Impact of processing history on rheological properties for branched polypropylene

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Abstract

The impact of applied processing history and the post-processing annealing procedure on the rheological properties of long-chain branched polypropylene (B-PP) have been studied intensively as compared with conventional linear polypropylene (L-PP) and low-density polyethylene (LDPE) produced by autoclave process. It was found that drawdown force, as a measure of melt elasticity for B-PP, is greatly depressed even by the short-time processing in an internal batch mixer, whereas the rheological properties of L-PP are unchanged by the processing history. Considering that the drawdown force is recovered to the original value during the post-processing annealing, the phenomenon is ascribed to the conformation change related to the branch structure, i.e. the alignment of long branches to a backbone chain, which is known as 'shear modification'. Further, it is demonstrated that the depression of the drawdown force for B-PP is more significant than that for LDPE. Moreover, it is also clarified that B-PP needs a longer post-processing annealing time to recover the drawdown force than LDPE. The difference in the recovery curves during the annealing suggests that B-PP has less relatively 'short' long branches.
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1. Introduction

It is widely accepted that isotactic polypropylene (PP) is one of the most important synthetic polymeric materials these days. The amount of the usage is still growing on the order of 6% per year because of the superior properties, such as excellent heat-resistance and stiffness, as well as the advantage of the cost performance. There are, however, still some problems for PP. One of the biggest problems is the lack of melt elasticity, which is ascribed to the linear structure of molecules. Because of the poor melt elasticity, the processing methods and thus the application for PP are sometimes limited in spite of the excellent mechanical properties. Therefore, considerable effort has been carried out to enhance the melt elasticity of PP.

Yamaguchi and Miyata have found that mixing with the critical gel whose molecular segment is miscible with PP leads to anomalously prominent strain-hardening in elongational viscosity as well as the marked swell ratio of extrudates, even though the amount of blend ratio is less than 3 wt% [1,2]. Since the viscous properties are hardly changed by mixing the gel, the technique would be widely available for various linear polymers [3,4].

Kolodka et al. have studied the rheological properties of the copolymers composed of ethylene–propylene macromonomer and propylene, and found that activation energy of the obtained graft copolymer, 51 kJ/mol, is higher than that of a conventional linear PP, about 40 kJ/mol [5]. Ye et al. also prepared the PP with long-chain branches by copolymerization of propylene and nonconjugated dienes by means of metallocene catalyst [6].

Further, the modification technique by peroxide and/or radiation has been studied extensively [7–14]. Such kind of PP is called high-melt-strength (HMS) PP, which is commercially available in a decade. HMS-PP shows good processability for various processing operations because of the enhanced strain-hardening in elongational viscosity. The origin of the marked strain-hardening is considered to be long-chain branches, although few papers characterize the branch structure [9,10]. Further, processability of various processing operations, such as extrusion foaming [11,12], thermoforming [13], and extrusion coating [14], has been investigated intensively for HMS-PP from the viewpoints of industrial application.

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The role of long-chain branches on the rheological and thus processability is well understood in a low-density polyethylene produced by radical polymerization. Because of the excellent processability, a low-density polyethylene has still a large share of polyethylene market irrespective of the poor mechanical properties compared with linear low-density polyethylene. The existence of long-chain branches, however, leads to 'shear modification', which is known as the rheological change by the processing, i.e. straining, operation as well as the thermal history [15–21]. For example, processing history in a single-screw extruder prior to forming depresses the melt elasticity to a great extent for a low-density polyethylene, especially, produced by autoclave process [19–22]. Therefore, understanding the modification of rheological properties in the extruder is required for the discussion on the relation with processability. In other words, processability can be controlled by the extrusion system as demonstrated by Yamaguchi et al. [20,21]. According to them, the low-density polyethylene extruded by a conventional full-flight screw configuration depresses the melt elasticity, although it can be extruded at a high out-put rate without gross melt fracture. On the other hand, the one extruded by kneading elements shows high melt elasticity, whereas it shows gross melt fracture leading to the reduction of the out-put rate at extrusion. The depression of melt elasticity, such as strain-hardening in elongational viscosity, is considered to be ascribed to the conformation change by the molecular orientation of branch part along to the backbone [16,18].

