Effect of Degree of Polymerization on Gelation and Flow Processability of Poly(vinyl chloride)

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ABSTRACT: The effect of degree of polymerization (DP) on the gelation and flow processability of poly(vinyl chloride) (PVC) was studied. Sheets with adjusted degree of gelation were prepared by rolling rigid pipe formulation suspension PVC compounds with DPs of 800, 1050 and 1300 by changing the milling temperature. Their degrees of gelation were measured with DSC and their capillary flow properties were measured with a capillary rheometer at 150, 170 and 190°C and the effect of DP on the relation between gelation and flow processabilities was studied. Because of the higher shearing heat during milling, the sample with the higher DP had a higher history temperature and thus tended to show a higher degree of gelation. The viscosity increased as the gelation increased. The dependency of viscosity on DP was higher at higher milling and extrusion temperatures and thus at a higher degree of gelation and a lower shear rate. This was assumed to be attributed to the more prominent uniform molecular flow as against the particle flow. The die swell increased with increasing the milling and extrusion temperatures and hence with increasing the gelation. A sample with a lower DP tended to show a larger die swell and this tendency was even more pronounced at the higher extrusion temperature. The melt fracture easily occurred when a sample with advanced gelation was extruded at low temperature. Whereas at low milling temperatures a sample with the lower DP showed a lower critical shear rate at onset of melt fracture, and thus easily generating melt fracture, at high milling temperatures it showed a higher critical shear rate and hence scarcely generated melt fracture. These experimental results were explained by the fact and concept that a sample with a lower DP shows a higher increase in the gelation during extrusion and/or the slighter feature of particle flow as against the uniform molecular flow at the same gelation level. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1915–1938, 2004

Key words: poly(vinyl chloride) (PVC); degree of polymerization; gelation; rheology; extrusion

INTRODUCTION

A suspension poly(vinyl chloride) (PVC) powder has a hierarchical particle structure with lamellar crystallites in the primary particles. At flow processing, the particle structure collapses by the action of heat and shear and approaches a unified homogeneous structure. Because PVC has a melting point near the decomposition temperature, it is generally melt processed at temperatures below the melting point and thus the crystallites partly melt, perfect gelation does not occur, and the particle structure partly remains. Accordingly at melt processing, the flow of PVC is caused not only by the "uniform flow" by the mutual movement of molecular chains but also by the "particle flow" by the slipping and rolling of particles (primary particles).[1–3] The proportion of uniform and particle flow is changed by the degree of gelation and flow conditions. In general, the higher gelation and flow temperature promote uniform flow. Accordingly, as shown in a previous study,[4] the flow processabilities of PVC are largely varied by the gelation. On the other hand in an article flow-processed from PVC powder or compound pellets, lamellar crystallites in the primary particles partly melt, diffuse, and recrystallize to form fringed micelle crystallites connecting the primary particles. Accordingly, as the melt-unification proceeds and the gelation is advanced, the mechanical properties are generally enhanced.

The material factors that affect the flow processability of PVC are the primary structures, such as molecular weight [degree of polymerization (DP)], its distribution, tacticity, copolymerization, and crosslinking; the formulations, such as thermal stabilizers, lubricants, reinforcing agents, and fillers; and the particle structures, such as particle size, its distribution, porosity, and bulk density, for example. These factors affect the gelation characteristics and affect directly or indirectly the flow processability through the change of the gelation. In a previous study,[4] the degree of gelation of a rigid pipe formulation PVC with a DP of 1050 was adjusted by changing the roll-milling temperature and time, the capillary flow characteristics were measured on the samples well-characterized in the gelation, and the effects of the gelation on the flow processabilities were systematically studied. In the present article, DP (molecular weight) was chosen and

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its effect on the relation between gelation and flow processabilities was studied with respect to flow processabilities, and capillary flow properties, such as viscosity, flow activation energy, die swell, melt fracture, and entrance pressure loss were studied. Because the meanings of these capillary flow properties in processability were described in the previous article,[4] they are not repeated here.

As for the effect of DP on the gelation characteristics, it is reported that the gelation time[5] and temperature[6] at the milling of suspension PVCs by use of a Brabender plastograph (Brabender Instruments, South Hackensack, NJ) linearly increase with increasing DP. It is also shown that the DSC low-temperature endotherm of an extrudate, which is a measure of gelation, is concomitantly lower as DP is higher at the same processing temperature and, conversely speaking, a sample with a higher DP must be processed at a higher temperature to obtain the same gelation level.[7]

Next, experimental results reported so far on the effect of DP on flow processabilities (rheological properties) are described.

Viscosity increases with increasing DP[2,8–12] and the dependency on DP is stronger at a higher extrusion temperature at a lower shear rate for the lower syndiotactic PVC. There are cases in extrusions at low temperatures and at high rates where the viscosity does not depend on DP[8,9,11,12] and it inversely decreases with increasing DP.[8] As for the non-Newtonian nature of flow, it generally becomes more notable with increasing DP and with lower extrusion temperatures.[8–10,12,13] The non-Newtonian dependency on the DP of a milled sample is weaker than that of a powder sample.[8] With respect to the flow activation energy, one at a constant shear rate decreases with increasing DP and shear rate[13–16] and its dependency on DP diminishes with increasing DP[13,15] and becomes independent of DP above about 800.[10,13] The flow activation energy at a constant shear stress increases with increasing DP and its dependency on DP diminishes with increasing DP.[15]

Die swell is generally larger when a polymer with a lower DP is extruded at a higher temperature.[2,3,9,12,17–19] A log–log plot of (die swell ratio – 1) versus viscosity for extrudates obtained at various extrusion temperatures gives a linear relation with negative slope and the absolute value of the slope increases with increasing DP.[13]

Entrance pressure loss is higher as DP and the milling temperature are higher[7,9,20] and the entrance pressure loss of extrudate milled at low extrusion temperatures below 180°C shows only a scarce dependency on DP at reextrusion at low temperatures below about 150°C.[20] The dependency of the entrance pressure loss on the DP of extrudate is weaker than that of the powder.[7] The end correction coefficient, which is a nondimensional measure of the entrance pressure

loss, increases with increasing shear rate. It is higher as DP is higher at high extrusion temperatures of about 200°C; its dependency on DP becomes weak and complex with lower extrusion temperatures, and becomes independent of DP at low extrusion temperatures of about 150°C.[9,12]

The critical shear rate at onset of melt fracture increases with increasing the extrusion temperature[12] and decreases with increasing DP.[12,13] The critical shear stress scarcely depends on the extrusion temperature and decreases with increasing DP.[12]

The critical draw ratio, which is a measure of melt extensibility, decreases with increasing DP[18] and a sample with higher DP shows inferior melt extensibility.

As mentioned above, a few studies have reported on the effect of DP on the gelation characteristics and numerous studies have reported on the effect of DP on the rheological characteristics. However, few studies have reported on the latter from the viewpoint of the former, that is, on the effect of DP on the relation between the gelation and rheological characteristics. The present study focused on just this aspect: that is, capillary flow properties were measured on sheets with adjusted degree of gelation by rolling rigid pipe formulation PVC compounds with various DPs at various milling temperatures and the effect of DP on the relation between gelation and flow processabilities was studied.

EXPERIMENTAL

Samples

Straight suspension PVC powders, grade ZEST 800Z (DP = 800), 1000Z (DP = 1050), and 1300Z (DP = 1300) produced by Shin Dai-ichi Vinyl Corp. (Japan) were used as raw materials. The DP of PVC is generally controlled by changing the polymerization temperature. DP increases as the polymerization temperature decreases. The stereoregularity of syndiotacticity also increases as the polymerization temperature decreases. Accordingly, the crystallinity of PVC increases with increasing DP.[21] We measured the crystallinity indices of three sample powders using the X-ray diffraction method proposed by Mitani et al.[22] Their values were 0.29, 0.28, and 0.27 for 800Z, 1000Z, and 1300Z, respectively, which are almost the same independent of DP in the range of the present investigation.

Formulation

A rigid pipe formulation was prescribed. The following additives were added to 100 weight parts (phr) of the PVC powder (in phr): tribasic lead sulfate, monohydrous, 1.5; lead stearate, 1.0; stearic acid, 0.2; cal-
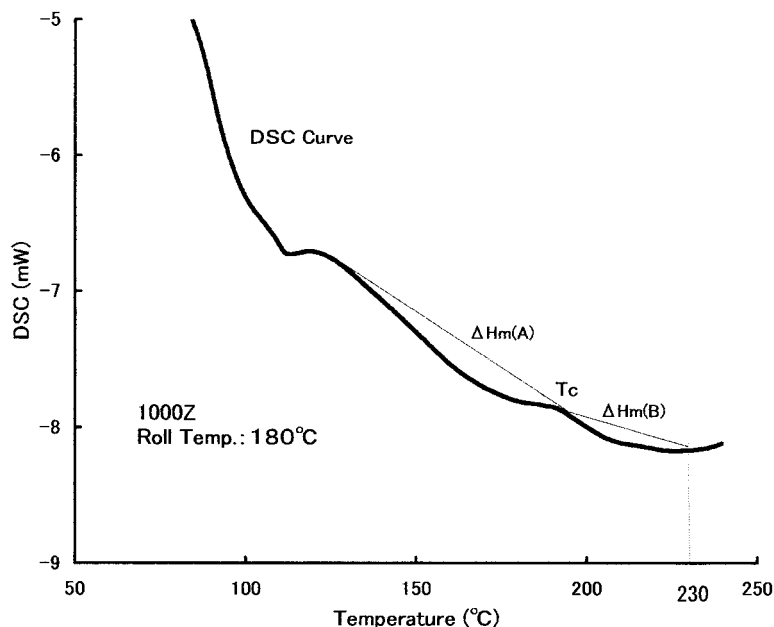
Figure 1 Measurement of degree of gelation by DSC.

cium stearate, 0.2; and acrylic processing aid, 0.5. These components were cold blended without heating in a 20-L Henschel mixer at high speed for 1 min and a powder compound was obtained.

Roll-milling

A 150 g sample of the powder compound was milled by use of a 6-in. test roll at 150, 160, 170, 180, 190, and 200°C for 1000Z and at 160, 180, and 200°C for 800Z and 1300Z for 5 min after the material rounded the roll and sheets of 0.6–0.7 mm thickness were prepared. The roll temperatures are the set points of roll surface temperatures. The rotation speeds of the front and back rolls were 17 and 21 rpm, respectively, and the mill gap was 0.4 mm. A rolling bank of material was observed. The folding back was carried out about 50 times during 5 min of milling. The basis of using a constant 5 min after the material rounded the roll is as follows: given that the degree of gelation and the appearance of the rolled sheet changed only slightly when the milling time was changed between 5 and 15 min as shown in the previous article,[4] the shortest time was chosen to suppress thermal degradation. The purpose of rolling in the present experiment was to adjust the degree of gelation—a shorter rolling time is better if the rolled sheet is uniform in gelation. We did not measure the resin temperature during rolling. The resin temperature was assumed to change with time in a complex manner according to the roll temperature and the DP of the resin. However, the resin temperature (maximum temperature reached) can be evalu-

ated by the history temperature Tc, mentioned in the next section.

Measurement of degree of gelation

To check the thermal degradation by DSC measurement, thermogravimetric analysis (TGA) was measured with the same apparatus on the same sample as used in DSC measurement as preliminary experiment. Because it became clear that the thermal degradation began to occur above about 250°C, the DSC measurement was carried out below 240°C.

A circular specimen of about 10 mg was cut from the rolled sheet and packed in a sealing Al sample pan. It was put in a DSC apparatus (DSC6200R-type manufactured by Seiko Instruments Inc., Tokyo, Japan) and the temperature was raised from 30 to 240°C at a rate of 20°C/min and a DSC thermogram was obtained. To prevent the thermal decomposition of PVC, the temperature was suddenly decreased to 30°C at a rate of 80°C/min as soon as it reached 240°C. The effect of annealing on gelation was studied as follows. The powder compound of about 10 mg was packed in a sealing Al sample pan and placed in a DSC furnace. The temperature was raised from 30°C to annealing temperatures (160, 170, 180, 190, and 200°C) at a rate of 40°C/min, held at the annealing temperatures for 5 min, and decreased to 30°C at a rate of 40°C/min. After this annealing process, the DSC thermogram was measured by the same manner as described above.

Figure 1 shows an example DSC thermogram of

1000Z sheet roll-milled at 180°C. The low-temperature endotherm ΔHm(A) was obtained as an area enveloped by the thermogram and a base line drawn so as to touch the shoulder around 120°C and the history temperature Tc. The high-temperature endotherm ΔHm(B) was obtained as an area enveloped by the thermogram and a base line drawn so as to connect Tc and 230°C (fixed). The degree of gelation was obtained as the absolute value of ΔHm(A) or as the ratio $G = \Delta Hm$(A)/[ΔHm(A) + ΔHm(B)]. It was assumed that the low-temperature endotherm ΔHm(A) originated from the fusion of fringed micelle crystals that melt-recrystallized during processing, that the high-temperature endotherm ΔHm(B) originated from the fusion of lamellar crystals that did not melt during processing, and that the history temperature Tc was the maximum temperature experienced by the resin.[23,24] DSC measurement was carried out five times on five specimens taken from various parts of the rolled sheet for each sample and the averaged value was adopted. The maximum standard deviation of ΔHm(A) was about 0.5 J/g at a roll temperature of 190°C and that of G was about 0.1 at a roll temperature of 170°C.

