscosity versus frequency for Polypropylenes PPB (MI = 1.8 dg/min) and PPL (MI = 1.5 dg/min).

broader than the PPL (Table 1). Second, the knots or entanglements in PPB also contribute to the shear-thinning pattern. It is, however, very difficult to separate contribution of each factor.

In oscillatory measurements of polymer melt flow, $\tan \delta$ has been used by many people for characterizing the elasticity of polymer (Yu, 1999; Park, 1999).

$$\tan \delta = \frac{G''}{G'} \quad (3)$$

It is the relative ratio of viscous shear modulus (G'') to elastic shear modulus (G') so that the lower value means the elasticity contributes more to the complex shear modulus than the viscous damping.

As clearly seen in Fig. 5, at low frequency regime (ca. smaller than 10 rad/sec), the $\tan \delta$ of PPB is smaller than the one of PPL but at high frequency region, the value

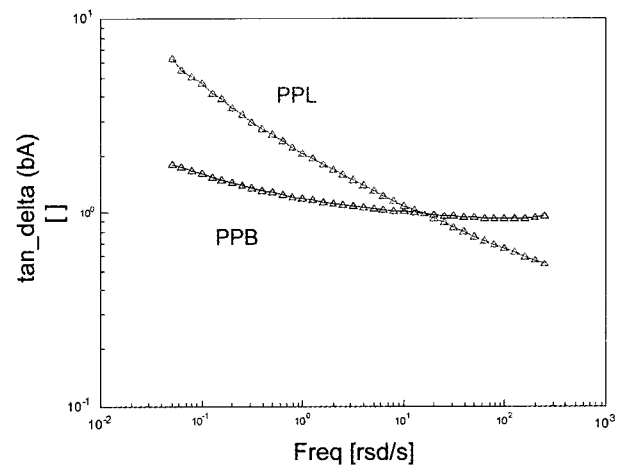


Fig. 5. The tangent delta versus frequency for Polypropylenes PPB (MI = 1.8 dg/min) and PPL (MI = 1.5 dg/min).

crosses over, resulting in a greater value of $\tan\delta$ than PPL. Considering the greater melt strength of PPB over whole take up speed range already observed under extensional flow mode, the cross-over of $\tan\delta$ of two polymers under oscillatory flow is interesting. It means, in a sense, the contribution of material elasticity on the flow properties not only depends on the flow rate but also flow field types, that is, extensional flow or shear flow.

To study the effect of shear flow history on the possible entanglement structure of PPB, multiple extrusion of PPB was performed. As mentioned the experimental section, a twin screw extruder ($L/D = 28$, Dia = 30 mm) was used. The mean residence time was around 80 sec. The material characterization results including molecular weight before and after the extrusion are listed in Table 2. The MI value of PPB, after twin screw extrusion, increased by more than two folds. Usually the increases in MI value after extrusion is interpreted in terms of chain scission due to thermal and shear cracking during the extrusion. However, this is not the case in this experiment. When checked the molecular weight and MWD of PPB (virgin pellets) and PPB-1 (extruded with TSE two times), the values are virtually the same. In other words, based on GPC results, any noticeable chain scission did not happen. It should be pointed out that before extrusion, plenty amount of antioxidants was dosed

Table 2. Material characterization results of polypropylenes before and after multiple extrusions

Material	Code	MFR dg/min	Mn g/mol	MWD	Die Swell
Branched PP (virgin)	PPB	2.0	65,400	4.7	2.8
Branched PP (second extrusion)	PPB-1	5.2	66,000	4.7	2.4

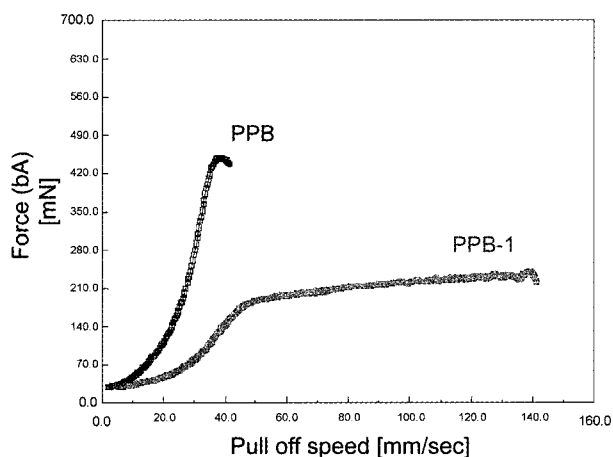


Fig. 6. The melt tension versus take up speed for polypropylenes having different Shear history PPB: virgin pellet, PPB-1: extruded with TSE.

to minimize the possible degradation. Fig. 6 shows the melt strength profile of PPB and PPB-1. In contrast to virtually the same values of the molecular weight and MWD of two polypropylenes in this experiment, the melt strength patterns are totally different. After the TSE extrusion of PPB, the melt strength significantly decreased, reflecting the partial loss of elasticity during the extrusion. It may be interpreted as the disentanglement of melt network by shear during extrusion.

It is evident that the elasticity of PPB, induced by chemical modification of linear polypropylenes is of physical nature so that it can be disentangled by external forces such as shear. The change in DSR (die swell ratio) value (Table 2) is also noteworthy, which indicates the possible change in elastic structure of PPB. However, the melt strength of PPB after multiple extrusion is still higher than PPL, implying the loss of elasticity during multiple extrusion is not so comprehensive. Therefore, although the disentanglement of PPB happens but still it retains part of network, resulting in still greater melt strength over PPL.

4. Concluding Remarks

The high melt strength of branched polypropylenes is strong advantage for extending their potential uses in industrial fields such as blow and thermoforming. According to this study, however, the rheological properties of branched polypropylene are very sensitive to the processing conditions such as flow type and shear history. Although the structure of branched PP is hard to pinpoint, The theoretical study on the rheological properties of the complicated polypropylenes is very important. Also, for securing consistently enhanced elasticity over broad processing conditions, incorporation of stronger network sources into polypropylene will be studied for future works.

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