Effect of Gelation on the Flow Processability of Poly(vinyl chloride)

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ABSTRACT: The processing of poly(vinyl chloride) (PVC) consists of fusion, flow, and solidification processes. In this study, we examined how gelation in the fusion process affected the processability in the following flow process. We prepared sheets with adjusted degrees of gelation (*G*s) by rolling a rigid-pipe-formulation PVC compound with a degree of polymerization of 1050 by changing the milling temperature and time. The rheological properties, including viscosity, die swell, melt fracture, and entrance pressure loss (ΔP_{ent}), of the sheets were measured with a capillary rheometer, and the effect of gelation on the flow processability was studied. The viscosity slightly increased as the milling temperature and time increased, and hence, *G* increased. The flow activation energy showed a maximum at a shear rate around 100 s^{-1} and increased with increasing gelation. The die swell was larger when a sheet with a more advanced gelation was extruded at a higher temperature. Melt fracture easily occurred when a sheet with an advanced gelation was extruded at a low temperature. The critical shear rate at the onset of melt fracture changed by over 3 decades, depending on *G*. ΔP_{ent} increased linearly with *G*. The dependence of the rheological properties on the gelation was in the following order: melt fracture $>$ die swell $\fallingdotseq$ ΔP_{ent} $>$ viscosity: The effect was larger for the elasticity than for the viscosity. The change in these rheological properties with increasing gelation was caused by a transition from particle flow to uniform molecular chain flow. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1808–1824, 2003

Key words: poly(vinyl chloride) (PVC); gelation; melt; rheology; extrusion

INTRODUCTION

When the quality of a plastic is determined, it is necessary to consider its processability, namely, its processing properties and the quality of the final part, that is, the product properties. In the processing of a plastic, the raw powder or pellets are melt-plasticized, shaped by flow and deformation in molten state, and cooled down; the shape is fixed; and a shaped article is obtained. In short, the plastic processing consists of three main processes: fusion, flow, and solidification. This article concerns the behavior in the flow process, namely, the flow processability. The flow processability includes many characteristics. It includes not only the viscosity but also the elastic characteristics, such as die swell, entrance pressure loss (ΔP_{ent}), and melt fracture, and the dependence on temperature and shear rate. In actual processing, these and other various rheological characteristics of raw materials, together with the processing machine and conditions, manifest complex phenomena. To rheologically break down and analyze the complex phenomena, the viscosity and other characteristics mentioned previously were used. The meanings of these rheological characteristics to the processability are described in Results and Discussion section.

Material factors that affect the flow processability of poly(vinyl chloride) (PVC) include the primary structures, such as molecular weight, molecular weight distribution, tacticity, copolymerization, and crosslinking; the formulations, such as thermal stabilizers, lubricants, reinforcing agents, and fillers; and the particle structures, such as particle size, particle size distribution, porosity, and bulk density. These factors affect the gelation characteristics in the fusion process and directly or indirectly affect the flow processability through changes in the gelation. In this study, the effect of the gelation characteristics [degree of gelation (*G*)] in the fusion process on the flow processability in the following flow process was examined. Namely, this study was concerned with the processability and product properties of PVC and with the effect of gelation on the melt processability.

Several studies[1–16] have been reported so far on the effect of gelation (milling) on the flow processability (rheological properties) of PVC. Uryu et al.[1] studied the effect of milling on the viscosity of rigid-formulation suspension PVC compounds and showed that the milling generally decreases the viscosity. They also showed that the dependence of slope of the flow curve, namely the structural viscosity exponent, on the

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degree of polymerization is weakened by milling. Furthermore, they suggested a rudimentary particle flow concept based on the experimental results that there are cases at high shear stresses where the resin with higher degree of polymerization shows lower viscosity than the resin with lower degree of polymerization.

Berens and Folt[2] studied the capillary flow properties of a suspension PVC and an emulsion PVC with an equivalent molecular weight distribution curve and showed experimentally that the former showed a higher viscosity and die swell and more easily generated melt fracture and that these rheological properties became more notable when the emulsion PVC powder was given such treatments as dissolution in a solvent, heating, milling, and compression molding. They proposed the particle flow concept and explained their experimental results by it. 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). The proportion of uniform and particle flow is changed by the degree of milling (gelation) and flow (measurement) conditions. In general, a higher gelation and flow temperature promote uniform flow. Because uniform flow is a flow where molecular chains diffuse each other and are well entangled, the viscosity is higher and the elasticity, such as die swell and melt fracture, is more notable there than in the case of slippery particle flow. Berens and Folt[3] also showed that the viscosity and die swell of the emulsion PVC increased with decreasing particle size and increasing compression temperature, whose cause they assigned to the weakened particle flow. Furthermore, in the ref. 4, they showed that with increasing particle size of the emulsion PVC, with increasing degree of polymerization, and with decreasing extrusion temperature, the particle flow became more notable, leading to a decreased viscosity and die swell and a suppressed melt fracture.

Shinagawa[5] prepared sheets with various degrees of milling by changing the roll-milling temperature and time from an Sn-formulation compound and a Pb-formulation compound of suspension straight PVC with a degree of polymerization of 1050 and measured their capillary flow properties. Shinagawa showed that for both formulation compounds, the viscosity increased, the melt fracture occurred easily with increasing milling, and these effects were more remarkable at lower extrusion temperatures. Shinagawa explained these experimental results by the particle flow concept.

Minoshima et al.[6] found that the viscosity, the end correction coefficient, and the ΔP_{ent} of an ethylene–vinyl chloride copolymer decreased with increasing roll-milling temperature and, hence, with increasing gelation, which was an inverse tendency of the emulsion straight PVC by Berens and Folt.

Fujiyama and Nagou[7] prepared compounds with various degrees of milling by changing the milling time with a Brabender plastograph from an Sn-formulation compound and a Pb-formulation compound of a suspension straight PVC with a degree of polymerization of 800 and measured their capillary flow properties. They showed that the viscosity and elasticity, such as die swell and melt fracture, became more notable with increasing milling time and, hence, gelation. These rheological properties were more remarkable for the Sn-formulation compound with easy gelling characteristics than for the Pb-formulation compound with poor gelling characteristics. These results were well explained by the concept of particle and uniform flow. However, the end correction coefficient, which is also a measure of elasticity, decreased with increasing milling and was higher for the Pb- formulation with poor gelation characteristics than for the Sn- formulation with good gelation characteristics. From this, it was considered that the end correction coefficient could not always be regarded as a measure of elasticity in the case of materials that show dilatant flow, such as the PVC compound. Fujiyama and Nagou[8] prepared compounds with various degrees of milling by changing the roll-milling temperature of a Pb-formulation compound of a poly(vinyl chloride–propylene)–polypropylene oxide graft copolymer and measured their capillary flow properties. They found that with increasing roll temperature and, hence, the gelation, the viscosity decreased, the ΔP_{ent} increased, and the die swell hardly changed. These results also could not be explained by the particle flow concept, as in the case of ethylene–vinyl chloride copolymer by Minoshima et al. mentioned previously. It seems that there exist complexities that cannot be explained by the particle flow concept in the cases of PVC copolymers.

Terselius et al.,[9] Krzewski and Collins,[10–12] Patel and Gilbert,[13] Summer and Rabinovitch,[14] and Obande and Gilbert[15] showed that with increasing processing temperature and, hence, gelation of rigid-formulation suspension PVC, ΔP_{ent} in the capillary flow increased in an S-shaped fashion. Terselius et al.[9] also reported that the die swell ratio (D/D_0) also showed a similar behavior to ΔP_{ent}.

Hinrichsen and Thorsteinsen[16] prepared sheets by changing the roll-milling temperature of window-frame-formulation suspension PVCs and measured their melt dynamic viscoelasticities. They showed that with increasing milling and, hence, gelation, the elasticity [dynamic modulus (G')], as measured against the viscosity [loss modulus (G'')], increased and tan δ (tan $\delta = G''/G'$) decreased when the measuring temperature was lower than the processing temperature, whereas G', as measured against G'', decreased and tan δ increased when the measuring temperature was higher than the processing temperature. Their results

indicate that tan δ was below unity at low measuring temperatures, increased with increasing measuring temperature, and showed a tan δ value above unity at high measuring temperatures (203°C). G'' is usually higher than G' and tan δ is above unity in the melt dynamic viscoelastic behaviors of homogeneous polymers without, for example, crosslinking. Tan δ of a PVC melt showed values below unity at low temperatures because the crystallites worked as crosslinking points and the elasticity was notable. Tan δ was lower and the elasticity was more notable for the sample with more enhanced gelation in low measuring temperatures because the primary particles of PVC were more tightly connected by fringed micelle crystallites for the sample with the more enhanced gelation. However, the fringed micelle crystallites melted at high measuring temperatures and approached a homogeneous structure similar to those of usual polymer melts, which lowered the elasticity and increased tan δ.

As mentioned previously, although the effects of gelation on the rheological properties of PVC melts have been extensively studied, systematic studies have been few, and unifying views have not yet been proposed. In this study, we adjusted G of a rigid-pipe-formulation PVC by changing the roll-milling temperature and time; the capillary flow characteristics were measured for the samples well-characterized in gelation, and the effects of gelation on the flow processability were systematically studied.

EXPERIMENTAL

Samples

A straight PVC powder, grade ZEST 1000Z, with a degree of polymerization of 1050 (Shin Dai-ichi Vinyl Corp., Shunan City, Japan) was used as the raw material.