Measurement of capillary flow properties

The relation between the volumetric flow rate Q and the extrusion pressure P was measured with a constant-extrusion speed plunger-type capillary rheometer Capirograph 1B type (Toyo Measurement Instruments Co., Japan) at 150, 170, and 190°C by use of a flat die with a capillary length L of 20 mm, a capillary diameter ($D_0 = 2R$ where R is the radius) of 1 mm, and $L/R = 40$. The barrel diameter was 9.55 mm. The sample amount was 20 g and the preheating time was 5 min. The measurement was performed with increasing flow rate. One run of measurements was finished in 30 min.

The apparent shear stress τ, the apparent shear rate $\dot{\gamma}$ at the wall, and the apparent viscosity η in capillary flow are given respectively in the following equations:

$$\tau = \frac{PR}{2L} \tag{1}$$

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \tag{2}$$

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{3}$$

From these, the flow curve (τ–$\dot{\gamma}$ or η–$\dot{\gamma}$) can be obtained. Although the pressure includes the entrance pressure loss, it was neglected because the die with a large L/R of 40 was used. The standard deviation of viscosity measurement was below about 5%.
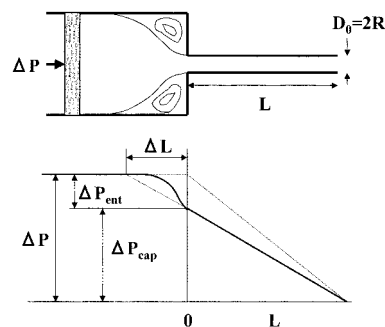

Figure 2   Measurement of entrance pressure loss ΔP_{ent}.

After the extrudate solidified, its diameter D at the part 5 mm from the front was measured with a micrometer and the ratio D/D_0, where D_0 is the capillary diameter, was designated the die swell ratio and used as a measure of die swell. The standard deviation of die swell measurement was below about 3%.

The appearance of the extrudate was observed with the naked eye and the occurrence of melt fracture was checked. The photograph of the extrudate was taken at a magnification of ×7.5 under a real-image microscope (SZH-type manufactured by Olympus Optical Co., Tokyo, Japan). The standard deviation of measurement of critical shear rate at onset of melt fracture was below about 50%.

As shown in the top part of Figure 2, when the PVC melt enters from a reservoir with a larger diameter into a capillary with a smaller diameter ($D_0 = 2R$) and length L, an entrance pressure loss ΔP_{ent} occurs as a result of the change of flow lines, as shown in the bottom part of the figure. The entrance pressure loss ΔP_{ent} mainly originates from the melt elasticity and in the case of PVC, it shows the degree of unification (homogenization) of resin and can be used as a measure of gelation. Although ΔP_{ent} can be obtained as the extrusion pressure measured by use of a die with L of 0, the strength of the die with zero length cannot endure the extrusion force. Therefore, in the present experiment, the extrusion pressure was measured by use of a flat die with a small length L (=1 mm) as against the diameter ($D_0 = 2$ mm) and the pressure was approximately equated with the entrance pressure loss. To prevent the effect of thermal history at measurement, the measurement was carried out at 140°C, which is 10°C lower than the lowest roll-milling temperature of 150°C. The shear rate at measurement of ΔP_{ent} was a single point of 7.6 s^{-1}. Because the extrusion pressure changed slightly by the amount of resin in the reservoir, it was measured at a piston end position 110 mm above the die. The sample amount was 15 g and the preheating time was 5 min. The standard deviation of entrance pressure loss measurement was below about 5%.

Because the thermal degradation of PVC compound was not negligible at temperatures above 200°C, the
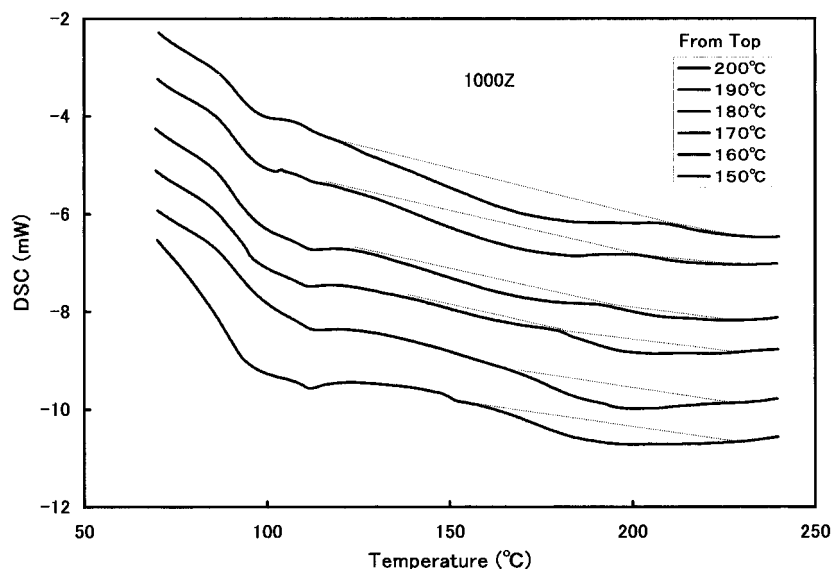
Figure 3 DSC curves of 1000Z sheets rolled at various temperatures.

capillary flow measurements were carried out at temperatures not exceeding 190°C. Although there might be a possibility that PVC melt slips at the die wall during flow, the data were treated as no slip. Furthermore, although shear heating might occur at high shear rates, it was neglected.

RESULTS AND DISCUSSION

Gelation

Figure 3 shows the change of DSC thermogram with the roll-milling temperature for 1000Z. With increasing temperature, the low-temperature endotherm ΔHm(A) appears, gradually increases, and the high-temperature endotherm ΔHm(B) gradually decreases. At the same time, the history temperature Tc increases.

Figure 4(a) shows the change of history temperature Tc with the roll-milling temperature. Tc increases linearly with increasing milling temperature and is about 10°C higher than the roll temperature. Tc tends to be lower for lower DP. This is assumed to be because a sample with lower DP generates less shearing heat during milling and attains a lower maximum temperature because of the lower viscosity. Figure 4(b) shows the change of Tc with the annealing temperature of powder compounds. Tc increases linearly with increasing annealing temperature and changes only slightly by DP. This means that the temperature experienced during annealing in DSC scarcely changes by DP.

Figure 5(a) shows the dependency, on the roll-milling temperature, of the degrees of gelation G = ΔHm(A)/[ΔHm(A) + ΔHm(B)] of samples with various DPs. The gelation begins around 160°C and ter-

minates around 200°C. 800Z seems to show slightly lower gelation than that of 1000Z and 1300Z. Figure 6(a) shows the dependency, on the roll-milling temperature, of the low-temperature endotherm ΔHm(A), which has been used as a measure of gelation since the earliest studies on gelation. Although a large difference is not observed, it tends to decrease with decreasing DP except for a single point of 1300Z milled at 200°C. From Figures 5(a) and 6(a), it may be said that a sample with lower DP tends to show lower gelation at the same milling temperature as a significant tendency. This is assumed to be because a sample with lower DP generates less shearing heat during milling and shows lower history temperature Tc, as shown in Figure 4(a). Although this tendency diminishes when the degree of gelation is plotted against the history temperature Tc, this tendency (the gelation decreases with decreasing DP) still remains. Obande and Gilbert[7] reported that the degree of gelation evaluated by the low-temperature endotherm ΔHm(A) of a suspension PVC extruded by use of a screw extruder decreases with increasing DP, compared with that at the same history (extrusion) temperature. This experimental result is an inverse tendency of the present one for roll milling. This difference originates in the milling machines: whereas they used a screw extruder, we used a roll. Because the milling time at the melt milling part in the screw extruder is shorter than that in the roll and the shearing force of the former is weaker than the latter, a large portion is supposed to gelate by the action of only heat and not to attain an equilibrium degree of gelation at that temperature. Because the gelation time and temperature are longer and higher, respectively, for a sample with higher DP (as shown by Suzuki[5] and Gonze[6]), it turns out that a sample
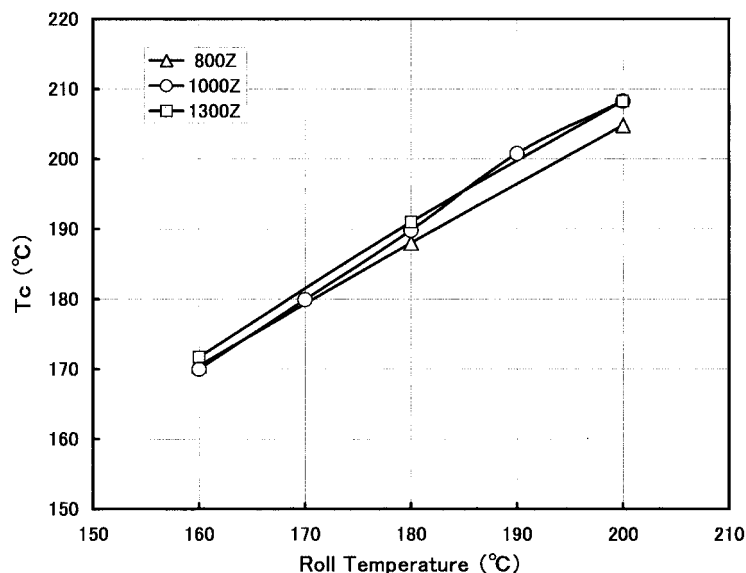
(a)
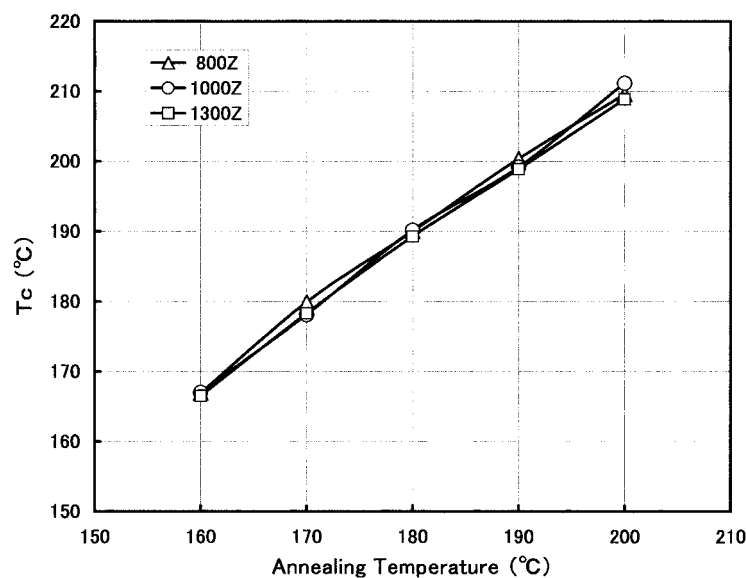
(b)

Figure 4 Dependency of history temperature Tc on (a) roll temperature and (b) annealing temperature.

with higher DP gives an extrudate with a lower degree of gelation, assuming that the gelation in a screw extruder is still in a state of progression.

Figures 5(b) and 6(b) show the dependencies, on the annealing temperature, of the degree of gelation G and the low-temperature endotherm $\Delta Hm(A)$ of powder compounds, respectively, which may be regarded as degrees of gelation caused by the action of only heat and of no shear. They increase with increasing the annealing temperature and decrease with increasing DP; that is, they show that the gelation by the action of heat alone occurs only with great difficulty with increasing DP, which is also assumed to be a cause of

lower gelation for a sample with higher DP. Contrary to this, because it is considered that the gelation progresses sufficiently to the equilibrium state in the roll milling, a sample with higher DP, which has a higher viscosity and thus is better milled, is assumed to show a higher degree of gelation. Based on the data of Figures 5(b) and 6(b) of powder compounds, the fact that the dependencies of G [Fig. 5(a)] and $\Delta Hm(A)$ [Fig. 6(a)] of rolled sheets on DP are not so fine and somewhat complex, although they tend to increase with DP, can be explained by a balance of the contradictory effects of shearing heat and natural gelation characteristic.