Because of the impact on the processability as demonstrated, shear modification behavior has to be comprehended when employing a branched polymer. As for HMS-PP, however, it has not been studied get to the best of our knowledge. In this study, we have clarified the importance of processing history, i.e. so-called shear modification phenomenon, for a commercially available branched polypropylene as compared with a linear PP and a low-density polyethylene produced by autoclave process, with the evaluation of the branch structure by dilute solution properties.

2. Experimental section

2.1. Materials

A branched polypropylene (B-PP), a linear polypropylene (L-PP) and a low-density polyethylene (LDPE) produced in an autoclave reactor were employed in this study. All samples are commercially available; B-PP is Pro-fax high melt strength polypropylene produced by Himont (MFR = 3.0 at 230 °C). Details in L-PP (MFR = 1.0 at 230 °C) and LDPE (MFR = 1.6 at 190 °C) were described in the previous papers [1,19,22–24].

The number- and weight-average molecular weights of B-PP, measured by gel permeation chromatography (GPC), are $M_n = 5.4 \times 10^4$, $M_w = 3.7 \times 10^5$, and $M_w/M_n = 6.9$, respectively, as a linear polypropylene standard, and those of L-PP are as follows; $M_n = 7.6 \times 10^4$, $M_w = 5.0 \times 10^5$, and $M_w/M_n = 6.6$. It was found from FT-IR and NMR measurements that both B-PP and L-PP are propylene homopolymers. NMR measurements

also revealed that the number of long ($\geq$ C6) branches for B-PP is less than 1 per 1000 carbon atoms, whereas that for LDPE is five.

2.2. Processing history

The processing history of B-PP and L-PP was applied by a 60 cm^3 internal batch mixer (Toyoseiki, Labo-Plastomill) at 190 °C under a nitrogen atmosphere at 30 rpm for various residence times with a small amount of thermal stabilizer. The same processing history was applied also for LDPE, but at 160 °C. The processed sample was immediately compressed into a sheet form by a compression-molding machine for 30 s at 130 °C for LDPE or at 190 °C for PP and then plunged into an ice-water bath to freeze the macroscopic molecular motion. Original pellets of each sample were also compressed into a sheet form.

2.3. Measurements

Oscillatory shear modulus and steady-state shear properties, such as shear stress and primary normal stress difference, were measured by a cone-and-plate rheometer (UBM, MR500) at various temperatures under a nitrogen atmosphere. Drawdown force, defined as the force needed for the extension of polymer extrudates at a constant draw ratio, was evaluated as an elastic parameter, because it is suitable to examine the time variation of melt elasticity during the post-processing annealing procedure, as demonstrated by Yamaguchi and Gogos [19]. A capillary rheometer equipped with the capillary die, having 8 mm in length and 2.095 mm in diameter and an entrance angle of π/2, was employed at 190 °C for all samples and at 160 °C for LDPE. In this study, the drawdown force, evaluated at the draw ratio of five, was monitored as a function of the post-processing annealing time t_a, i.e. the residence time in the capillary rheometer, because the rheological properties are dependent on the thermal history during the measurements [19–22]. We defined $t_a = 0$, the time of 2 min after putting the sample into the cylinder.

Dilute solution properties, such as shrinking factors, $g = (\langle R^2 \rangle_{branch}/\langle R^2 \rangle_{linear})$ and $g' (= [\eta]_{branch}/[\eta]_{linear})$, and the b-factor $(= \log[g']/\log[g])$, were evaluated by gel permeation chromatography equipped with a viscometer and a light-scattering apparatus. A linear polypropylene and a high-density polyethylene were employed as linear polymers.