Formulation

A rigid-pipe-formulation was prescribed. The following were added to 100 phr of the PVC powder: monohydrous tribasic lead sulfate (1.5 phr), lead stearate (1.0 phr), stearic acid (0.2 phr), calcium stearate (0.2 phr), and an acrylic processing aid (0.5 phr). 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

To study the effect of roll-milling temperature, 150 g of the powder compound was milled with a 6-in. test roll at 150, 160, 170, 180, 190, and 200°C for 5 min after the material rounded the roll, and sheets 0.6–0.7 mm thick were prepared. To study the effect of roll-milling time, we milled 150 g of the powder compound at 180°C for 5, 10, and 15 min after the material rounded the roll.

Measurement of the degree of gelation

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 differential scanning calorimeter (DSC6200R, Seiko Instruments, Inc., Chiba, Japan), the temperature was raised from 30 to 240°C at a rate of 20°C/min, and a differential scanning calorimetry (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.

Figure 1 shows as an example a DSC thermogram of the sheet roll-milled at 180°C. The low-temperature endotherm [ΔH_m(A)] was obtained as an area enveloped by the thermogram and a base line, which was drawn so as to touch the shoulder around 120°C and the history temperature (T_c). The high-temperature endotherm [ΔH_m(B)] was obtained as an area enveloped by the thermogram and a base line, which was drawn so as to connect T_c and 230°C (fixed). The degree of gelation was obtained as the absolute value of ΔH_m(A) or as the ratio $G = \Delta H_m(\mathrm{A})/[\Delta H_m(\mathrm{A}) + \Delta H_m(\mathrm{B})]$. We assumed that ΔH_m(A) originated from the fusion of fringed micelle crystals that melt-recrystallized during processing, that ΔH_m(B) originated from the fusion of lamellar crystals that did not melt during processing, and that T_c was the maximum experience temperature of the resin.[17,18] DSC measurement was carried out five times for each sample, and the averaged value was adopted. The maximum standard deviation of ΔH_m(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.

Morphology observation

The rolled sheet was immersed in liquid nitrogen, thoroughly cooled, and fractured by bending. The fractured surface was vacuum-evaporated with gold and observed with a scanning electron microscope (JSM-5600LV, JEOL, Tokyo, Japan) at a magnification of 1000× under an acceleration voltage of 15 kV.

Measurement of the 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, Toyo Measurement Instruments Co., Ltd., Tokyo, Japan) at 150, 170, and 190°C with a straight die with a capillary length (L) of 20

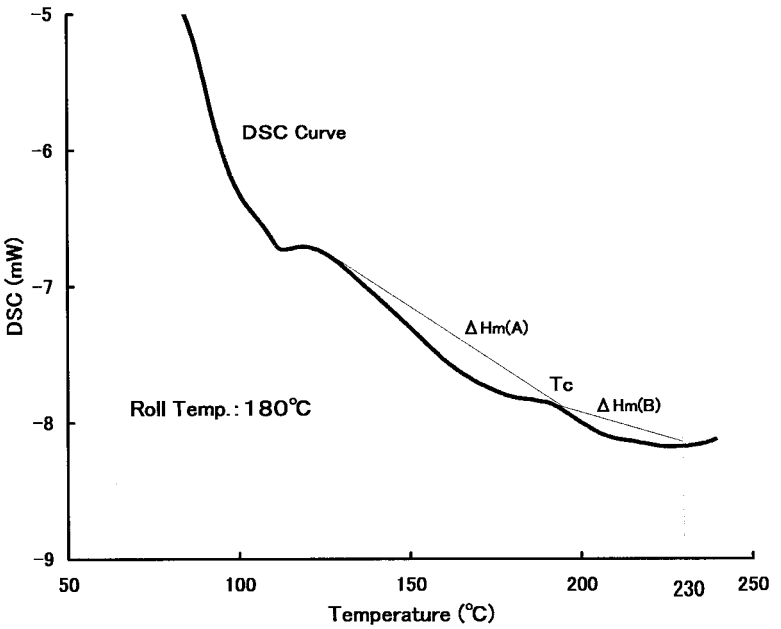


Figure 1 Measurement of degree of gelation by DSC.

mm, a capillary diameter ($D_0 = 2R$, where R is the radius) of 1 mm, and an L/R of 40. The sample amount was 20 g, and the preheating time was 5 min

The apparent shear stress (τ), the apparent shear rate ($\dot{\gamma}$) at the wall, and the apparent viscosity (η) in the capillary flow are given by eqs. (1), (2), and (3), respectively:

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

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

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

From these equations, the flow curve ($\tau - \dot{\gamma}$ or $\eta - \dot{\gamma}$) was obtained.

After the extrudate solidified, its diameter (D) at the part 5 mm from the front was measured with a micrometer, and D/D_0 was used as a measure of die swell.

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, Olympus Optical Co., Ltd., Tokyo, Japan).

As shown in the upper part of Figure 2, when the PVC melt entered from a reservoir with a larger diameter into a capillary with a smaller diameter ($D_0 = 2R$) and length, L, an enerance pressure loss, ΔP_{ent} occurred because of the change in the flow lines, as shown in the lower part of the figure. ΔP_{ent} mainly originates from the melt elasticity, and in the case of PVC, it shows a degree of unification (homogenization) of the resin and can be used as a measure of gelation. Although ΔP_{ent} can be obtained as P with a die with $L = 0$, the strength of the die with $L = 0$ cannot endure the extrusion force. Therefore, in this experiment, P was measured with a die with a small L (1 mm) as measured against the diameter ($D_0 = 2$ mm), and the pressure was approximately regarded as ΔP_{ent}. To prevent the effect of thermal history at measurement, the measurement was carried out at 140°C, which was 10°C lower than the lowest roll-milling temperature of 150°C. The shear rate at measurement of ΔP_{ent} was one point of 7.6 s^{-1}. Because the extrusion temperature changed a little with 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.

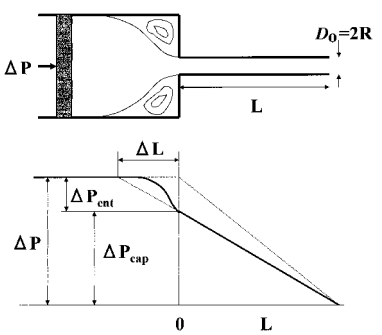


Figure 2 Measurement of ΔP_{ent}. ΔP: total pressure loss; ΔP_{cap}: pressure loss in capillary; L: capillary length.

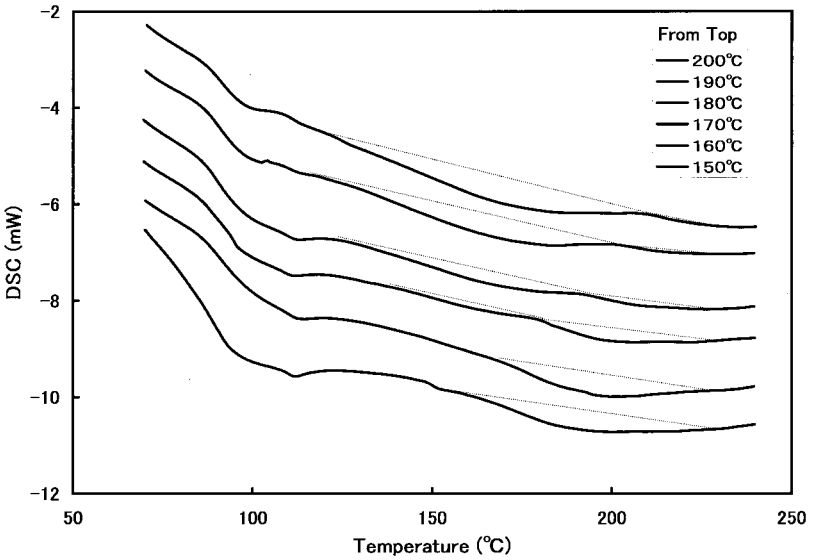


Figure 3 DSC curves of sheets milled at various roll temperatures.

Because the thermal degradation of the PVC compound became not negligible at temperatures above 200°C, the capillary flow measurements were carried out at temperatures not exceeding 190°C. Although the possibility exists that PVC melt slipped at the die wall during flow, the data were treated as no-slip. Furthermore, although shear heating might have occurred at high shear rates, it was neglected.

RESULTS AND DISCUSSION

Degree of gelation

Figure 3 shows the changes in the DSC thermogram with roll-milling temperature. With increasing temperature, ΔH_m(A) appeared and gradually increased, and ΔH_m(B) gradually decreased. At the same time, T_c rose.

Figure 4 shows the dependence on the roll-milling temperature of $G = \Delta H_m(A)/[\Delta H_m(A) + \Delta H_m(B)]$ and ΔH_m(A), the latter of which was often used as a degree of gelation in early times, of the rolled sheet. The gelation began around 160°C and terminated around 200°C when evaluated by G, whereas it still increased even at 200°C when evaluated by ΔH_m(A).