(a)

(b)
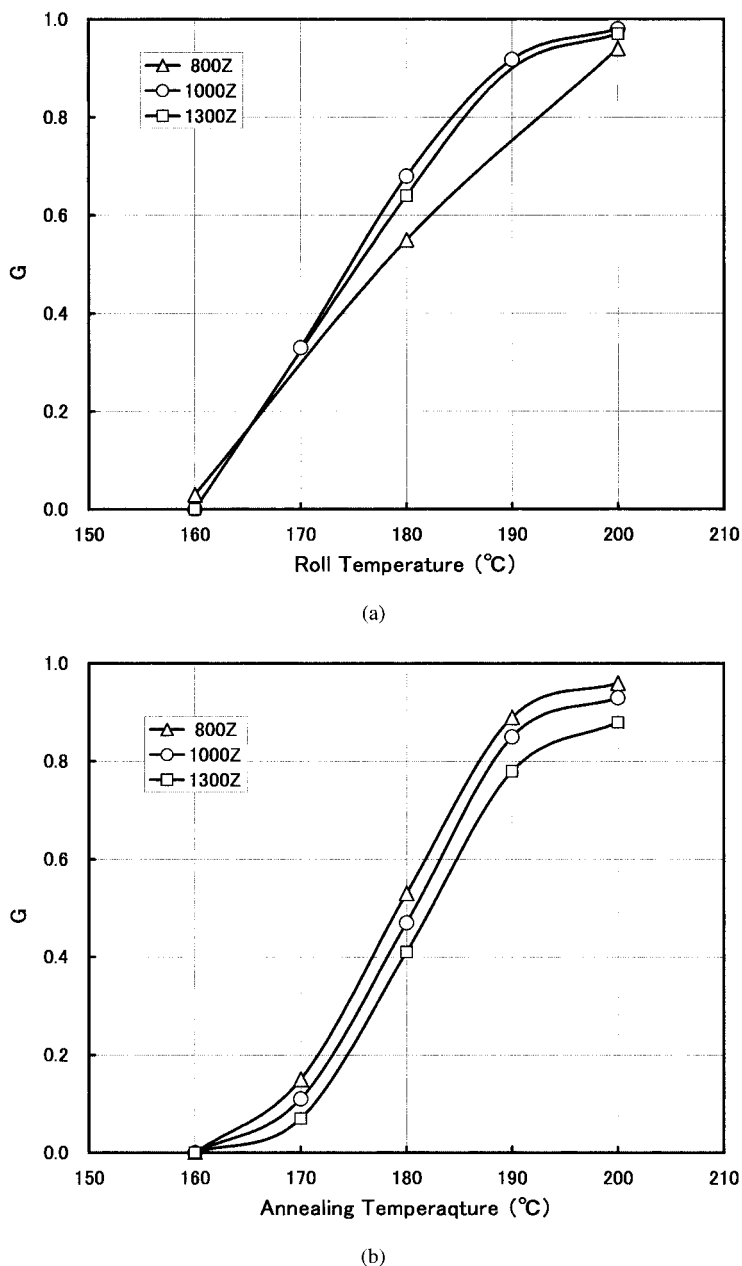
Figure 5 Dependency of degree of gelation G on (a) roll temperature and (b) annealing temperature.

Flow curve (viscosity)

Figure 7 exemplifies the change, with the extrusion temperature, of a flow curve represented in the form of the change of viscosity with shear rate for 1000Z sheet milled at 180°C. The viscosity decreases with increasing the extrusion temperature and shear rate, showing non-Newtonian behaviors. The degree of the decrease of viscosity with increasing the shear rate (i.e., its non-Newtonian nature) changes at shear rates around 200 s^{-1}, shows breaking points, and the non-Newtonian behavior of the high-shear rate side was more pronounced than that of low-shear rate side.

To study the temperature change of viscosity, the viscosity η at each shear rate was plotted against the reciprocal absolute temperature T. Straight lines were obtained and the Arrhenius equation represented by the following form holds:

$$\eta = A \exp \frac{\Delta Ha}{RT} \qquad (4)$$

where A is a constant independent of temperature, R is the gas constant, and ΔHa is the flow activation energy.

Figure 8(a), (b), and (c) show the variation of ΔHa obtained from the Arrhenius plots with shear rate and milling temperature for 800Z, 1000Z, and 1300Z, respectively. ΔHa shows maxima at shear rates around
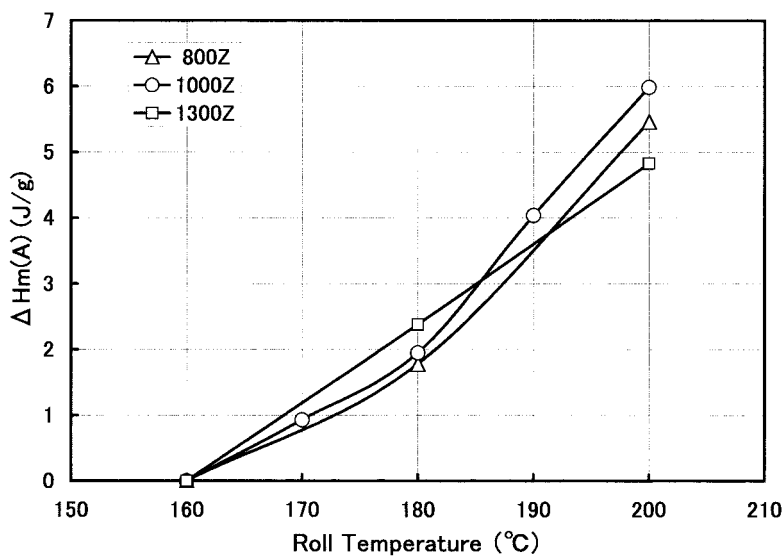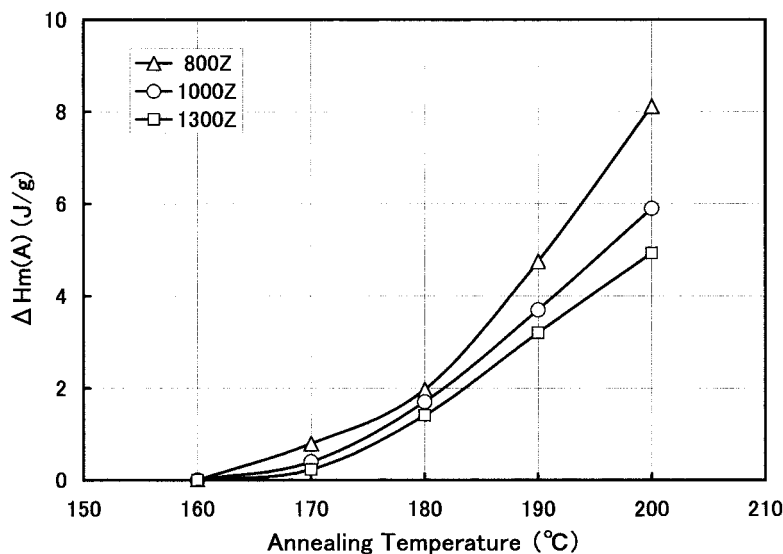
Figure 6 Dependency of low-temperature endotherm ΔHm(A) on (a) roll temperature and (b) annealing temperature.

10^2 s^{-1} and then decreases; 800Z shows weaker maxima than those of the others. Samples milled at high temperatures and having enhanced gelations show high ΔHa values at high shear rates around 10^4 s^{-1}. As for the effect of gelation, samples milled at high temperatures and having enhanced gelations tend to show high ΔHa values. This tendency is particularly notable at high milling temperatures of 190 and 200°C. Figure 9 shows the comparison of ΔHa among samples in the case of milling at 160°C. ΔHa scarcely depends on DP. The same results were obtained in the cases of other milling temperatures.

Collins and Krier[25] measured the viscosity of an Sn formulation rigid suspension PVC compound in a temperature range of 160–240°C and a shear rate

range of 0.3–150 s^{-1} and evaluated the changes of the flow activation energy with shear rate and stress. The activation energies at low- and high-temperature regions differ from each other and the former is lower than the latter; whereas the latter decreases with shear rate, the former shows a maximum at a shear rate around 15 s^{-1}. The temperature at transition from the low-temperature region to the high-temperature region increases with increasing shear rate. They regard the flow at the low-temperature region with low activation energies as a flow of domain or particulate and that at the high-temperature region with high flow activation energies as a flow of molecular chains. They assume that the fact that the transition temperature from the particulate to molecular flows increases with
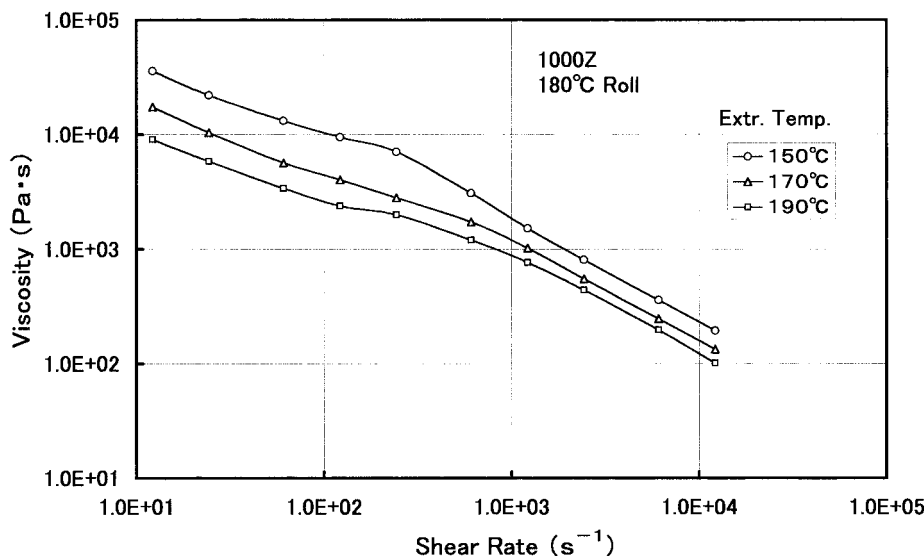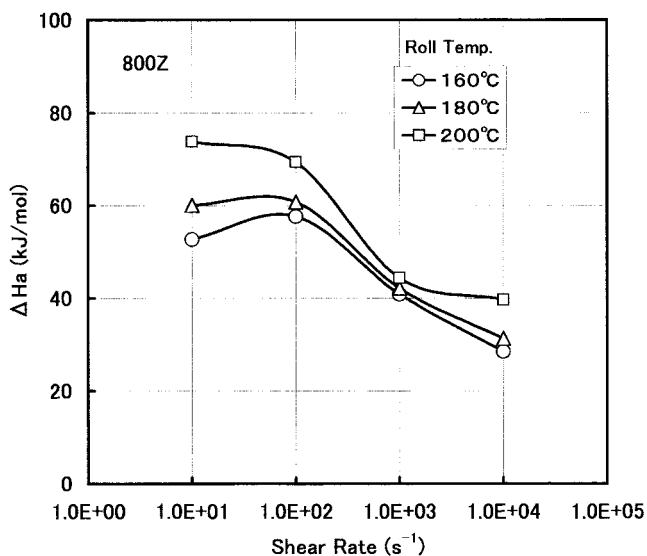
Figure 7 Temperature change of flow curve.

shear rate is because, with increasing shear rate, the molecular orientation increases and the dissolution to molecular chains becomes more difficult. The extrusion temperature range was 150–190°C and the shear rate range was 10–10,000 s^{-1} in the present investigation, which enters in the low-temperature region of the experiment by Collins and Krier. The change of the flow activation energy with shear rate in the present study shows maxima like those in their experiment. The shear rate at the maxima was around 100 s^{-1} in the present study, whereas it was around 15 s^{-1} in their result, the former being slightly higher. The absolute values of the activation energy in the present experiment were between those of their high- and low-temperature regions. These facts are assumed to be attributed to the differences in DP and formulation. The fact that samples milled at high temperatures and having enhanced gelations tend to show high flow activation energy in the present experiment was assumed to be because, with increasing gelation, the particle structure collapses and approaches a unified homogeneous structure, which leads to the molecular flow at the high-temperature region of Collins and Krier. This inference is consistent with the results of viscosity, die swell, melt fracture, and entrance pressure loss described below. As for the dependency of the flow activation energy on DP, it is reported that the flow activation energy at the constant shear rate decreases with increasing DP and shear rate[13–16] and its dependency on DP diminishes with increasing DP[13,15] and becomes independent of DP above about 800.[10,13] Because DPs of the present study were above 800, it is reasonable that the flow activation energy only slightly depends on DP.

Next, the change of flow curve with gelation will be examined. Figure 10(a), (b), and (c) show the changes,

with milling temperature, of flow curve of 1000Z measured at 150, 170, and 190°C, respectively. At shear rates below the breaking points, the viscosity tends to increase with increasing milling temperature and thus the gelation. This tendency is even more pronounced at lower extrusion temperatures and gradually becomes virtually unrecognizable with increasing extrusion temperature. Similar results were also obtained for other samples.

The fact that the viscosity increases with increasing roll-milling temperature and thus with enhanced gelation is assumed to be because with enhancing the gelation the particle structure collapses and the particle flow shifts to a uniform flow. From the facts that the change of gelation by the milling temperature strongly affects the flow curve at low extrusion temperatures and scarcely affects it with increasing extrusion temperature, it is assumed that gelation proceeds during the extrusion (measurement): Because gelation scarcely proceeds at low extrusion temperatures, gelation of the original sample affects the flow curve. On the other hand, because the gelation proceeds well at high extrusion temperatures, the difference in gelation of the original samples becomes slight and thus the effect of gelation of the original sample becomes less.