3. Results and discussion

3.1. Viscoelastic properties for original materials

Oscillatory shear moduli for B-PP at 190 °C are plotted in Fig. 1 as compared with those for L-PP represented by solid lines. B-PP shows lower moduli especially in the high frequency region, whereas both materials show similar storage modulus G' in the low frequency region. Moreover, modulus at the cross point, i.e. $G' = G''$, for B-PP is quite lower than that for L-PP. These results indicate that B-PP has broad relaxation spectra. Considering that M_w/M_n is not such different between
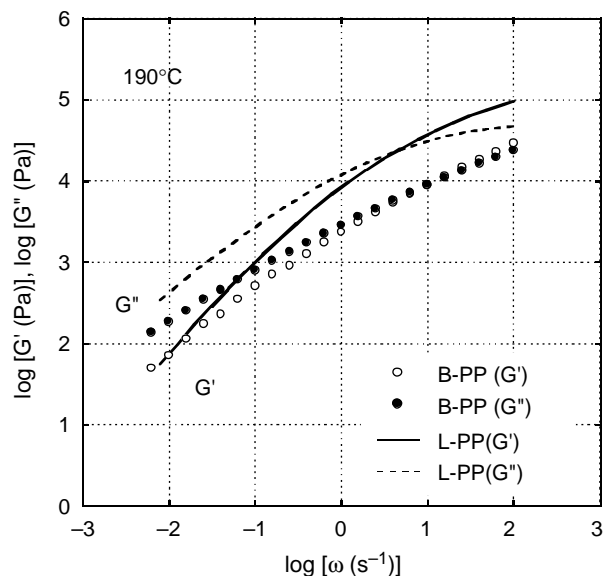
Fig. 1. Oscillatory shear moduli, such as storage modulus (open circle) and loss modulus (closed circle), for B-PP (symbols) as compared with L-PP represented by solid lines at 190 °C.

B-PP and L-PP, the broad relaxation spectra for B-PP is owing to the existence of long-chain branches.

Van Gurp–Palmen plot [24], i.e. loss angle δ versus absolute value of complex modulus G^*, of B-PP, shown in Fig. 2, demonstrates that simple time-temperature superposition principle is not applicable for B-PP, whereas L-PP shows thermorheological simplicity as mentioned in the previous paper [1]. It is interesting to note that a branched polyethylene also shows thermorheological complexity [24–27], whereas a linear polyethylene does not as far as the temperature difference is not so huge. As similar to the reports for branched polyethylene [25–27], low modulus region is found to be more sensitive to temperature also for B-PP.
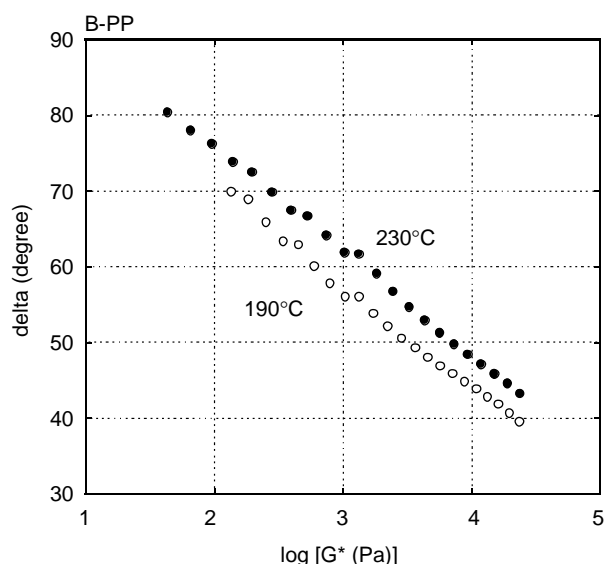

Fig. 2. Van Gurp–Palmen plot, i.e. loss angle versus absolute value of complex modulus G^*, for B-PP at 190 °C (open circles) and 230 °C (closed circles).
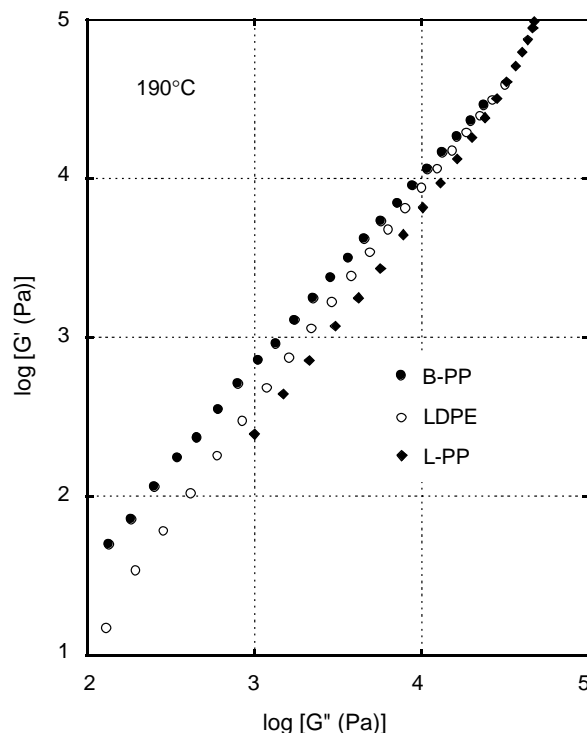

Fig. 3. Shear storage modulus G' versus loss modulus G'' for samples at 190 °C; closed circle B-PP; open circle LDPE; closed diamond L-PP.