Figure 5 shows the dependence of G and ΔH_m(A) on roll-milling time at a roll temperature of 180°C. Both increased with time, and G increased by about 0.15 when the time was prolonged from 5 to 15 min. As shown by the fact that the gelation increased with increasing rolling time at the same roll temperature,

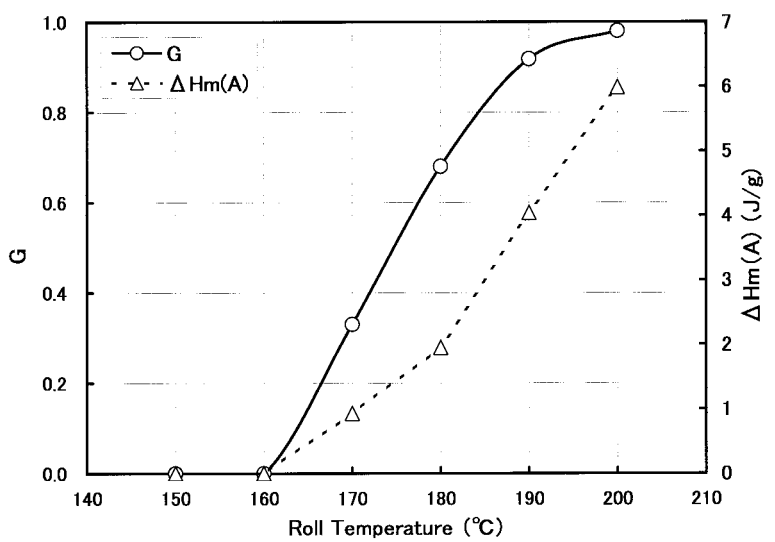


Figure 4 Dependence of G and ΔH_m(A) on roll temperature.

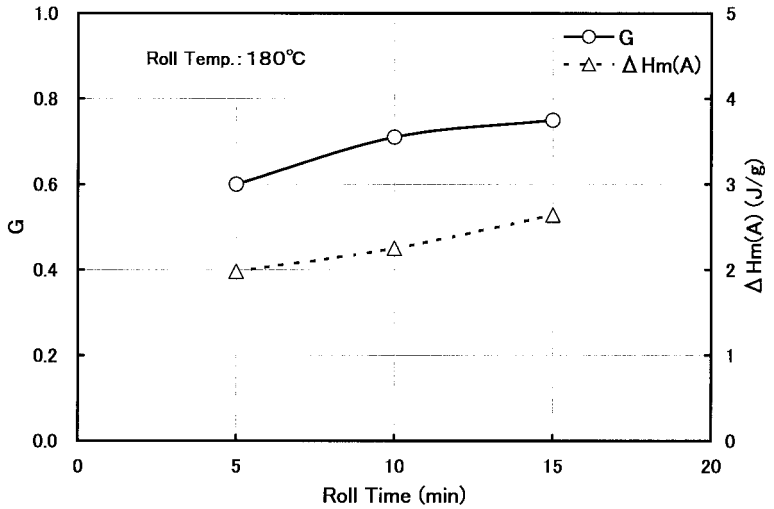


Figure 5 Dependence of G and ΔH_m(A) on roll time.

the gelation was decided not only by the temperature but also by the shear (mechanical force).

Morphology observation

Figure 6 shows the changes in the cryogenic fractured surface of the milled sheet with roll-milling temperature. Primary particles with a diameter of 1–2 μm were observed at low milling temperatures, and the particle structure gradually became obscure with increasing milling temperature and approached a homogeneous structure.

Flow curve (viscosity)

The rheological characteristic that should be considered first in the evaluation of the flow processability of a polymer is the viscosity. The viscosity is represented by the flow curve. To evaluate the flow processabilities in various processing methods, the viscosity at the corresponding shear rate range can be measured. For example, the mixing torque of a screw extruder and the injection pressure of injection molding can be evaluated by the shear viscosity at high shear rates, and the lower the value is, the smaller the processing power is. However, the drawdown after leaving a die at extrusion and blow-molding and the drawdown at pressure/vacuum formation are evaluated by the viscosity at low shear rates.

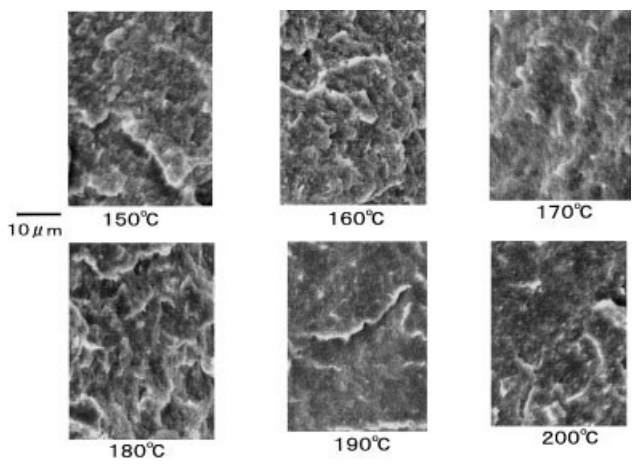


Figure 6 Changes in fracture surface morphology with roll temperature.

Figure 7 exemplifies the change, with the extrusion temperature, of the flow curve represented in the form of the changes in the viscosity with shear rate for the sheet milled at 180°C. The viscosity decreased with increasing extrusion temperature and shear rate, showing non-Newtonian behaviors. The degree of the decrease in viscosity with increasing shear rate, namely, the non-Newtonianity, changed at shear rates around 200 s^{-1} and showed breaking points, and the non-Newtonianity of the high-shear-rate side was more remarkable than that of the low-shear-rate side.

To study the temperature change in the viscosity, η at each shear rate was plotted against the reciprocal absolute temperature (T). Straight lines were obtained, as shown in Figure 8, for the sheet milled at 180°C, and the Arrhenius equation represented by the following form held:

$$\eta = A\exp\frac{\Delta H_a}{RT} \tag{4}$$

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

Figure 9 shows the variation of ΔH_a obtained from Arrhenius plots with shear rate and milling temperature. ΔH_a showed maxima at shear rates around 10^2 s^{-1} and then decreased. Samples milled at high tem-

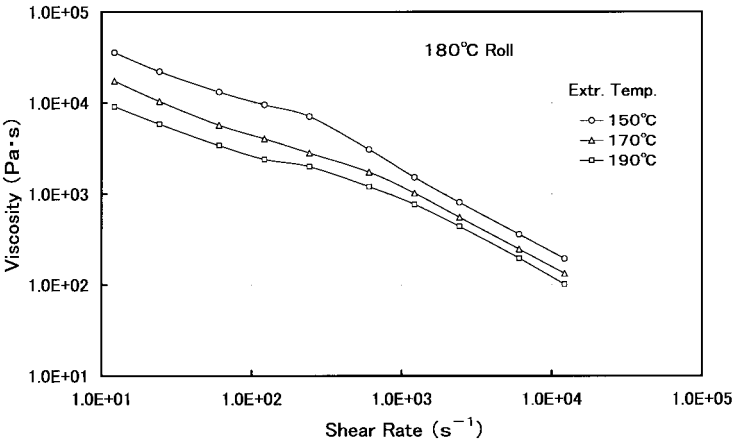


Figure 7 Temperature change of the flow curve.

peratures and with enhanced gelations showed high ΔH_a's at high shear rates around 10^4 s^{-1}. As to the effect of gelation, samples milled at high temperatures and with enhanced gelations tended to show high ΔH_a's. This tendency was particularly notable at the high milling temperatures of 190 and 200°C. Figure 10 shows the effect of milling time on ΔH_a. With increasing milling and, hence, gelation, ΔH_a increased. This change was particularly notable at milling times from 5 to 10 min.

Collins and Krier[19] measured the viscosity of an Sn-formulation rigid suspension PVC compound in the temperature range 160–240°C and the shear rate range 0.3–150 s^{-1} and evaluated the changes in ΔH_a with shear rate and stress. The activation energies at low-temperature and high-temperature regions differed from each other, and the former was lower than the latter. Although the latter decreased with shear rate, the former showed a maximum at a shear rate around 15 s^{-1}. The temperature at transition from the low temperature region to the high-temperature region increased with increasing shear rate. They regarded 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 assumed that the fact that the transition temperature from the particulate to molecular flows increased with shear rate was because with increasing shear rate, the molecular orientation increased, and the dissolution to molecular chains became more difficult. The extrusion temperature range was 150–190°C, and the shear rate range was 10–10000 s^{-1} in this experiment, which was in the low-temperature region of the experiment by Collins and Krier. The change in ΔH_a with shear rate in this experiment showed maxima like in their experiment. The shear rate at the maxima was around 100 s^{-1} in this experiment, whereas it was around 15 s^{-1} in their results, the former being slightly higher. The absolute values

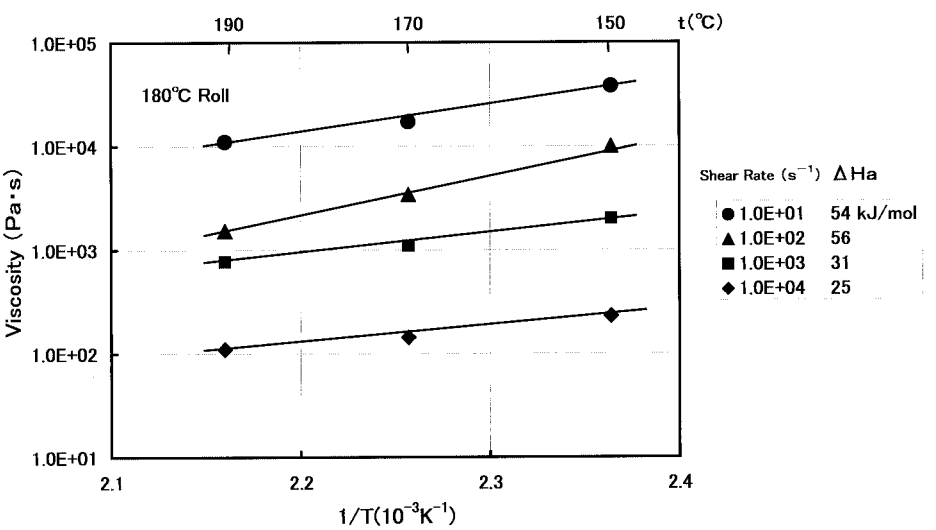


Figure 8 Temperature change of the viscosity (Arrhenius plot).