Figure 11(a), (b), and (c) show the changes, with DP, of flow curves of sheets milled at roll temperatures of 160, 180, and 200°C, respectively. Figure 12(a), (b), (c), and (d) show the dependencies, on DP, of viscosities at shear rates of 12.2, 122, 1220, and 12,200 s^{-1}, respectively, using the roll-extrusion temperatures as parameters. The viscosity increases with increasing DP and its dependency on DP is stronger at higher roll temperature and lower shear rate. This is the direction of transition from the particle to uniform molecular flow

(a)
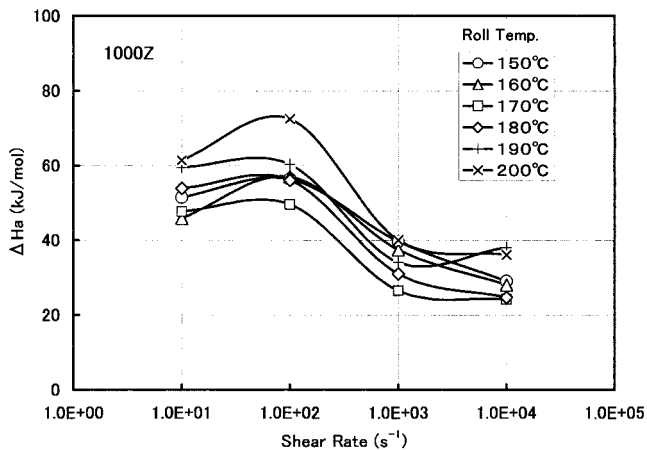
(b)
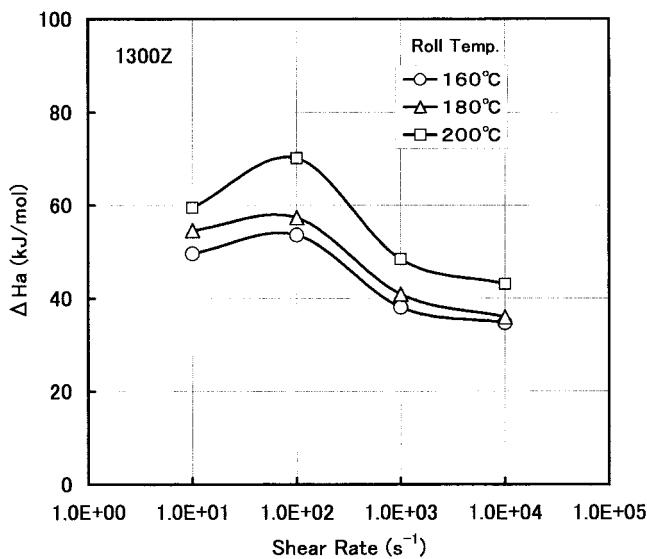
(c)

Figure 8 Change of flow activation energy ΔHa with roll temperature and shear rate for (a) 800Z, (b) 1000Z, and (c) 1300Z.
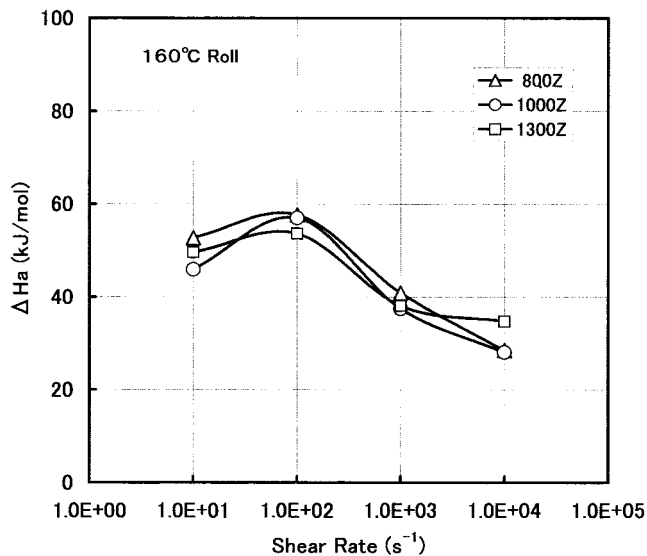

Figure 9 Comparison of change of flow activation energy ΔHa with shear rate among samples rolled at 160°C.

as shown in the previous study.[4] Because the particle flow is a flow caused by the slipping and rolling of particles (primary particles), molecular structures such as DP do not affect it and thus DP scarcely influences the viscosity when the feature of particle flow is prominent. On the other hand, in the case of uniform molecular flow, because molecular chains are well entangled and the flow is caused by the mutual movement of molecular chains, the viscosity is higher as DP is higher, like the usual resins. In this way, it can be explained that the dependency of viscosity on DP becomes more notable when the proportion of the uniform flow, as against the particle flow, increases. It is clear from Figure 12(a), where the most prominent uniform molecular flow is assumed to occur, that the dependency of viscosity on the roll-milling temperature is higher as DP is higher and the extrusion temperature is lower. In the case of an extrusion temperature of 190°C, the viscosity of 1300Z with the highest DP is higher as the milling temperature is higher, and thus the degree of gelation is greater as in the case of extrusion temperatures below 170°C, although the degree is low. 1000Z shows similar viscosities independent of the milling temperature; 800Z shows a reverse tendency, where the viscosity is lower as the milling temperature is higher and thus the degree of gelation is higher. This means that when 800Z with the lowest DP is extruded at low shear rates such as 12.2 s^{-1}, the viscosity decreases with increasing gelation; that is, it is said that the dependency of viscosity of PVC on DP differs depending on DP, extrusion temperature, and extrusion rate. Although antipodal results, where, with increasing gelation, the viscosity increased[1–4,26,27] and decreased,[8,28,29] are reported as
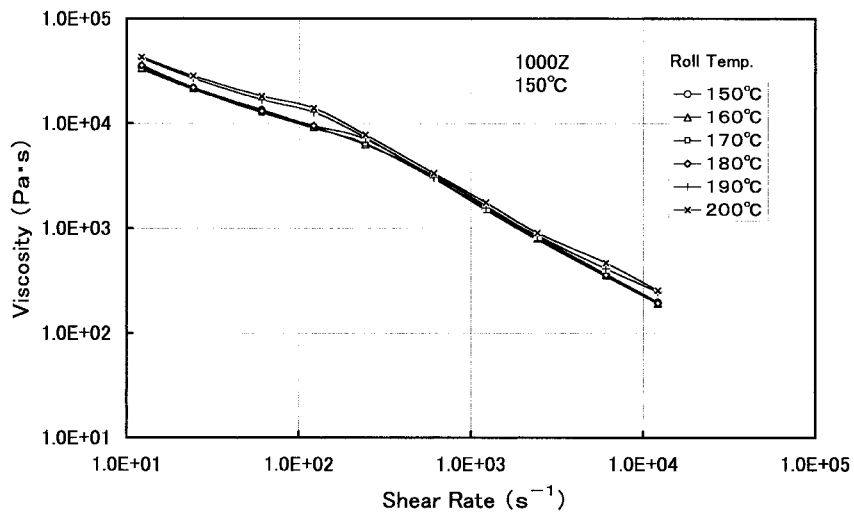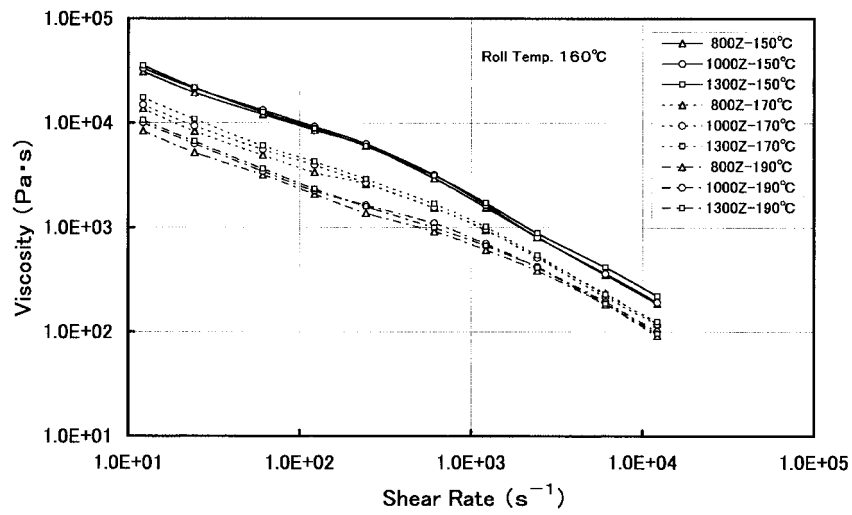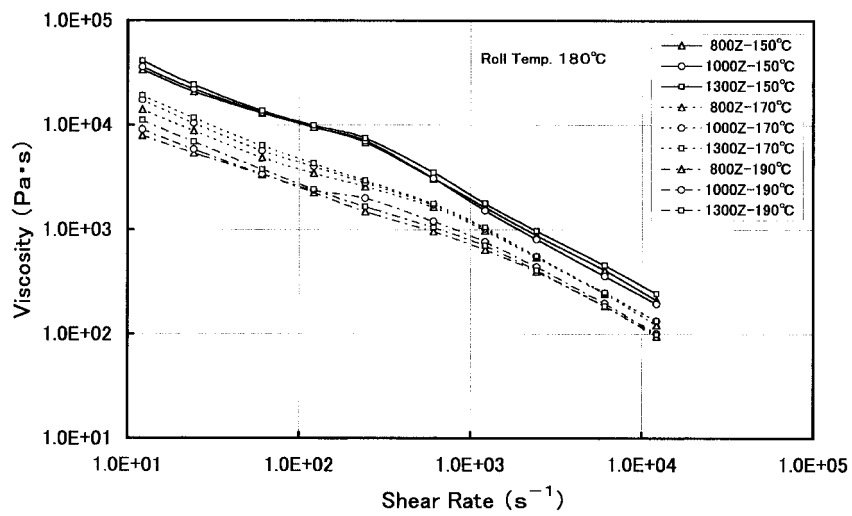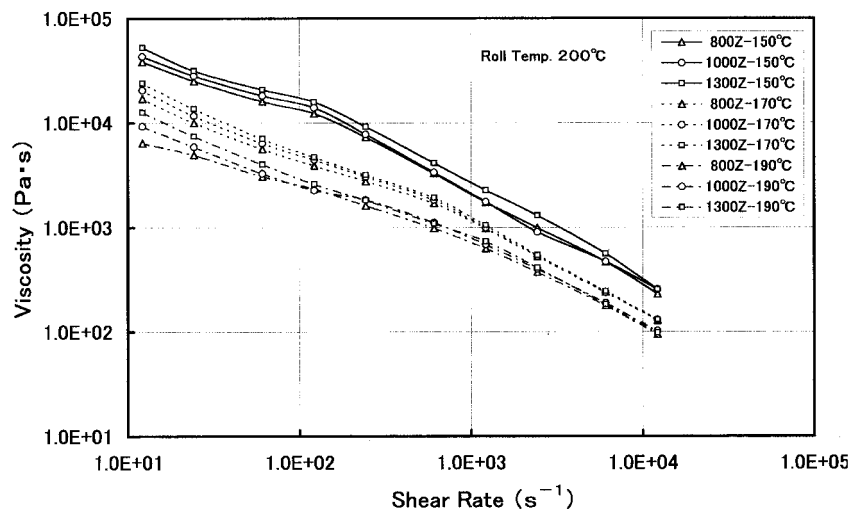
(a)
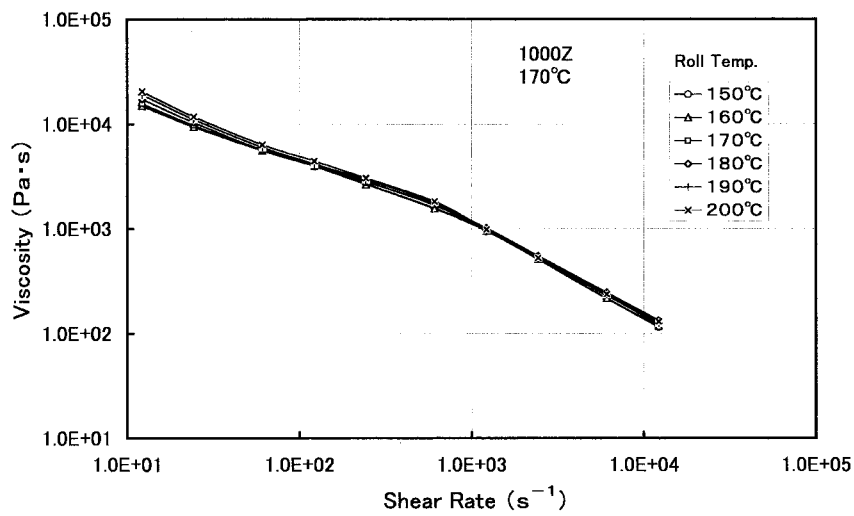
(b)
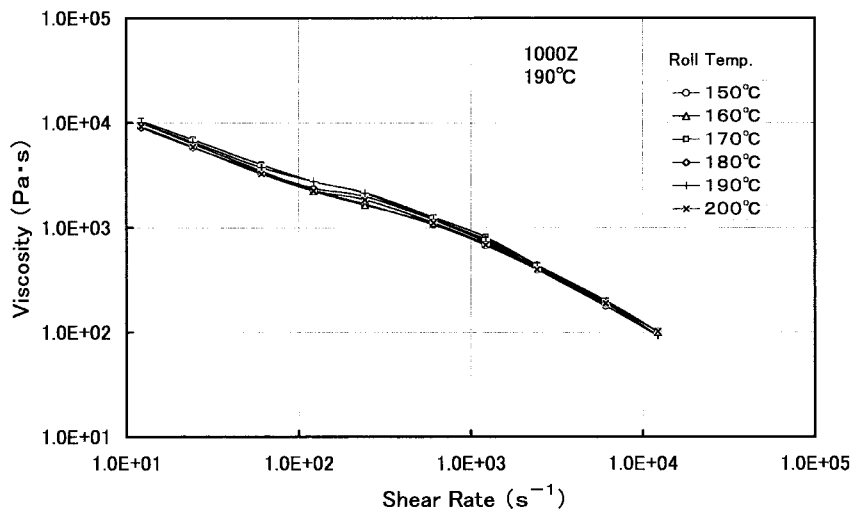
(c)