The apparent flow activation energy is calculated from the shift factors obtained by different ways. Firstly, we evaluated the shift factor from the master curves in which vertical shift is also considered, and found that activation energy for B-PP is quite high, 95.2 kJ/mol, as compared with that for L-PP, 39.4 kJ/mol. Secondly, the shift factor was evaluated ignoring the vertical shift, which gave the value of 65–75 kJ/mol. The inaccuracy of the activation energy is ascribed to the inaccuracy of the shift factor due to the thermorheological complexity. The value, 65–75 kJ/mol, is still significantly higher than that for L-PP. The difference in flow activation energy between a linear polymer and a branched polymer is also similar to the case of a polyethylene; 25–35 kJ/mol for a linear polyethylene and 50–60 kJ/mol for a branched polyethylene.

Fig. 3 shows the plot of storage modulus G' versus loss modulus G'' for B-PP, L-PP, and LDPE at 190 °C. In the linear viscoelastic region, B-PP shows strong melt elasticity than the others. The result is attributed to the broad distribution of relaxation time as discussed in Fig. 1.

The steady-state properties under shear flow, such as shear stress and primary normal stress difference, for B-PP at 230 °C are shown as a function of shear rate in Fig. 4 with the result of L-PP. The shear stress of L-PP is almost twice as high as that of B-PP. This is reasonable because L-PP has lower MFR, i.e. higher molecular weight, than B-PP. Regarding the primary normal stress difference, however, B-PP exhibits higher values than L-PP, demonstrating that B-PP shows prominent elastic property.
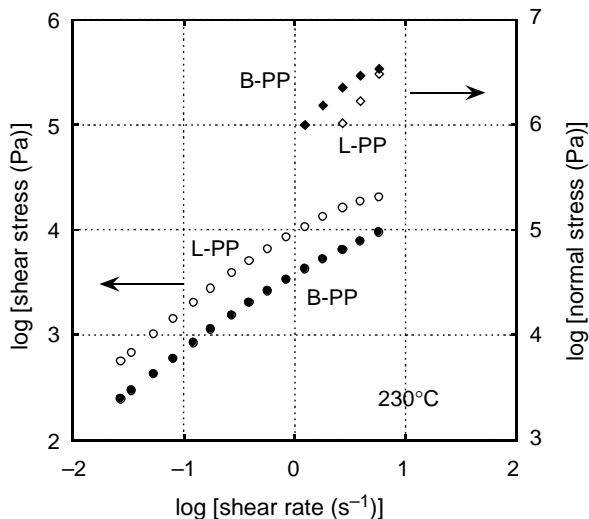
Fig. 4. Shear stress (circles) and primary normal stress difference (diamonds) for B-PP (closed symbols) and L-PP (open symbols) at 230 °C as a function of shear rate.

Fig. 5 shows the absolute value of complex shear viscosity at 160 and 190 °C for LDPE with that for B-PP at 190 °C. In some of the following experiments, rheological properties of B-PP at 190 °C are compared with those of LDPE at 160 °C. As seen in the figure, viscosity of LDPE at 160 °C is higher than that of B-PP at 190 °C, although they seem to be similar values in the very low angular frequency region.

Drawdown force at a draw ratio of five is listed in Table 1 with the apparent flow activation energy for all samples employed. As seen in the table, drawdown force for B-PP is almost twice as high as that for L-PP. Because B-PP shows lower shear viscosity than L-PP, the result indicates the appearance of marked strain-hardening in elongational viscosity for B-PP.