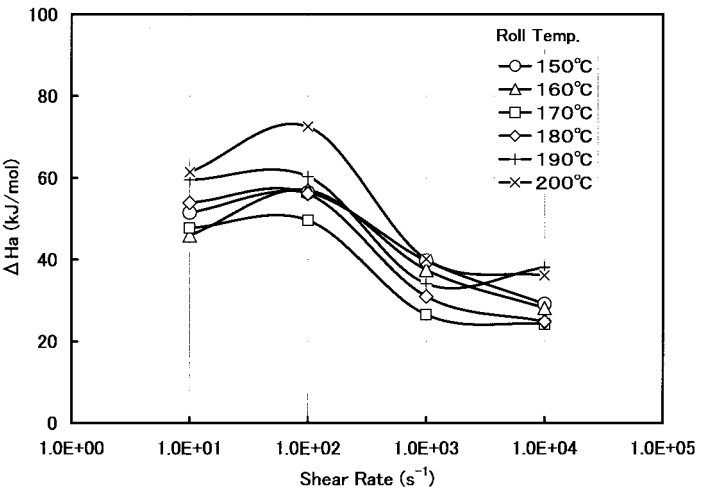


Figure 9 Changes in ΔH_a with roll temperature and shear rate.

of the activation energy in this experiment were between those of their high-temperature and low-temperature regions. These facts were assumed to be due to differences in the degree of polymerization and formulation. The fact that samples milled at high temperatures and with enhanced gelations tended to show high ΔH_a in this experiment was assumed to be because with increasing gelation, the particle structure collapsed and approached a unified homogeneous structure, which led to 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 ΔP_{ent} described later.

ΔH_a represents the degree of temperature changes in the viscosity and other rheological characteristics, and a high ΔH_a of a polymer indicates large changes in the viscosity and other rheological properties with temperature changes. Accordingly, whereas high ΔH_a has the merit of providing a large drop in viscosity with a small temperature increase, it also provides large changes in the processing behaviors with a change in processing conditions (processing temperature) and is not favorable from the view point of processing stability. Because ΔH_a increased with milling at high temperatures for a long time and, hence, with increasing gelation, it may be said that it is favorable not to enhance the gelation too much from the view point of processing stability.

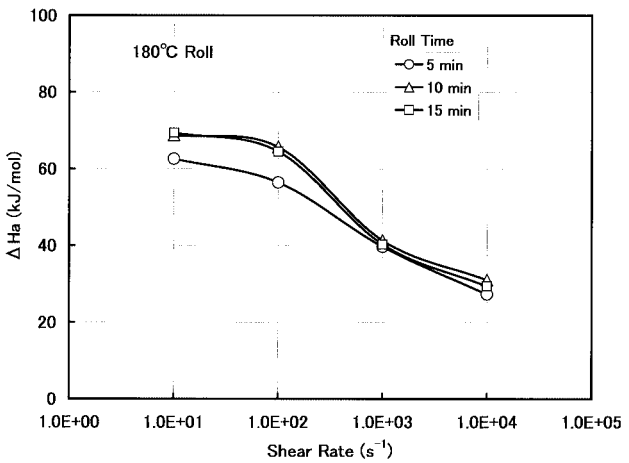


Figure 10 Changes in ΔH_a with roll time and shear rate.

Next, the changes in the flow curve with gelation are discussed. Figure 11(a–c) shows the changes in the flow curve, with milling temperature, measured at 150, 170, and 190°C. At shear rates below the breaking points, the viscosity tended to increase with increasing milling temperature and, hence, gelation. This tendency was more notable at the lower extrusion temperature and gradually became unrecognizable with increasing extrusion temperature. Figure 12(a–c) shows the effect of milling time on the flow curve. The viscosity slightly increased with increasing milling time and, hence, gelation. This tendency was more remarkable at the lower extrusion temperature, and there was little difference at an extrusion temperature of 190°C. These experimental results agree with the results of Shinagawa.[5]

The fact that the viscosity increased with increasing roll-milling temperature and time and, hence, with enhancing gelation was assumed to be because with enhancing gelation, the particle structure collapsed and the particle flow shifted to the uniform flow, as mentioned in the Introduction. Because the change in gelation by the milling temperature and time strongly affected the flow curve at low extrusion temperatures and affected it less with increasing extrusion temperature, we assumed that the gelation proceeded during the extrusion (measurement): because the gelation scarcely proceeded at low extrusion temperatures, the gelation of the original sample affected the flow curve. However, because the gelation proceeded well at high extrusion temperatures, the difference in gelation of

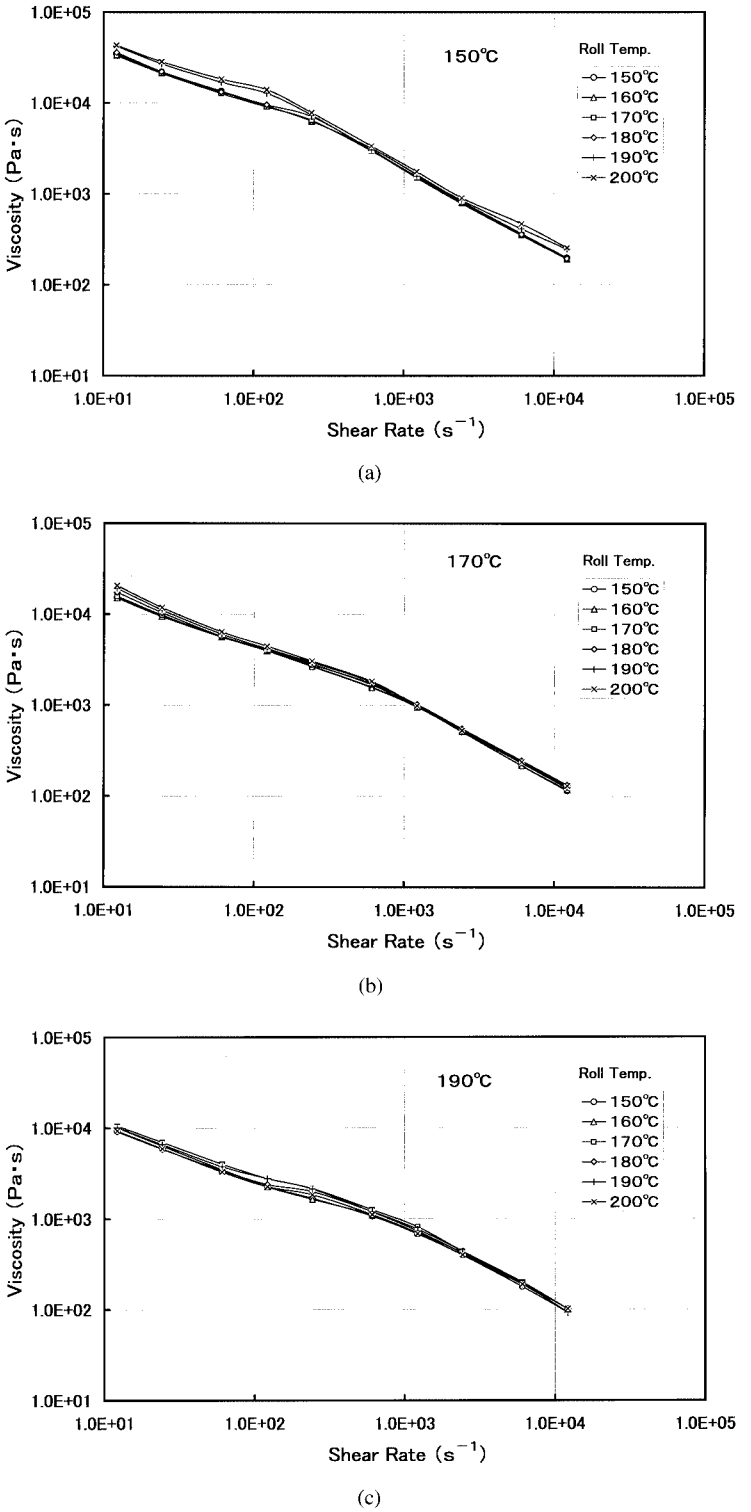
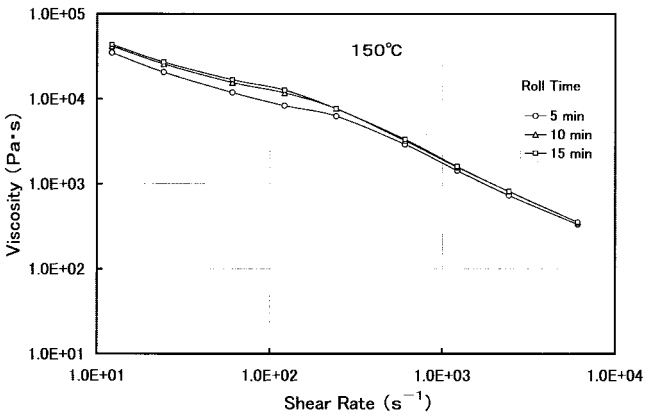