Figure 10 Flow curves of 1000Z sheets milled at various roll temperatures measured at (a) 150°C, (b) 170°C, and (c) 190°C.
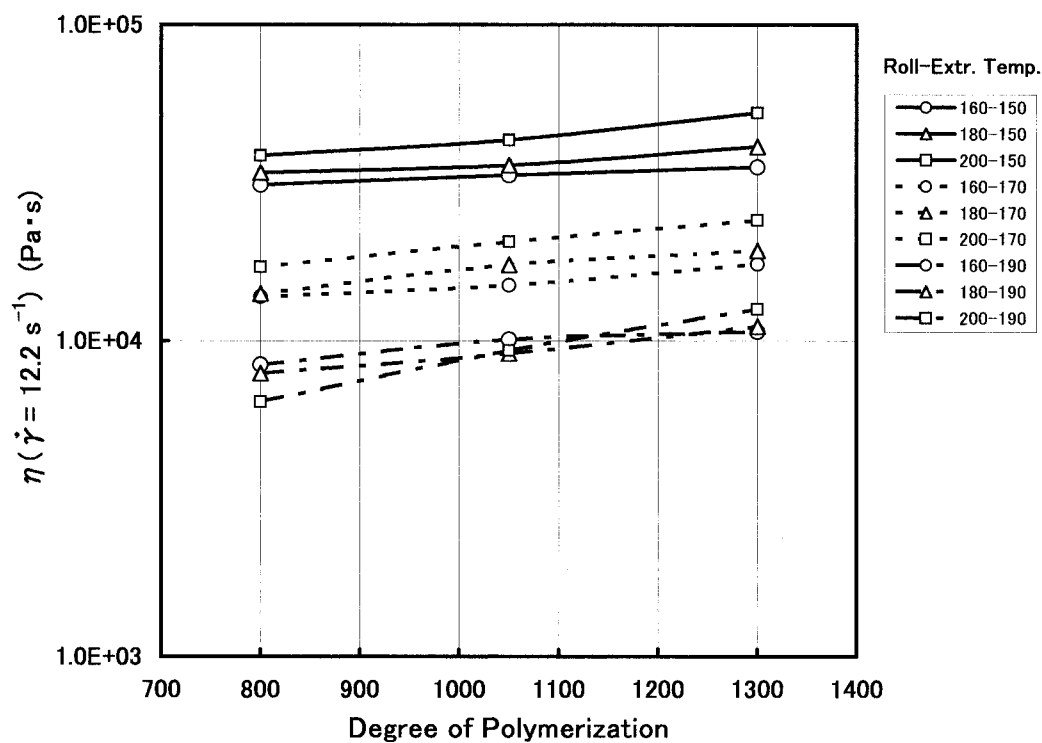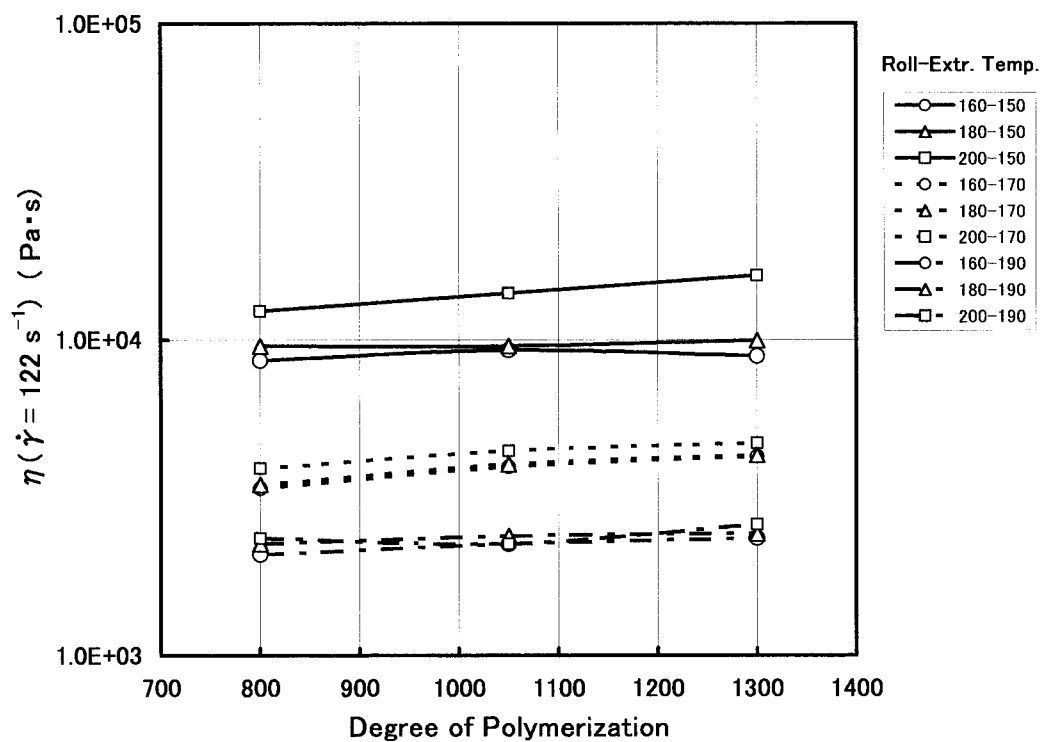
(a)

(b)

(c)

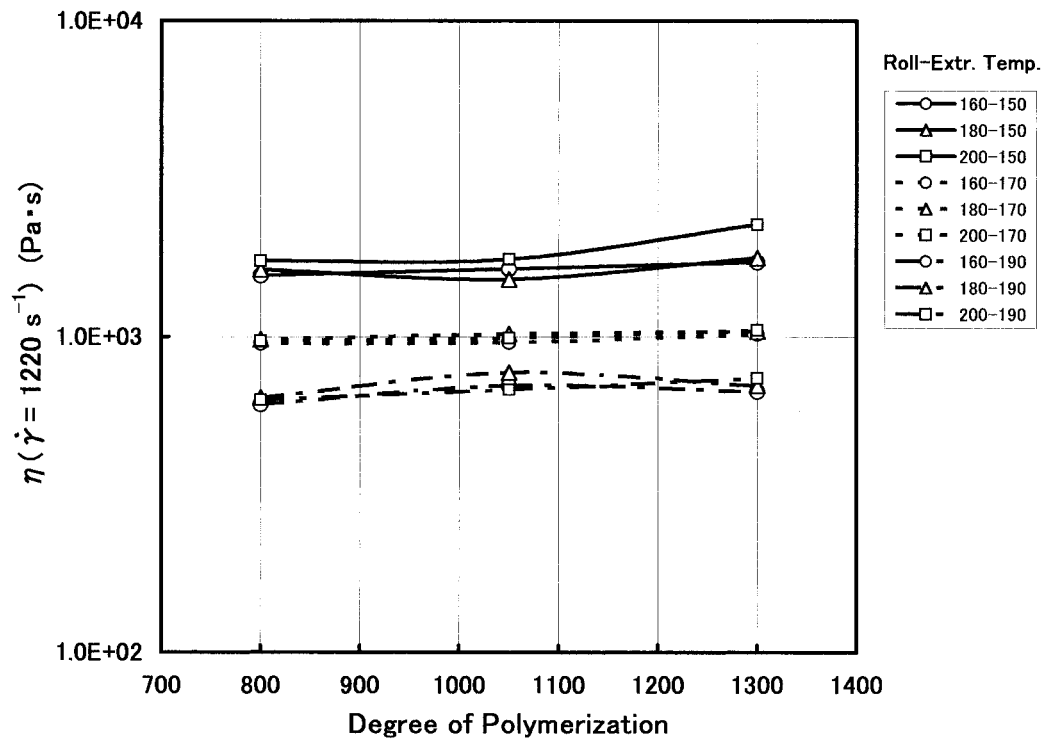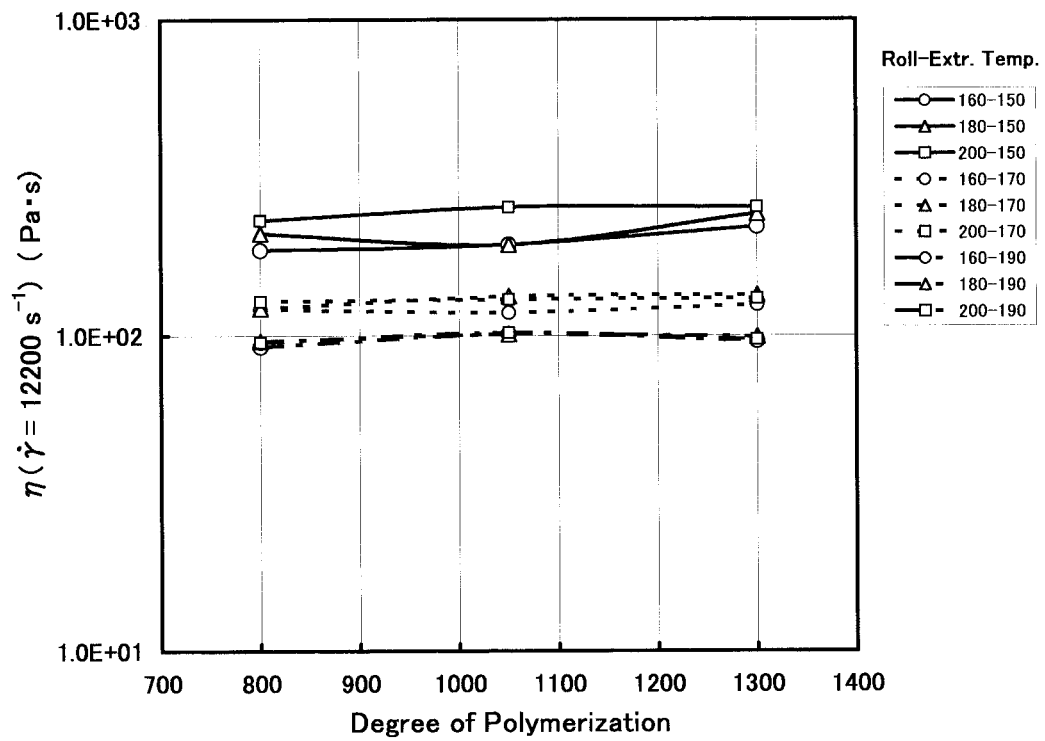**Figure 11**   Comparison of flow curve among samples rolled at (a) 160°C, (b) 180°C, and (c) 200°C.

(a)

(b)

Figure 12 Dependency of viscosity on degree of polymerization at (a) $\dot{\gamma} = 12.2$ s^{-1}, (b) $\dot{\gamma} = 122$ s^{-1}, (c) $\dot{\gamma} = 1220$ s^{-1}, and (d) $\dot{\gamma} = 12,200$ s^{-1}.

(c)

(d)

Figure 12 (*Continued from the previous page*)

shown in the introduction of the previous article,[4] this difference is assumed to originate from the differences in DP, extrusion temperature, and extrusion rate. Furthermore, it must be noted that in actual processing that the effects of DP and gelation on the viscosity robustly appear at low shear rates in extrusion processing, whereas these effects decrease at high shear rates in injection molding as shown in Figures 11 and 12.
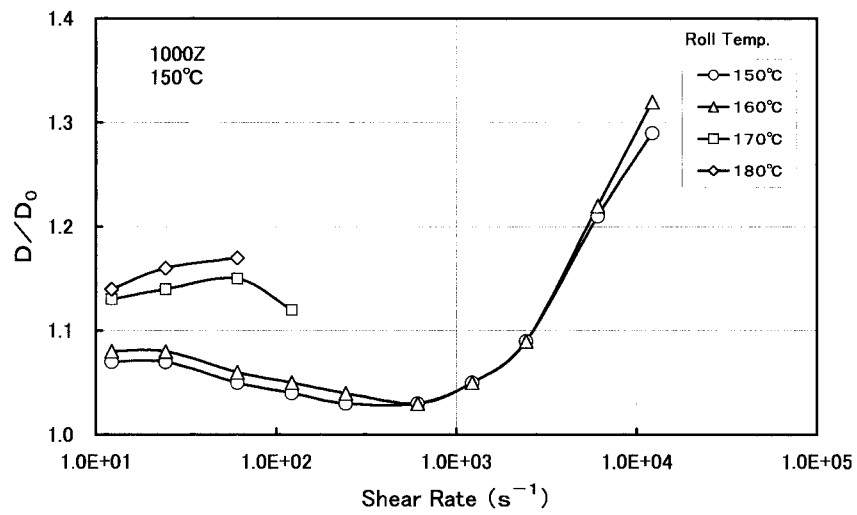
Die swell

Figure 13(a), (b), and (c) show the changes, with shear rate, of die swell ratio D/D_0 of 1000Z sheets milled at various temperatures and extruded at 150, 170, and 190°C, respectively. In the cases of extrusions at 150°C [Fig. 13(a)] and 170°C [Fig. 13(b)], melt fractures as mentioned later occurred and smooth extrudates could not be obtained for the samples milled at 190 and 200°C and hence their die swells could not be evaluated. For the extrusion at 150°C [Fig. 13(a)], the samples milled at 150 and 160°C show a similar and small die swell and the die swell increases with increasing the milling temperature from 170 to 180°C. For the samples milled at 150 and 160°C, because the degrees of gelation are both 0, as shown in Figure 5(a), the die swell curves show very similar shapes and values. For the extrusion at 170°C [Fig. 13(b)], the samples milled at 150 and 160°C also show similar and small die swell ratios that are slightly larger than those of extrusion at 150°C. The die swell increases with raising the milling temperature from 170 to 180°C. For the extrusion at 190°C [Fig. 13(c)], the samples milled at temperatures below 180°C show similar die swell curves and the samples milled at 190 and 200°C show higher values. The gelations of all samples milled at temperatures below 180°C are assumed to be increased to that at 190°C during extrusion at 190°C. Other experiments showed that the resin temperature increases by about 10°C higher than the roll temperature. It may be observed from Figure 13(a)–(c) that the die swell ratios of samples milled at temperatures greater than 10°C lower than the extrusion temperature increased to that of a sample milled at a temperature about 10°C lower than the extrusion temperature: The die swell ratio of the sample milled at 150°C is increased to that at 160°C in the extrusion at 170°C and the die swell ratios of the samples milled at 150, 160, and 170°C are increased to that at 180°C in the extrusion at 190°C. The die swells of the samples milled at 190 and 200°C could be measured in the extrusion at 190°C [Fig. 13(c)] and there is almost no difference between them. The reason for this is because the degrees of gelation G of both samples are nearly 1.0; they are sufficiently gelated and thus show similar die swells.