3.2. Processing history of internal mixer

Fig. 6 shows the time variation of the torque and the resin temperature in the internal mixer for B-PP. After taking a maximum, the torque decreases to a steady value. It takes about
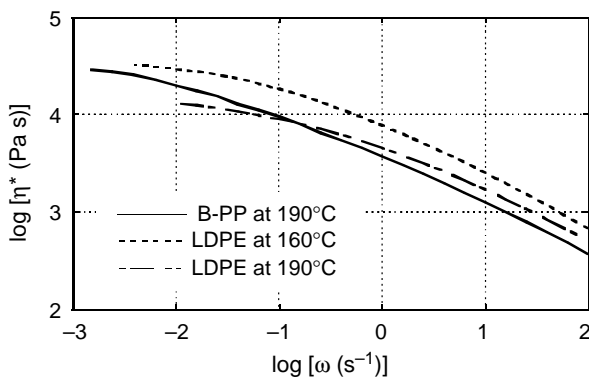
Table 1
Flow activation energy and drawdown force

Sample	Drawdown force (mN)		Flow activation energy (kJ/mol)
	190 °C	160 °C	
B-PP	210	–	65–75,[a] 95.2[b]
L-PP	110	–	39.4
LDPE	145	285	53.4

[a] Horizontal shift only.
[b] Horizontal as well as vertical shift.

120 s to reach the steady-state. The resin temperature is kept around at 190 °C, which is the set temperature, suggesting viscous dissipation can be ignored in this experimental processing machine. The magnitude of a steady torque is as follows; 0.27 kg m for B-PP, 0.95 kg m for L-PP (at 190 °C), and 0.97 kg m for LDPE (at 160 °C). The order in the torque well corresponds with the viscosity at the resin temperature for each material. The magnitude of the torque and the residence time in the mixer are crucial parameters for 'shear modification', because suppression of melt elasticity is decided by the applied stress and the residence time in the processing machine [19]. From the viewpoint of applied stress, LDPE has more intensive processing history than B-PP as far as the processing time in the mixer is the same.

The drawdown force, as a measure of melt elasticity, is evaluated as a function of the post-processing annealing time, i.e. the residence time in the capillary rheometer. Although the drawdown force of L-PP having the processing, i.e. straining, history in the internal batch mixer is the same as that of the original pellet, B-PP is found to be very sensitive to the processing history like LDPE. Fig. 7 exemplifies the growth curves of drawdown force, i.e. the time variation of recovery process of melt elasticity for the B-PP processed by the mixer. Further, the drawdown force for all samples with different processing times in the mixer seems to recover to the same, original value, suggesting that the number of long-chain branches and the molecular weight are unchanged. This is also confirmed by GPC that M_n and M_w are hardly changed by the processing history. Therefore, the rheological modification by the applied processing history as well as the post-processing

Fig. 5. Comparison of absolute value of complex viscosity η^* of B-PP at 190 °C (solid line) with those of LDPE at 160 °C (dotted line) and at 190 °C (dashed-and-dotted line) plotted against the angular frequency ω.
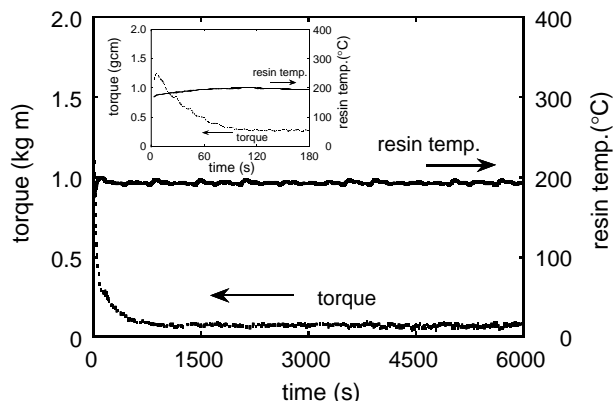

Fig. 6. Time variation of torque and resin temperature in the internal batch mixer for B-PP. The set temperature is 190 °C.
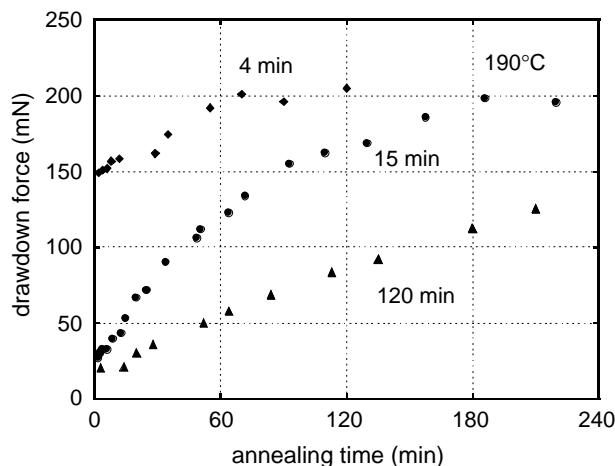
Fig. 7. Growth curves of drawdown force during the post-processing annealing procedure for the samples processed by the internal mixer for 4 min (diamond), 15 min (circle) and 120 min (triangle) at 190 °C.