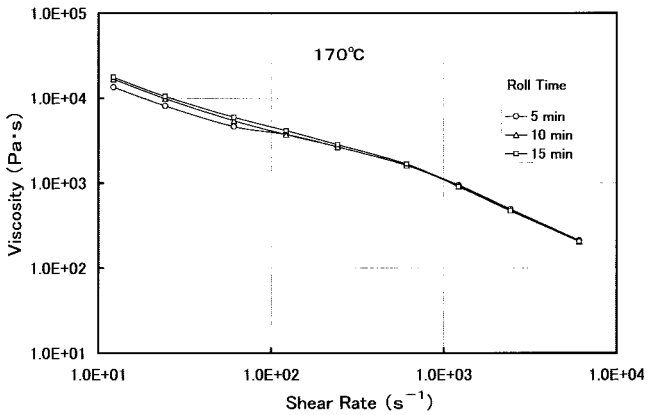
Figure 11 Flow curves of sheets milled at various roll temperatures, measured at: (a) 150, (b) 170, and (c) 190°C.

the original samples became slight, and hence, the effect of gelation of the original sample became less.

With this knowledge, ΔH_a in Figures 9 and 10 are discussed again. For samples milled at low temperatures or for a short time and with low gelations, the increase in gelation during the extrusion was slight at low extrusion temperatures and became higher with increasing extrusion temperature. Accordingly, the increase in viscosity caused by the increase in gelation during the extrusion increased with increasing extrusion temperature, and ΔH_a was apparently calculated too low. With increasing gelation of original sample,



(a)



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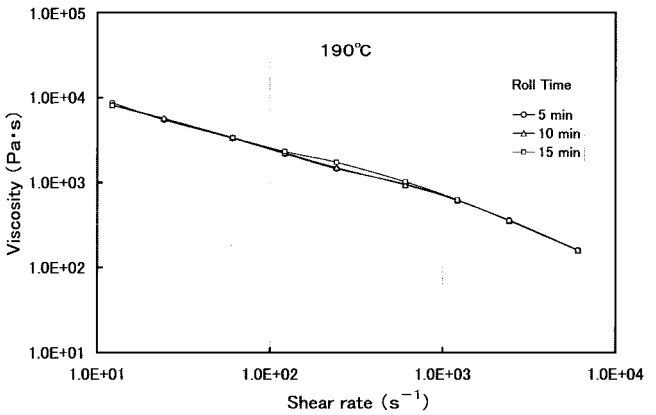


(c)

Figure 12 Flow curves of sheets milled for various roll times measured at (a) 150, (b) 170, and (c) 190°C.

because the increase in gelation during the extrusion became small, the effect on ΔH_a decreased. In other words, ΔH_a did not increase with increasing gelation, but the flow activation energies of samples with low gelations were evaluated at lower than the actual values. Next, the maxima of ΔH_a at shear rates around 100 s^{-1} are discussed again. Because the increase in viscosity by the increase in gelation was larger at the lower shear rate, the effect of the increase in gelation during the extrusion appeared larger at the lower shear rate, as shown in Figures 11 and 12. Therefore, there is a possibility that the activation energies at a shear rate of 10 s^{-1} were evaluated too low. Accordingly, the activation energies may have become lower than those at a shear rate of 100 s^{-1}. Although the cause of the increase in ΔH_a with an increase in the gelation and the existence of its maxima in the shear rate dependence may not have totally originated from this effect, we are sure that this effect partly attributed to it.

Die swell

The phenomenon in which an extrudate of a polymer melt swells at the die exit is called the die swell or Barus effect. Its cause is the recovery, at the die exit, of melt orientation, which was formed at the die entrance where the polymer melt enters from a flow path with a larger cross-section into the flow path with a smaller cross-section. The die swell is generally evaluated by the ratio of the extrudate diameter (D) to the bore diameter of the die D_0, D/D_0, which is called the die swell ratio or the memory effect value. Because of the die swell, the diameter of extrudate becomes larger than the bore diameter of the rod die, the diameter and thickness of extrudate becomes larger than those of the tube die, and the side of the extrudate swells and rounds in cases of profile dies, such as triangular and cross-shaped dies. Accordingly, the die swell is an important technical factor in extrusion, particularly in contour extrusion, and a polymer with a D/D_0 near to unity gives an extrudate with a shape true to the shape of the die cross-section and is favorable.

Figure 13(a–d) shows the changes in D/D_0 of samples milled at 150, 160, 170, and 180°C with extrusion temperature. The change in D/D_0 with shear rate showed valleys or peaks, which is a characteristic of PVC.[3,4,7,20–23] The D/D_0's of common resins, such as polypropylene and polyethylene, monotonously increase with shear rate. The D/D_0 increased as the extrusion temperature increased, and this tendency weakened with increasing milling temperature. The fact that the D/D_0 increased with increasing extrusion temperature is also a characteristic of PVC,[4,20,21,23–27] and the D/D_0's of common resins decrease with increasing extrusion temperature. In the case of insufficient gelation, because PVC flowed by slipping and rolling in the particulate state, its flow was a plastic flow, and the storage of elastic recoverable strain at the entrance of the capillary was small, and hence, the elastic recovery at the capillary exit was weak, leading to a small die swell. With increasing gelation, melt unification proceeded, and the PVC melt became elastic because of the well-entangled molecular chains and stored a large elastic recoverable strain at the entrance

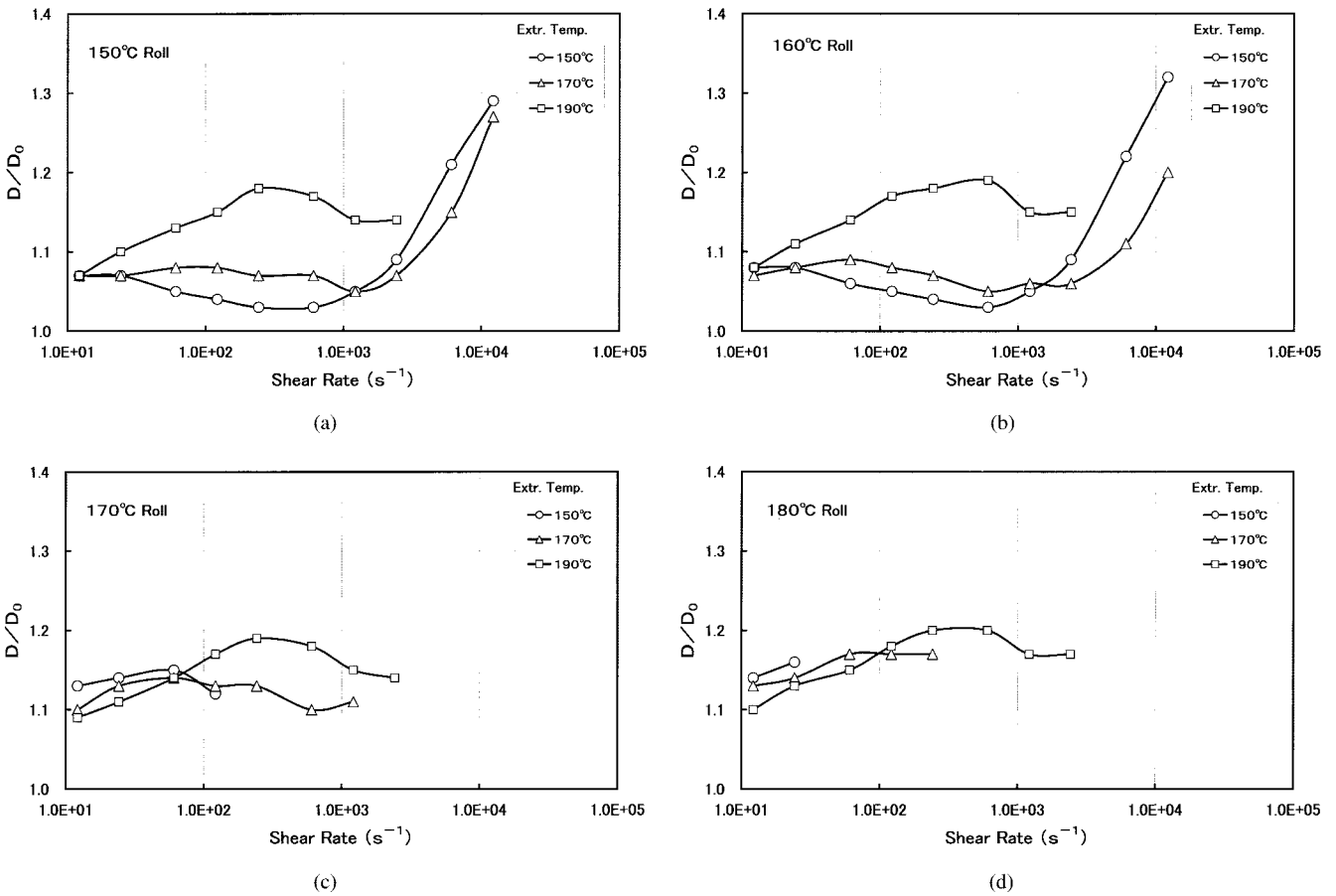
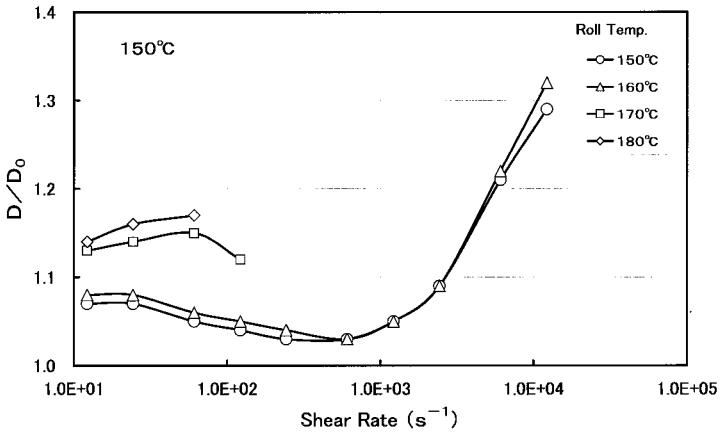


Figure 13 Changes in D/D_0 with temperature and shear rate for sheets rolled at (a) 150, (b) 160, (c) 170, and 180°C.