The fact that the die swell ratio increases with increasing milling temperature is assumed to be because, with increased gelation, the particulate structure collapses and approaches the unified homogeneous structure. In the case of insufficient gelation, because PVC flows in a slippery manner by sliding and rolling in the particulate state, its flow is a plastic flow and the storage of elastic recoverable strain at the entrance of capillary is small, and thus the elastic recovery at the capillary exit is weak, leading to a small die swell. With increasing gelation, the melt-unification proceeds, PVC melt becomes elastic because of the well-entangled molecular chains, and stores large elastic recoverable strain at the entrance of capillary. Accordingly, the elastic recovery after emerging from the capillary is substantial, leading to a large die swell. The effect of milling temperature on the die swell is more prominent than that on the viscosity mentioned in the preceding section. It can thus be said that the die swell, which is a melt elastic property, is more significantly affected by the gelation and in its turn by the flow mode than the viscosity, which is a melt viscous property.

Figure 14(a), (b), and (c) show the changes, with shear rate, of die swell ratio D/D_0 of each sample sheet milled at 160°C and extruded at 150, 170, and 190°C, respectively. The die swell increases with increasing extrusion temperature. This increase is assumed to originate from the increase in gelation during extrusion. With respect to the dependency of die swell on DP, the die swell is higher as DP is lower and the dependency becomes more notable with elevating the extrusion temperature. From this fact, it is assumed that the increase in gelation during extrusion is even more pronounced as DP is lower and/or that the feature of the particle flow is weaker as DP is lower. Figure 15 shows results for the case of a milling temperature of 180°C, showing similar tendencies to the case of the milling temperature of 160°C, with the die swell generally being enhanced. Figure 16 shows a result for the case of a milling temperature of 200°C and an extrusion temperature of 190°C. The die swell further increases and becomes almost independent of DP. In this case, because both the milling and extrusion temperatures are high, gelation is sufficiently enhanced as shown in Figure 5(a), and thus the flow there approaches a uniform molecular flow; the flow behavior is assumed to approach that for the usual resins where the die swell increases with increasing molecular weight. It is assumed that when the milling and extrusion temperatures further increase and gelation is further enhanced, the die swell increases with increasing DP (i.e., Fig. 16 is considered to depict the ongoing change). Figure 17 shows the dependency of the die swell ratio at a shear rate of 122 s^{-1} on DP by use of the milling–extrusion temperatures as parameters. Because the changes of die swell ratio with shear rate show complex tendencies, with valleys and peaks as shown in Figures 14–16, such plots may be meaningless. However, they have a merit of being able to see the dependency of die swell ratio on DP at a glance. Figure 17 shows that the die swell decreases with increasing DP in almost all conditions. This tendency diminishes at DPs above 1000Z and a reverse tendency can be seen at maximum milling–extrusion temperatures of 200–190°C.
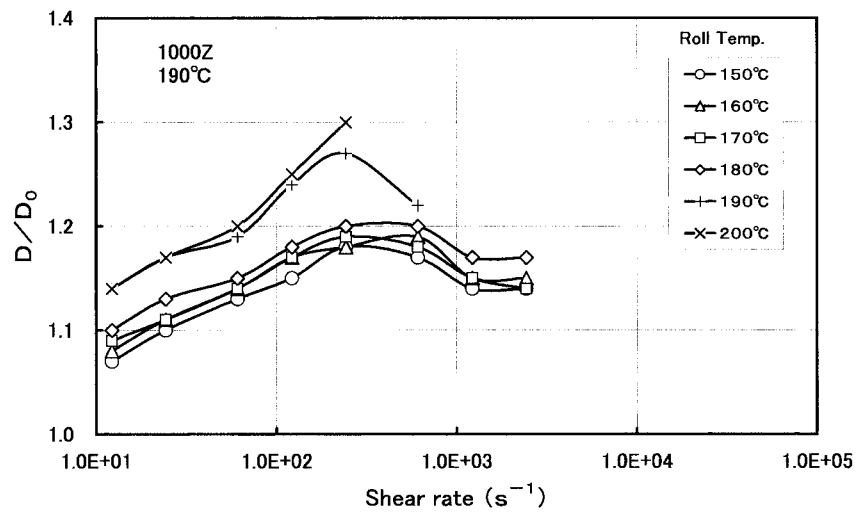
As mentioned in the introductory remarks, it has thus far been reported that the die swell is larger as a
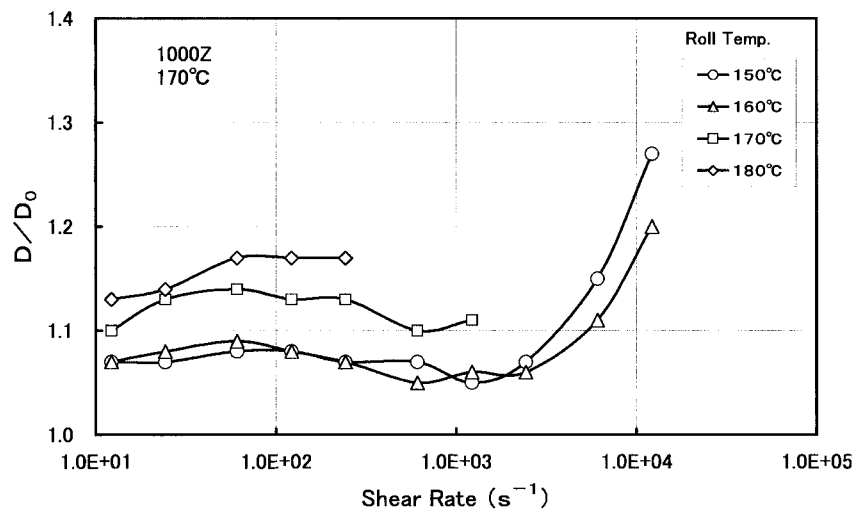
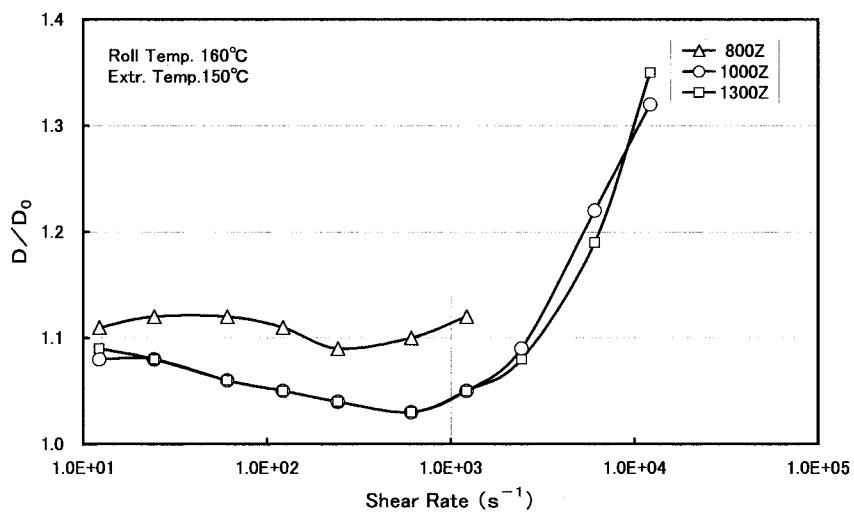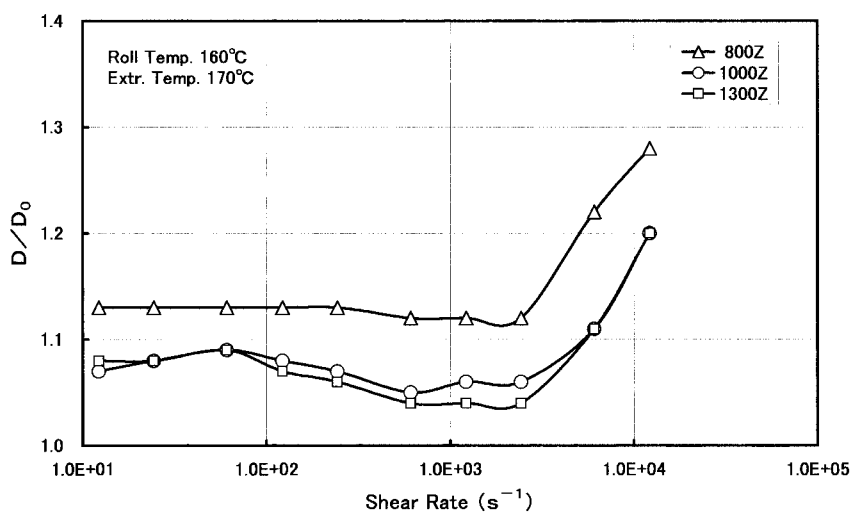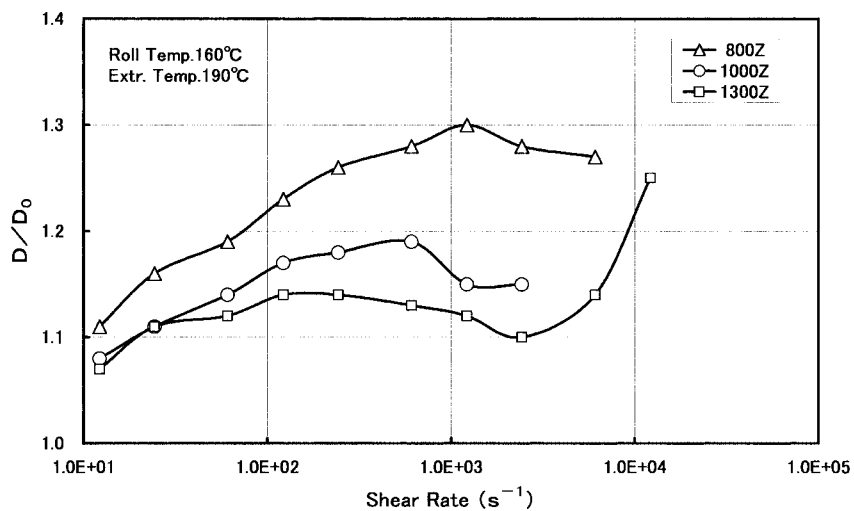**Figure 13**　Change of die swell ratio D/D_0 with roll temperature and shear rate measured for 1000Z at (a) 150°C, (b) 170°C, and (c) 190°C.
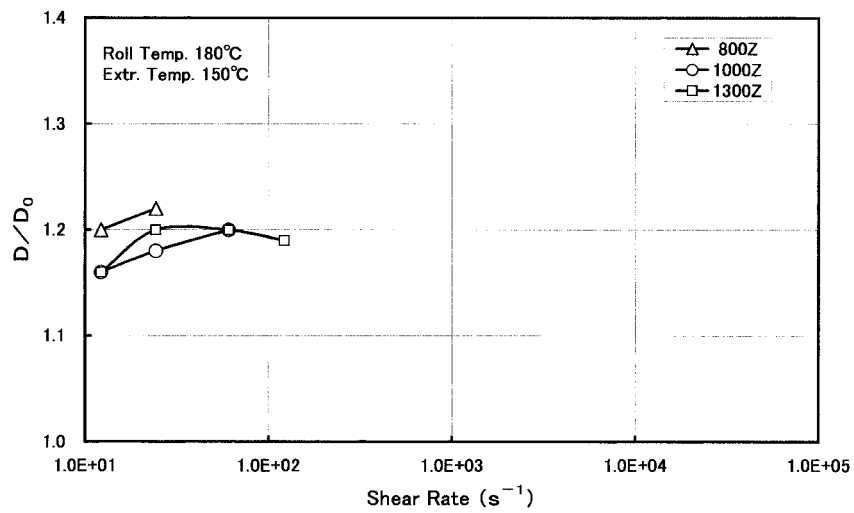
Figure 14 Comparison of change of die swell ratio D/D_0 with shear rate among samples (a) rolled at 160°C, extruded at 150°C; (b) rolled at 160°C, extruded at 170°C; and (c) rolled at 160°C, extruded at 190°C.
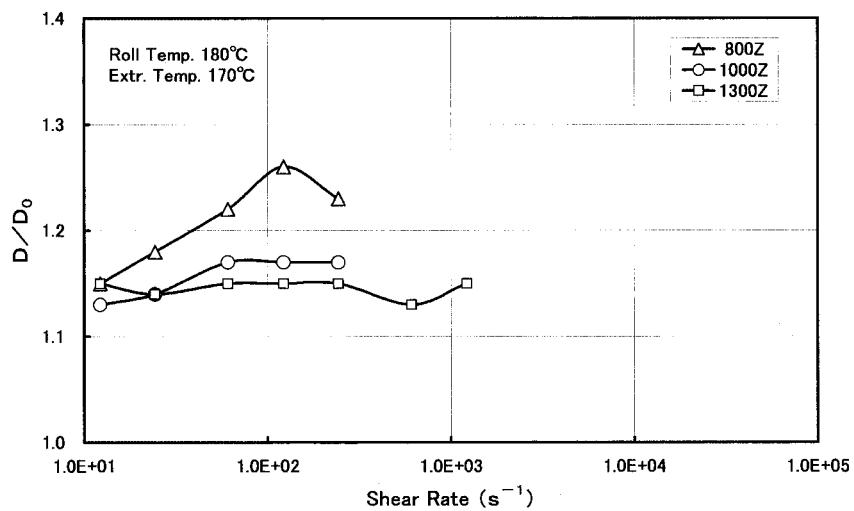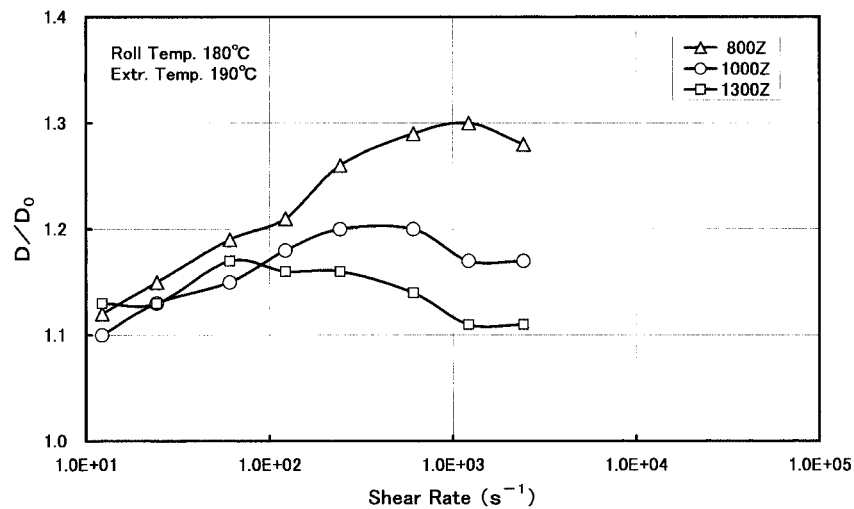
Figure 15 Comparison of change of die swell ratio D/D_0 with shear rate among samples (a) rolled at 180°C, extruded at 150°C; (b) rolled at 180°C, extruded at 170°C; and (c) rolled at 180°C, extruded at 190°C.
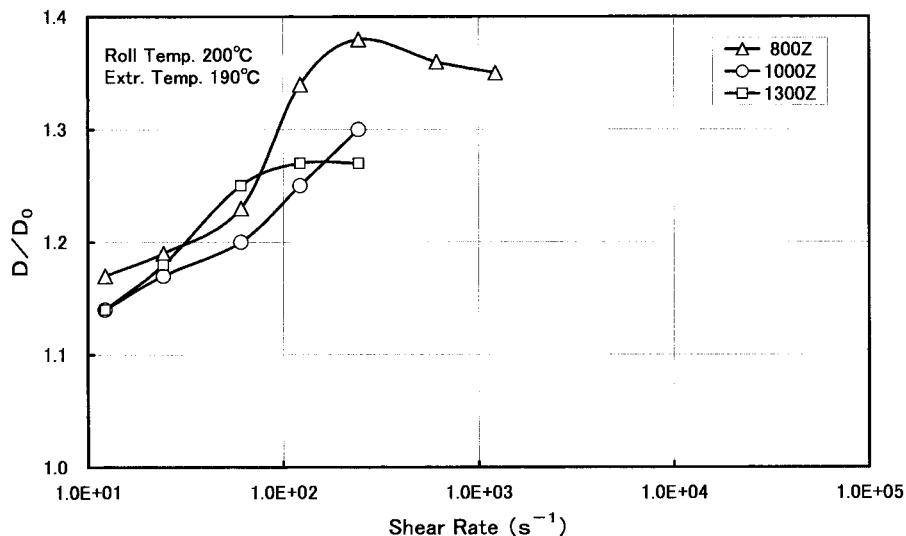
Figure 16 Comparison of change of die swell ratio D/D_0 with shear rate among samples rolled at 200°C, extruded at 190°C.