annealing procedure is not originated from the molecular scission and/or crosslink reaction, but from the conformation change of molecules as similar to the case of a low-density polyethylene [16,18,21].

Moreover, it was found that the drawdown force at $t_a = 0$ is significantly low, which is even lower than that for L-PP (110 mN). Further, only 4 min processing depresses the drawdown force to a great extent. According to Yamaguchi et al. [20], 15 min-processing-history in the internal batch mixer has the almost same effect as a single-screw extrusion on the depression of melt elasticity for the LDPE. Further, several researchers have demonstrated that such kind of processing history greatly affects the post-die processing, such as the surface irregularity of extrudates and drawability [15–17,20,21]. The results indicate that processability of B-PP could be greatly influenced by processing history in a single-screw extruder prior to the die. Therefore, the relation between rheological properties and processability has to be discussed considering the processing history in a processing machine. Furthermore, careful attention has to be paid for processing machines including screw segments and operating variables from the industrial point of view.

In order to compare the recovery profile, normalized drawdown force, defined as the ratio of the tentative drawdown force to that of the original pellet, is plotted in Fig. 8. The post-processing annealing is performed at 190 °C for both materials. It is clearly shown that normalized drawdown force at $t_a = 0$ for the B-PP is lower than that for the LDPE as far as the processing time is the same. It is interesting results because lower torque is required for B-PP in the mixer. For the better understanding of the slow recovery, the growth curves of normalized drawdown force for the B-PP at 190 °C is plotted with that for the LDPE annealed and measured at 160 °C, in which both samples have 120 min—residence time under the rotation of blades in the mixer. As Fig. 9 shows, it takes a longer time for the B-PP to recover the drawdown force, in spite of the lower viscosity than LDPE at 160 °C.
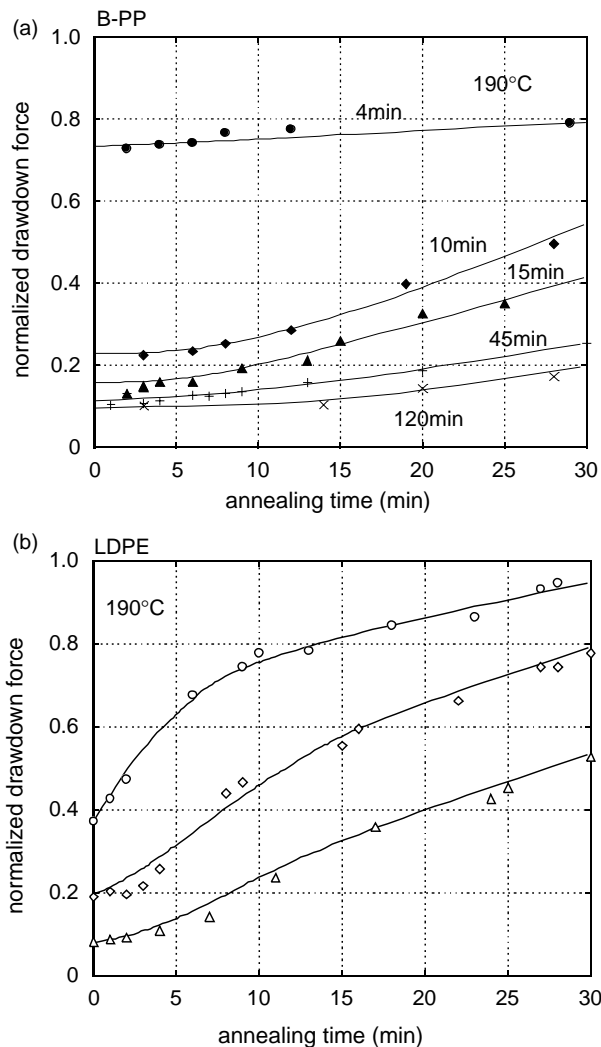