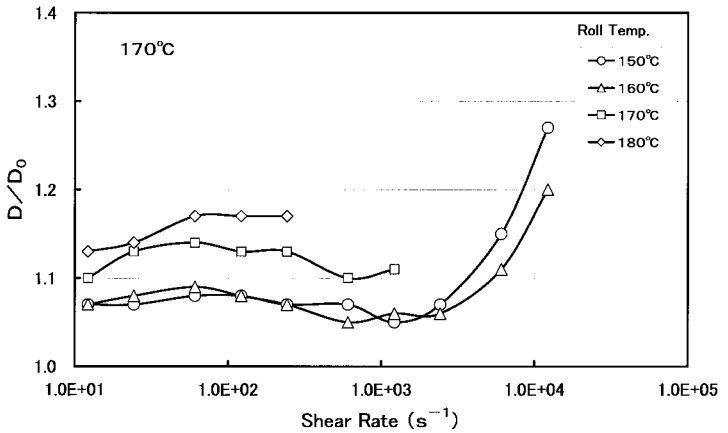
of capillary. Accordingly, the elastic recovery after the emergence from the capillary was large, leading to a large die swell. The fact that the dependence of D/D_0 on the extrusion temperature weakened with increasing milling temperature was assumed to be due to the progress of gelation during the extrusion. In the case of the sample milled at a low temperature, its gelation was originally low, as shown in Figure 4, and increased with increasing extrusion temperature, and hence, the die swell was larger as the extrusion temperature increased. With increasing milling temperature, because the gelation of the original sample had already proceeded, the progress of gelation during the extrusion was slight, the difference of the gelation by the extrusion temperature was small, and hence, the dependence of die swell on the extrusion temperature became small. When the milling temperature was 150 and 160°C, as shown in Figure 13(a,b), because the G values were both 0, as shown in Figure 4, the changes in the die swell with the extrusion temperature showed a very similar tendency. The maximum milling temperature shown in Figures 13 was 180°C in Figure 13(d), and the die swell curves measured at 190°C, which was higher than the maximum milling temperature of 180°C, showed very similar shapes and values independent of the milling temperature. This was assumed to be because the milling histories had vanished because the extrusion temperature was higher than the milling temperature. Although when the milling temperature was 180°C, shown in Figure 13(d), the die swell scarcely depended on the extrusion temperature, further increased milling temperatures might completely melt crystallites and finish the gelation and, hence, lead to the usual behavior where the die swell decreases with increasing extrusion temperature.

From this knowledge, the experimental results[4,20,21,23–27] reported so far, that the D/D_0 of PVC increases with increasing the extrusion temperature, can be explained by the gelation hypothesis: these results can be explained by the idea that the gelation proceeds during the extrusion, and hence, the die swell increases.

Figure 14(a–c) shows the changes, with shear rate, of D/D_0 of rolled sheets milled at various temperatures and extruded at 150, 170, and 190°C. For extrusions at 150°C [Fig. 14(a)] and 170°C [Fig. 14(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



(a)



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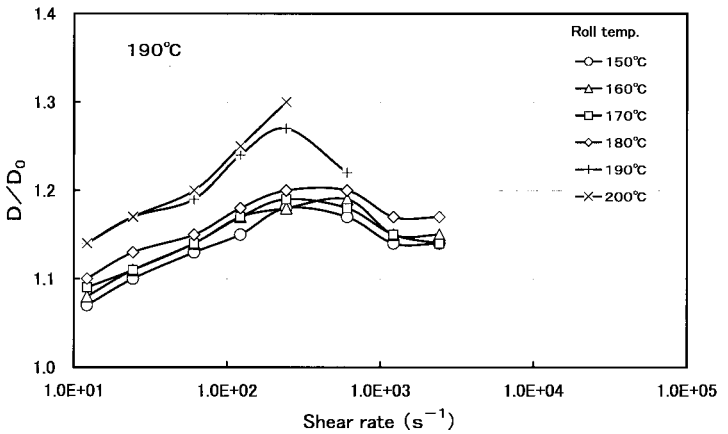
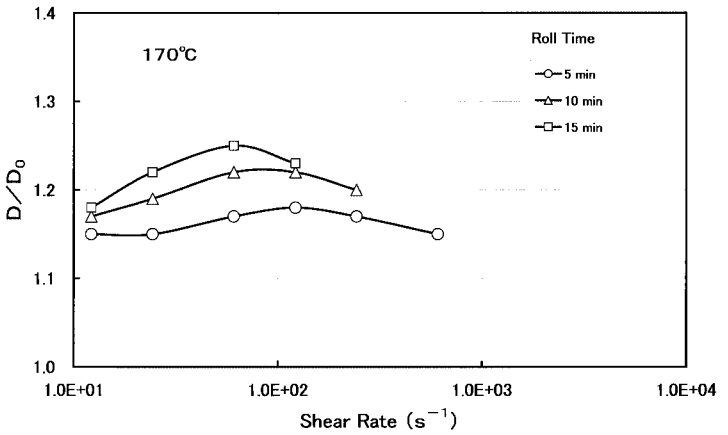


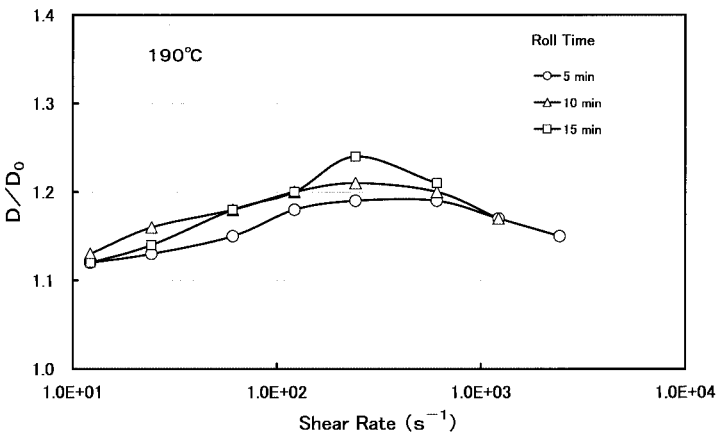
(c)

Figure 14 Changes in D/D_0 with roll temperature and shear rate measured at (a) 150, (b) 170, and (c) 190°C.

could not be evaluated. For the extrusion at 150°C [Fig. 14(a)], the samples milled at 150 and 160°C showed similar and small die swells, and the die swell increased with increasing milling temperature from 170 to 180°C. For the samples milled at 150 and 160°C, because the G values were both 0, as shown in Figure 4, the die swell curves showed very similar shapes and values. For the extrusion at 170°C [Fig. 14(b)], the samples milled at 150 and 160°C also showed similar and small D/D_0's, which were slightly larger than those of the extrusion at 150°C. The die swell increased with increasing milling temperature from 170 to 180°C. For the extrusion at 190°C [Fig. 14(c)], the samples milled at temperatures below 180°C showed



(a)



(b)

Figure 15 Changes in D/D_0 with roll time and shear rate measured at (a) 170 and (b) 190°C.

similar die swell curves, and the samples milled at 190 and 200°C showed higher values. The gelations of all samples milled at temperatures below 180°C were assumed to be raised to that at 190°C during extrusion at 190°C. Other experiments showed that the resin temperature rose by about 10°C higher than the roll temperature. As shown in Figure 14(a–c), the D/D_0's of samples milled at temperatures more than 10°C lower than the extrusion temperature were raised to that of a sample milled at a temperature about 10°C lower than the extrusion temperature: The D/D_0 of the sample milled at 150°C was raised to that at 160°C in the extrusion at 170°C, and the D/D_0's of the samples milled at 150, 160, and 170°C were raised 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. 14(c)], and there was almost no difference between them. The reason for this was the G values of both samples were nearly 1.0: They were completely gelated and, hence, showed similar die swells.