resin with a lower DP is extruded at a higher temperature.[2,3,9,12,17–19] These studies lack in providing a perspective on gelation; however, viewed from the knowledge of the present study, both conditions are in the direction of advancing the gelation and of shifting from particle flow to uniform molecular flow, which can explain the effect of the degree of gelation on the die swell from the concept of the particle and uniform flows. The phenomena and hypothesis that the increase in gelation during extrusion is made more difficult as DP is higher and/or that the feature of the particle flow as against the uniform molecular flow is stronger as DP is higher, at the same level of gelation, are thus elucidated.

Melt fracture

Figure 18 shows as an example of the changes, with shear rate, of photographs of extrudates obtained by extruding sheets of various DPs milled at 180°C at an
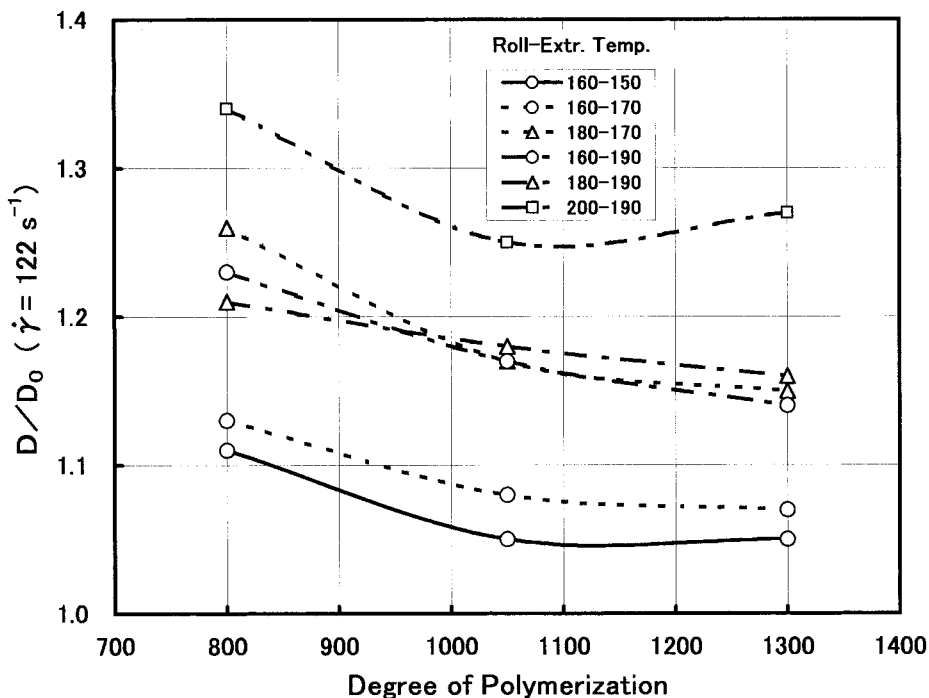

Figure 17 Dependency of die swell ratio D/D_0 at $\dot{\gamma} = 122$ s^{-1} on degree of polymerization.
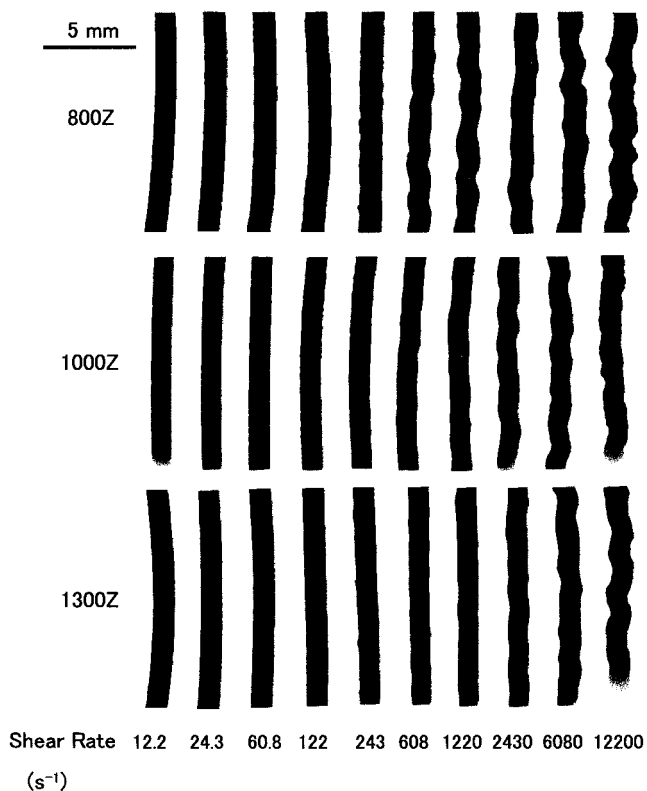
Figure 18 Shape of extrudate rolled at 180°C, extruded at 170°C.

extrusion temperature of 170°C. At low shear rates the extrudates are smooth; they begin to distort with increasing shear rate to around 60.8, 122, and 243 s^{-1} for 800Z, 1000Z, and 1300Z, respectively; and the distortion increases with increasing shear rate. Accordingly, the critical shear rates $\dot{\gamma}_c$ are 60.8, 122, and 243 s^{-1} for 800Z, 1000Z, and 1300Z, respectively, in this case.

From this it may be said that a resin with a higher DP generates melt fracture only with a greater degree of difficulty.

Figure 19 shows the change of the critical shear rate $\dot{\gamma}_c$ with the milling temperature using DP and the extrusion temperature as parameters. The arrows indicate the critical shear rates over or under the measuring limits of shear rate of the apparatus used. Figure 20 shows the dependency of the critical shear rate on DP using the milling–extrusion temperatures as parameters. The critical shear rate is lower as the extrusion temperature is lower. It also decreases with increasing milling temperature and thus the gelation. As for the effect of DP, compared at the same milling–extrusion temperatures, although a sample with a higher DP shows the higher critical shear rate and hardly generates the melt fracture at milling temperatures below 180°C, it shows the lower critical shear rate and easily generates the melt fracture in the cases of milling–extrusion temperatures of 200–190°C. (In the cases of extrusion temperatures below 170°C, the tendency is not obvious because the critical shear rates are below the measuring limit.)

The fact that the critical shear rate at onset of the melt fracture $\dot{\gamma}_c$ increases with increasing extrusion temperature is general for thermoplastic resins and is reported also for PVCs.[12,13,30] The fact that with increasing gelation the melt fracture occurs easily is fragmentarily reported by Berens and Folt,[1] Shinagawa,[26] and Fujiyama and Nagou.[27] According to Paradis,[31] the elastic energy that the PVC melt has stored when entering into the capillary from the reservoir is consumed by the elastic recovery of die swell. However, when the extrusion rate increases and the stored energy becomes excessive, it cannot maintain itself and a part of it is lost in the form of melt fracture.
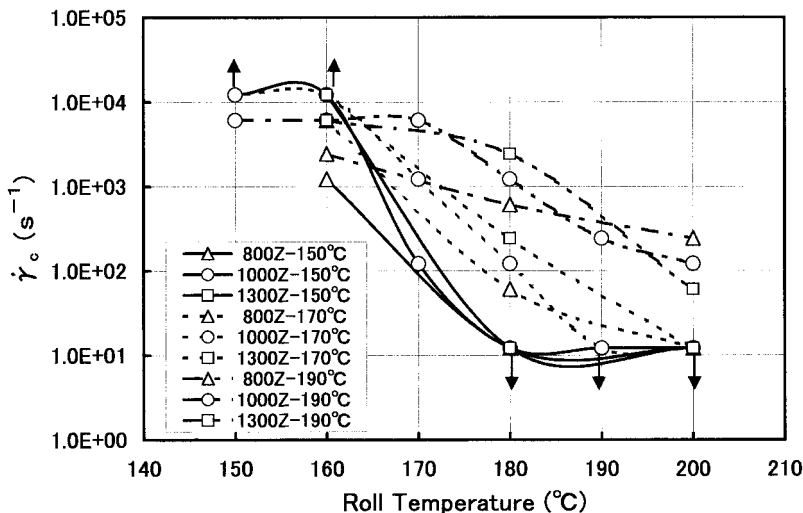