Fig. 8. Normalized drawdown force for B-PP (a) and L-PP (b) as a function of the post-processing annealing time in the capillary rheometer at 190 °C.
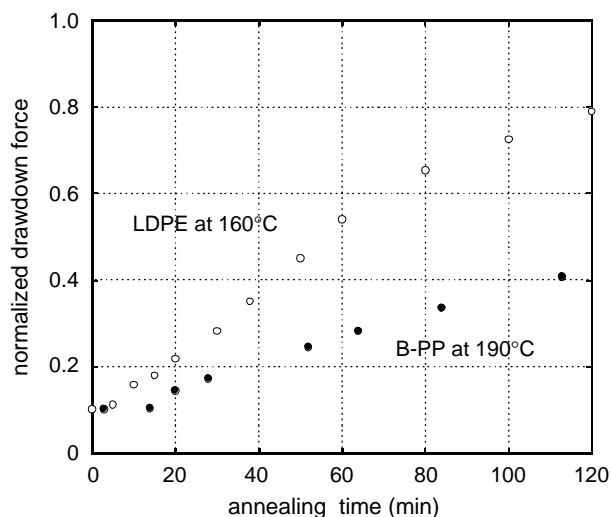

Fig. 9. Normalized drawdown force for B-PP at 190 °C and L-PP at 160 °C as a function of the post-processing annealing time in the capillary rheometer.

The difference in the recovery curve would be ascribed to the branch structure. In other words, the post-processing recovery curves involve the information on the molecular shape. According to Münstedt [16], the alignment of long-chains to a main backbone chain is responsible for the shear modification. Based on the tube model [28], the applied stress drags the branches into the tube of a backbone chain as pointed out by Leblans and Bastiaansen [18]. In the recovery process, therefore, conformation change, i.e. an escape of branch part from the tube of a backbone chain, takes place due to the entropy loss around the branch points. Following the molecular interpretation, taking a long time to recover the drawdown force is ascribed to deep alignment of branch part or alignment of a long branch to the backbone. The idea is similar to the concept that a branched polymer has a long reptation time [28]. Consequently, it can be estimated that LDPE, which shows prompt and prolonged recovery processes in the post-processing annealing, has relatively low-molecular-weight branches, but higher than entanglement molecular weight M_e, as well as high-molecular-weight branches. The relatively 'short' branches are responsible for the initial increment of drawdown force by the recovery of molecular conformation, whereas high-molecular-weight branches are the origin of the slow recovery. Further, hierarchical branch structure could be also responsible for the late process. It is generally accepted from the polymerization process that branch part of LDPE has daughter branches, i.e. hierarchical branch structure. In case, it takes a longer time for the whole branch part to recover to the initial stable conformation. On the other hand, B-PP has less comparatively 'short' long-branches than the conventional autoclave LDPE. Although such discussion here is carried out only qualitatively, further fundamental studies on a model branch polymer could make it possible to predict the magnitude of shear modification and its recovery on the basis of an advanced molecular model.

3.3. Dilute solution properties

As pioneering works performed by Tackx and Tacx [29] and Beer et al. [30] have demonstrated, dilute solution properties as a function of molecular weight give important information on branch structure. In this study, dilute solution properties are also evaluated for the detail characterization of branch structure besides NMR measurements. From the dilute solution properties, the characteristic of branch structure is commonly expressed in terms of Zimm–Stockmayer model [31–33]. According to the model, shrinking factor, g, is defined as the ratio of the radius of gyration of a branched molecule to that of a linear molecule having the same molecular weight. Another shrinking factor, g', is defined as the ratio of the intrinsic viscosities:

$$g = \frac{\langle Rg^2 \rangle_{\text{branch}}}{\langle Rg^2 \rangle_{\text{linear}}}. \tag{1}$$