Next, the effect of roll-milling time on the die swell is discussed. Figure 15(a,b) shows the changes, with the milling time, in D/D_0's extruded at 170 and 190°C. For the extrusion at 150°C, because smooth extrudates could not be obtained because of the melt fractures, the die swell could not be measured. The D/D_0 increased with increasing milling time and, hence, gelation. This tendency was more notable at the lower extrusion temperature. The effect of gelation during the extrusion also appeared here. The milling temperature of the samples for the effect of milling time in Figures 15 was 180°C, and hence, the effect of gelation during the extrusion at 170°C was small. Because the resin temperature was about 10°C higher than the roll temperature, the increase in gelation during the extrusion was small, even in the extrusion at 190°C. From the fact that despite this, the die swell increased with increasing milling time, we assumed that the die swell was affected not only by the gelation by heat (temperature) but also by the gelation by shear (milling).

Berens and Folt[3] studied the effect of gelation on the capillary flow properties of emulsion PVCs and showed that the die swell increased with increasing compression temperature and, hence, gelation. They also showed that the die swell was larger as the degree

of polymerization decreased and the particle size decreased, which they assumed to be due to the transition from the particle flow to the uniform molecular flow. Fujiyama and Nagou[7] adjusted the gelations of suspension PVCs with an Sn- formulation and a Pb-formulation by changing the milling time with a Brabender plastograph and studied the effect of gelation on the capillary flow properties. They found that for both formulations, a sample with a long milling time and, hence, with a well advanced gelation showed a higher D/D_0 than the other three samples with short milling times and insufficient gelations. Because the D/D_0's of three samples with insufficient gelations showed similar values, it was assumed that their die swells increased with increasing gelation during extrusion at 190°C, as in this study. Terselius et al.[9] showed that the D/D_0 of a rigid-pipe-formulation suspension PVC increased in an S-shaped fashion with increasing processing temperature of the roll or Brabender plastograph.

The fact that the D/D_0 increased with increasing milling temperature and time was assumed to be because with increasing gelation, the particulate structure collapsed and approached a unified homogeneous structure, which shifted the particle flow, in which primary particles flow in a slippery manner by slipping and rolling each other, to the uniform flow in which molecular segments of entangled molecular chains flow by sliding each other. The effect of milling temperature and time on the die swell was more prominent than that on the viscosity mentioned in the preceding section. Namely, the die swell, which is a melt elastic property, was more affected by the gelation and, in turn, more by the flow mode than the viscosity, which is a melt viscous property.

Because the advanced gelation increased the die swell, it would be preferable not to mill too much in the extrusion processing, particularly in the profile extrusion from the viewpoint of dimensional precision.

Melt fracture

When the extrusion rate is increased and exceeds a critical point in the extrusion of a thermoplastic polymer, the extrudate begins to show defects, such as sharkskin, spiraling, bambooing, and irregular shape, which are generically called melt fracture. Various theories have been proposed for the cause of melt fracture, and they have generally regarded the elasticity of the polymer melt as the origin. The shear rate and stress at which a melt fracture begins to occur are called the *critical shear rate* ($\dot{\gamma}_c$) and *critical shear stress*, respectively. In the case of extrusion, if a melt fracture occurs, the extrudate is inferior in product quality. Accordingly, the extrusion must be carried out at a speed below the $\dot{\gamma}_c$.

Figure 16(a)shows as an example the change, with shear rate, in an extrudate obtained by extrusion of the sheet milled at 170°C at an extrusion temperature of 170°C. At low shear rates, the extrudates were smooth; they began to get distorted with increasing the shear rate to around 1220 s^{-1}, and the distortion increased with increasing shear rate. Accordingly, $\dot{\gamma}_c$ was 1220 s^{-1} in this case. Figure 16(b) shows as an example the change, with milling temperature, in an extrudate obtained by the extrusion of sheets milled at various temperatures at an extrusion temperature of 170°C and a shear rate of 1220 s^{-1}. At low milling temperatures, the extrudates were smooth; they began to get distorted with increasing milling temperature to around 170°C, and the distortion increased with increasing milling temperature. Figure 16(c) shows as an example the change, with extrusion temperature, in an extrudate obtained by extruding the sheet milled at 170°C at a shear rate of 1220 s^{-1}. At low extrusion temperatures, the extrudate was severely distorted, became gradually smoother with increasing extrusion temperature, and was completely smooth at an extrusion temperature of 190°C.

Figure 17 shows the change in $\dot{\gamma}_c$ with milling temperature with the extrusion temperature as a parameter. The arrows indicate the $\dot{\gamma}_c$'s over or under the measuring limits of the shear rate of the apparatus used. The $\dot{\gamma}_c$ decreased as the extrusion temperature decreased. It also decreased with increasing milling temperature and, hence, gelation. This means that the melt fracture initiated at the lower extrusion rate when a sample with more advanced gelation was extruded at the lower temperature. Figure 18 shows the effect of milling time on $\dot{\gamma}_c$. $\dot{\gamma}_c$ decreased and the melt fracture easily occurred with increasing milling time and gelation. Because the same raw material showed the $\dot{\gamma}_c$'s differing by even over 3 decades with different degrees of milling (gelation), it is necessary not to mill too much in extrusion processing.

The effect of milling temperature and time and, hence, gelation on the melt fracture was larger than that on the die swell. The dependence on the gelation was remarkable, in the following order: melt fracture $>$ die swell $>$ viscosity.

The fact that $\dot{\gamma}_c$ at the onset of the melt fracture increased with increasing extrusion temperature is general for thermoplastic resins and was also reported for PVCs.[22,23,28] The fact that with increasing gelation, the melt fracture easily occurred was fragmentarily reported by Berens and Folt,[2] Shinagawa,[5] and Fujiyama and Nagou.[7] According to Paradis,[29] the elastic energy that the PVC melt has stored when entering into the capillary from the reservoir is consumed by the elastic recovery of the die swell. However, when the extrusion speed increases and the stored energy

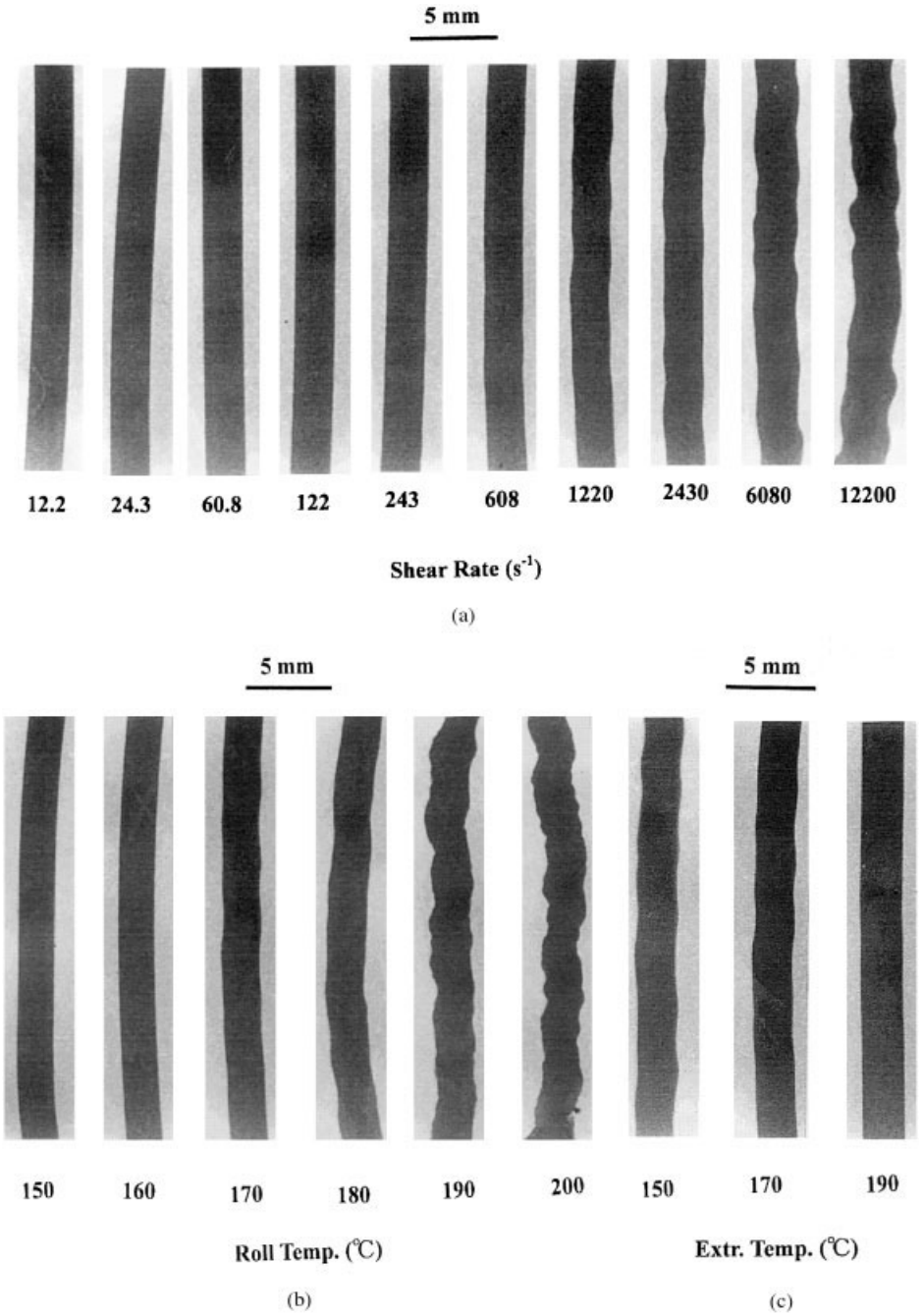


Figure 16 Changes in extrudate appearance with (a) shear rate for samples milled at 170°C and extruded at 170°C, (b) roll temperature for samples extruded at a shear rate of 1220 s^{-1} at 170°C, and (c) extrusion temperature for samples milled at 170°C and extruded at 1220 s^{-1}.

becomes excessive, it cannot hold itself, and a part of it is lost in the form of melt fracture. If the gelation of PVC was insufficient because it flows in a slippery manner by the particle flow, the stored elastic energy at the entrance of capillary was small, and the melt fracture did not easily occur. With increasing gelation, the PVC melt became more elastic by the entanglement of molecular chains and stored much elastic energy, and hence, the melt fracture easily occurred.