Figure 19 Comparison of dependency of critical shear rate $\dot{\gamma}_c$ at onset of melt fracture on roll temperature among samples.
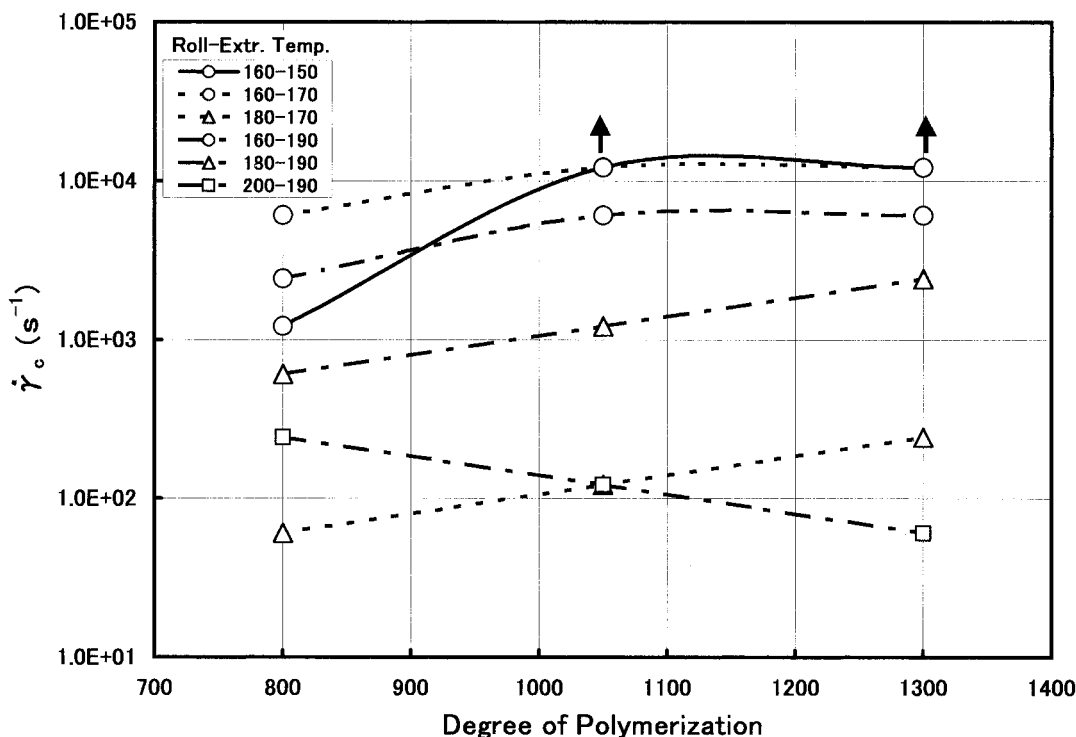
Figure 20 Dependency of critical shear rate $\dot{\gamma}_c$ at onset of melt fracture on degree of polymerization.

If the gelation of PVC is insufficient, because it flows in a slippery manner by the particle flow, the stored elastic energy at the capillary entrance is small and thus the melt fracture occurs only with difficulty. With increasing gelation, the PVC melt becomes more elastic by the entanglement of molecular chains and stores more elastic energy and thus the melt fracture occurs easily.

As for the dependency of the critical shear rate at onset of melt fracture on DP, a resin with a higher DP shows a lower critical shear rate and more easily generates melt fracture for the usual thermoplastic resins. The same tendency was also reported for PVC.[12,13] However these studies lack in providing a perspective on gelation. Examining the dependency of the critical shear rate on DP in Figures 19 and 20 from the perspective of gelation, samples milled at roll temperatures below 180°C have low degrees of gelation and are thus assumed to robustly show the feature of particle flow. Accordingly, a sample with a higher DP, in which the increase in gelation during extrusion scarcely occurs or the feature of the particle flow is assumed to be even stronger at the same gelation level, shows a higher critical shear rate and can scarcely generate melt fracture. On the contrary, in the case of high milling (200°C) and extrusion temperatures, because gelation proceeds sufficiently and the material approaches a unified homogeneous structure, like the usual thermoplastic resins, it is assumed that the critical shear rate is decreased and the melt frac-

ture more easily occurs with increasing DP, also like the usual resins. In the same way as in the case of die swell in the previous section, the phenomena and hypothesis that the increase in gelation during extrusion is made more difficult as DP is higher and/or that the feature of the particle flow as against the uniform molecular flow is stronger as DP is higher, at the same level of gelation, are thus elucidated.

Entrance pressure loss

Figure 21 shows the dependency of the entrance pressure loss ΔP_{ent} of each sample on the milling temperature. The entrance pressure loss increases with milling temperature. The entrance pressure loss of 1000Z sheet milled at a low temperature of 150°C is lower than that of unmilled powder. This is assumed to be because linking structures between the primary particles in the polymerized powder are collapsed mechanically by milling at a low temperature. Although the degree of gelation G reaches a maximum around 200°C, as shown in Figure 5(a), the low-temperature endotherm $\Delta Hm(A)$ continues to increase with the milling temperature, like the entrance pressure loss as shown in Figure 6(a). Terselius et al.,[32] Krzewski and Collins,[33–35] Patel and Gilbert,[36] Summer and Rabinovitch,[20] and Obande and Gilbert[37] showed that with increasing the processing temperature and hence the gelation of rigid formulation suspension PVC, the entrance pressure loss in the capillary flow increases in
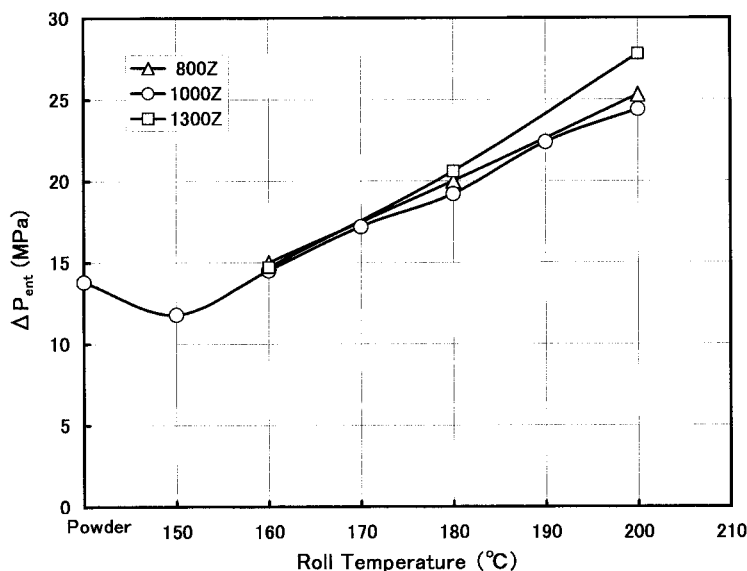
Figure 21 Comparison of dependency of entrance pressure loss ΔP_{ent} on roll temperature among samples.

an S-shaped fashion. In the present experimental results, although the degree of gelation G shows an S-shaped change [as shown in Fig. 5(a)], the sign of leveling off at the higher side was not observed in the entrance pressure loss ΔP_{ent} as shown in Figure 21. The leveling off may be observed at higher milling temperatures. The dependency of ΔP_{ent} on DP is slight, although 1300Z with the highest DP seems to show slightly higher values.

Figure 22(a) and (b) show the relationships between the entrance pressure loss ΔP_{ent} and the degree of gelation G and the low-temperature endotherm $\Delta Hm(A)$, respectively. ΔP_{ent} shows good, nearly linear correlations with G and $Hm(A)$ except for one point at G and $\Delta Hm(A)$ of 0 for the sample milled at 150°C. The correlations are only slightly dependent on DP. From these facts, it may be said that the entrance pressure loss measured at a lower temperature below the processing temperature can be used as a measure of the degree of gelation regardless of DP. Because the entrance pressure loss is also a physical quantity concerned with melt elasticity, like the die swell and melt fracture, it is assumed that its value is low when the gelation is insufficient and the particle flow occurs and is high when the gelation and molecular entanglement proceed sufficiently and a uniform flow occurs.

The entrance pressure loss is also a measure of melt elasticity[33] and increases with increasing the gelation caused by the increased milling temperature as shown above. Accordingly the entrance pressure loss is used as a measure of gelation. The degree of dependency of the entrance pressure loss on the gelation is similar to that of the die swell. The dependency of the rheological properties on gelation is in the order of melt fracture > die swell ≒ entrance pressure loss > viscosity.

The effect of transition from the particle flow to the uniform flow caused by the increased gelation appears more notably in the elasticity (melt fracture, die swell, entrance pressure loss) than in the viscosity.

CONCLUSIONS

Sheets with adjusted degree of gelation were prepared by rolling rigid pipe formulation suspension PVC compounds with DPs of 800, 1050, and 1300 by changing the roll milling temperature. Their degrees of gelation were measured with DSC and their capillary flow properties were measured with a capillary rheometer and the effect of DP on the relation between gelation and flow processabilities was studied.

1. Because of the difference in shearing heat at roll milling, a sample with a lower DP showed a lower history temperature and hence a lower degree of gelation.
2. The flow activation energy at constant shear rate increased with advancing gelation and depended only slightly on DP in the range of the present study.
3. The viscosity increased by elevating the milling temperature and this tendency was more substantial at the lower extrusion temperature. The viscosity increased with DP and the dependency on DP was even more pronounced at the higher milling and extrusion temperatures and hence with advancing the gelation. The dependency was also more notable at the lower shear rate. The viscosity was constant, independent of DP at low milling (160°C) and extrusion (150°C) temperatures. It scarcely depended on DP, in-
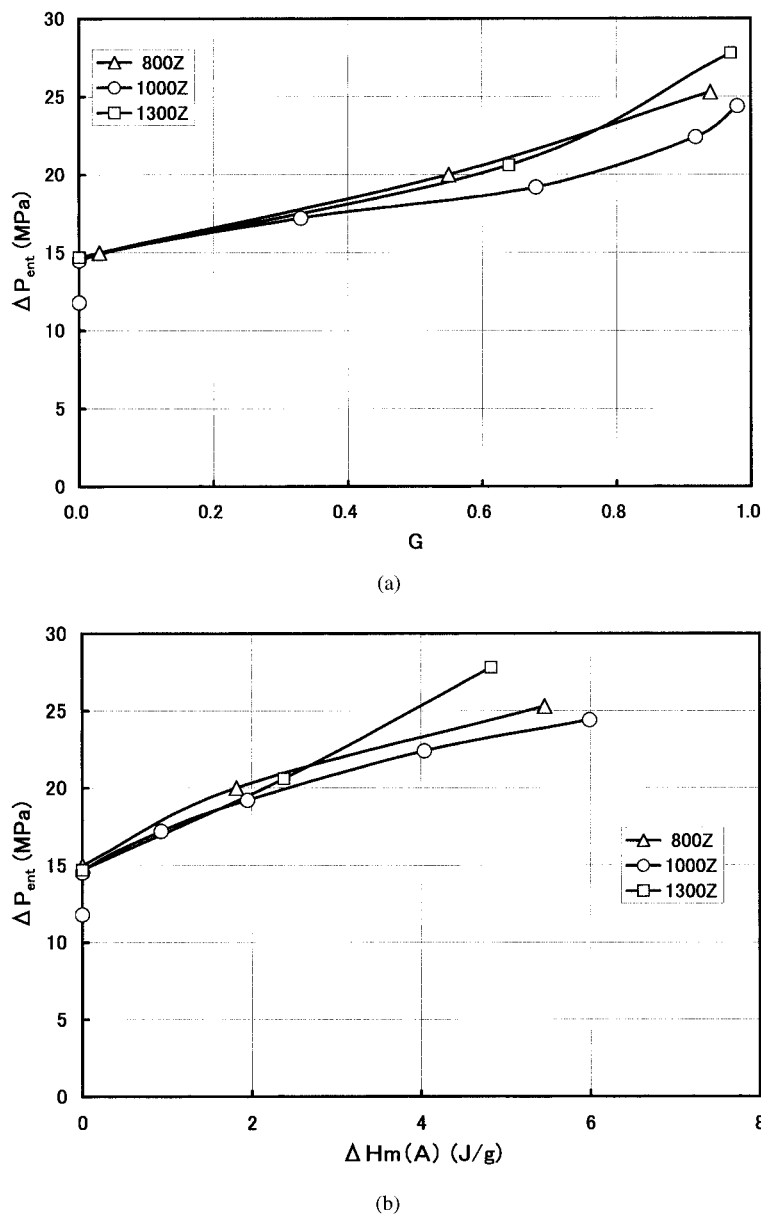
(a)

(b)

Figure 22 Relation between entrance pressure loss ΔP_{ent} and (a) degree of gelation G and (b) low-temperature endotherm ΔHm(A).

dependent of the milling and extrusion temperatures at high shear rates. These were assumed to be because, by shifting from low milling and extrusion temperatures to high ones and hence with advancing gelation, and by decreasing the shear rate, the particle flow shifted to a uniform molecular flow.

4. The die swell increased with elevating the milling and extrusion temperatures and hence with advancing gelation. It increased with decreasing DP and this tendency was even more pronounced at the higher extrusion temperature. From this it is assumed that the increase in the gelation during extrusion is the more prominent

or the feature of the particle flow is the weaker for a resin with the lower DP. In the case of high milling (200°C) and extrusion (190°C) temperatures and hence of advanced gelation, the effect of DP becomes slight. In this case, it is assumed that the particle flow is small and the uniform flow is prominent.

5. The melt fracture is the more prominent when a sheet milled at the higher roll temperature is extruded at the lower extrusion temperature. While at low milling temperatures (< 180°C) a sample with the lower DP shows the lower critical shear rate at onset of melt fracture and hence easily generates melt fracture, at high

milling temperatures (200°C) it shows the higher critical shear rate and hence hardly generates melt fracture. This is assumed to be because the particle flow becomes little and the uniform flow becomes prominent as in the case of usual thermoplastic resins.

6. The entrance pressure loss measured at a low temperature of 140°C increases with the milling temperature and hence with the degree of gelation. Because it is scarcely affected by DP, it can be used as a measure of gelation even for resins with different DPs.

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