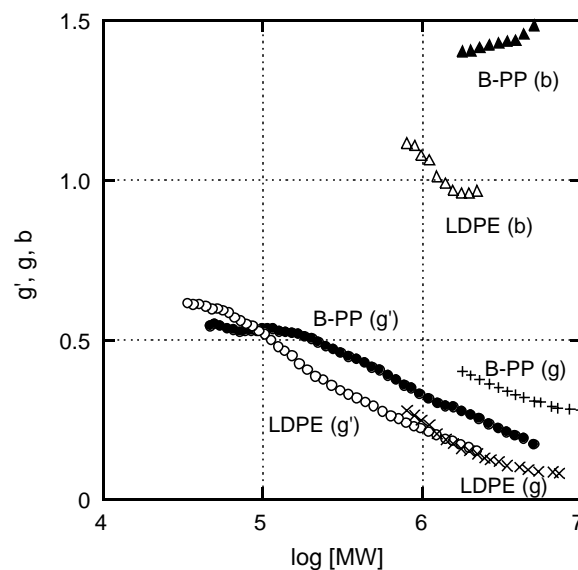$$g' = \frac{[\eta]_{\text{branch}}}{[\eta]_{\text{linear}}}. \tag{2}$$

Fig. 10. Shrinking factors, g and g', and b-parameter as a function of molecular weight; ($\bullet$) g' for B-PP, ($+$) g for B-PP, ($\blacktriangle$) b for B-PP, ($\bigcirc$) g' for LDPE, ($\times$) g for LDPE, and ($\triangle$) b for LDPE.

Moreover, both shrinking factors are connected each other by b-parameter as follows

$$b = \frac{\log g'}{\log g}. \tag{3}$$

where the b-parameter, also called as the drainage factor, gives the information on the shape of molecules; 1.5 for comb-shaped polymers with long distance between neighbor branches and 0.5 for star-shaped polymers [29,31–34]. Further, b-parameter increases with increasing the distance between neighbor branches and decreasing the length of branches, which has been also confirmed by model polyolefins [35].

Fig. 10 shows the shrinking factors and b-parameter for B-PP and LDPE. It is clarified that shrinking factors for both materials are lower than 1, demonstrating both are branched polymers. The deviation from the linear polymer is more prominent for LDPE, i.e. lower shrinking factors. Assuming that both materials have the same branch structure, B-PP has fewer branches than LDPE. Although this seems to be in accordance with the result of NMR measurements, the difference in the number of long branches ($\geq$C6) is too large. As well known, NMR measurements cannot differentiate the length of branches having more than C6. Therefore, it is expected that most long-branches evaluated by NMR are short, i.e. lower molecular weight than M_e, which does not play an important role, at least, on the shear modification behavior.

Further, it is also found that b-parameter for LDPE is lower, suggesting LDPE has more star-like structure. Considering the recovery curves from the processed sample, it is concluded that LDPE has more hierarchical branch structure than B-PP.

Further, it should be worth mentioning that g' for B-PP is lower than that for LDPE in the low molecular weight fraction. The results indicate that even B-PP has relatively 'short' branches as well as long branches.

4. Conclusion

The effect of applied processing, i.e. straining, history on the rheological properties, especially drawdown force as an elastic parameter, for B-PP has been studied as compared with those for L-PP and LDPE. B-PP having broad relaxation spectra depresses the melt elasticity prominently by the applied processing history in an internal batch mixer, whereas the rheological properties of L-PP are unchanged. Further, the rheological change for B-PP is found to be more sensitive than that for autoclave LDPE, in spite of the lower kneading torque for B-PP. Since the molecular weight and the distribution is not affected by the processing history, the depression of melt elasticity is ascribed to 'shear modification', i.e. alignment of long branches to the backbone by the conformation change of molecules. Considering that B-PP shows more prominent 'shear modification' behavior than autoclave LDPE, the processing history even in an extruder prior to the die equipped could affect the processability to a great extent.

Further, it was also found that the recovery process of melt elasticity in the post-processing annealing procedure for B-PP is considerably slow, suggesting that longer branches align to the backbone. As compared with B-PP, LDPE shows prompt recovery to some degree although it takes a long time to fully recover to the initial value. The results suggest that B-PP has less relatively 'short', but longer than M_e, long branches than LDPE. The difference in the recovery process during the post-processing annealing is interpreted, assuming that hierarchical branch structure is more developed for LDPE.

Dilute solution properties indicate that B-PP has less long branches with more comb-shape structure than LDPE. This result also support that LDPE has hierarchical branch structure as compared with B-PP.

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