Enerance pressure loss

In the case where the shape of flow path in a processing machine changes by contraction or divergence, a pressure drop occurs because of the change in flow lines. This is the enerance pressure loss, ΔP_{ent}. Namely, a high ΔP_{ent} means that the pressure loss at the point where the shape of flow path changes by the contraction or divergence is larger as measured

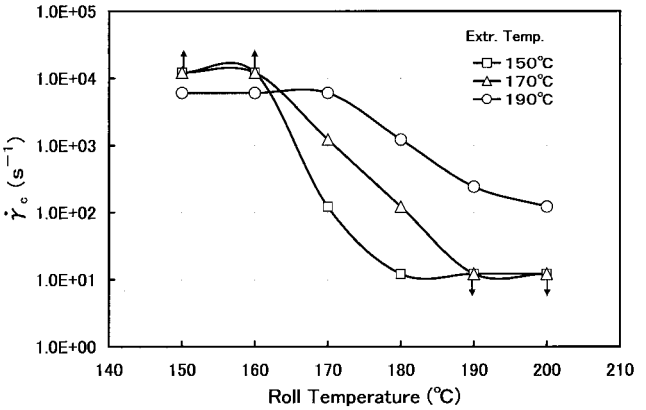


Figure 17 Dependence of $\dot{\gamma}_c$ at the onset of melt fracture on roll temperature.

against the pressure loss at the straight flow path. Because ΔP_{ent} represented the degree of melt unification in the case of PVC, it could be used as a measure of the gelation.

Figure 19 shows the dependence of ΔP_{ent} on the milling temperature. ΔP_{ent} increased with milling temperature. ΔP_{ent} of the sheet milled at a low temperature of 150°C was lower than that of unmilled powder. This was assumed to be because linking structures between the primary particles in polymerized powder were collapsed mechanically by milling at a low temperature. Figure 20 shows the dependence of ΔP_{ent} on the milling time. ΔP_{ent} increased with milling time. Although G reached the top around 200°C, as shown in Figure 4, ΔH_m(A) continued to increase with milling temperature like ΔP_{ent}. Terselius et al.,[9] Krzewski and Collins,[10–12] Patel and Gilbert,[13] Summer and Rabinovitch,[14] and Obande and Gilbert[15] showed that with increasing processing temperature and gelation of rigid-formulation suspension PVC, ΔP_{ent} in the capillary flow increases in an S-shaped fashion. In these experimental results, although G showed an S-shaped change, as shown in Figure 4, the signs of leveling off

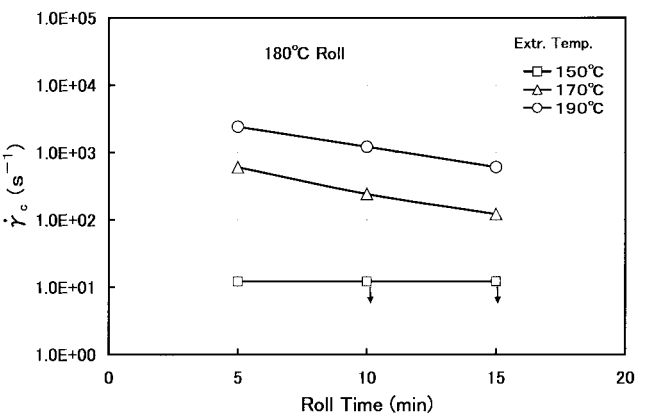


Figure 18 Dependence of $\dot{\gamma}_c$ at the onset of melt fracture on roll time.

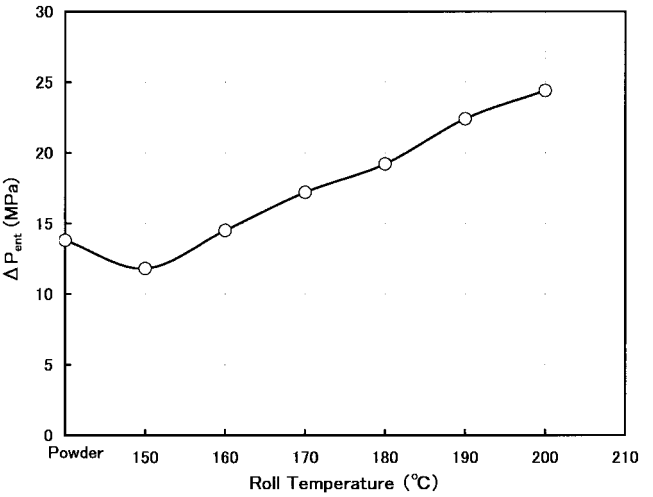


Figure 19 Dependence of ΔP_{ent} on roll temperature.

at the higher side were not observed in ΔP_{ent}, as shown in Figure 19. The leveling off may be observed at higher milling temperatures.

Figure 21 shows the relation between ΔP_{ent} and G or ΔH_m(A). Although ΔP_{ent} showed a positive correlation with G, the relation was off from a linear relationship at regions of high and low G. On the contrary, ΔP_{ent} showed a nearly linear good correlation with ΔH_m(A), except for one point at ΔH_m(A) = 0 for the sample milled at 150°C. From the fact that although the G values of the samples milled at 150 and 160°C were both 0, ΔP_{ent} increased considerably with increasing milling temperature from 150 to 160°C, the rheologically evaluated G have changed even if the thermally evaluated one did not. Because ΔP_{ent} is also a physical quantity concerned with melt elasticity like the die swell and melt fracture, we assumed that its value was low when the gelation was insufficient and that the particle flow occurred and was high when the gelation

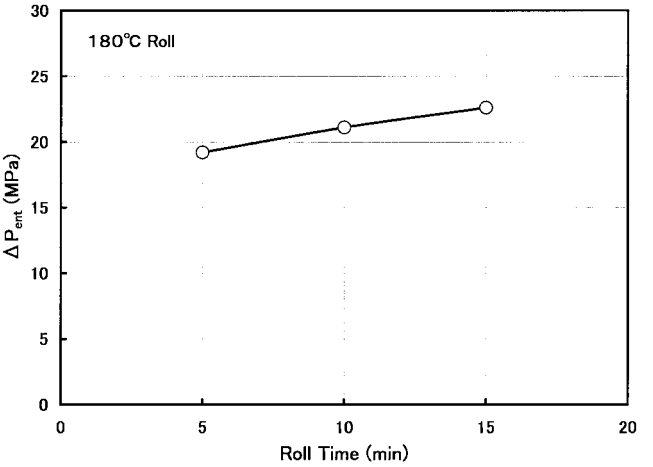


Figure 20 Dependence of ΔP_{ent} on roll time.

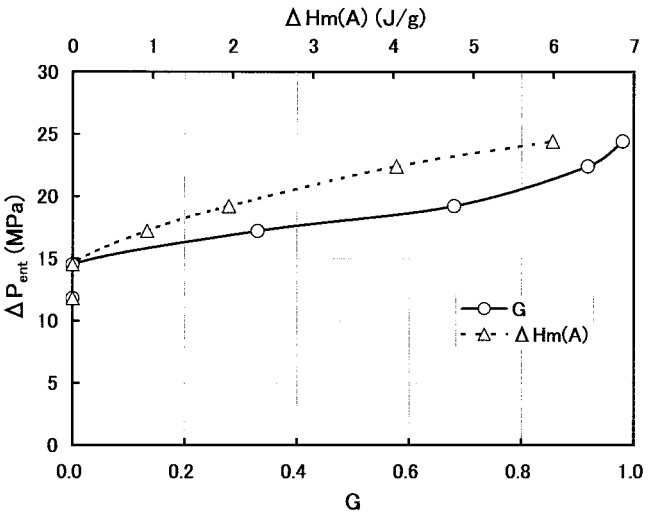


Figure 21 Relation between ΔP_{ent} and G or ΔH_m(A).

and molecular entanglement proceeded sufficiently and the uniform flow occurred.

ΔP_{ent} is also a measure of melt elasticity[10] and increased with increasing gelation, which was caused by the increased milling temperature and time, as shown previously. Accordingly, ΔP_{ent} was used as a measure of gelation. The degree of dependence of ΔP_{ent} on the gelation was similar to that of the die swell. The dependence of the rheological properties on the gelation was in the following order: melt fracture $>$ die swell $\fallingdotseq$ ΔP_{ent} $>$ viscosity. The effect of the transition from the particle flow to the uniform flow caused by the increased gelation was more notable in the elasticity (melt fracture, die swell, ΔP_{ent}) than in the viscosity.

CONCLUSIONS

The fact that the processing conditions (gelation) strongly affect the flow processabilities, such as viscosity, and particularly elasticities, such as die swell, melt fracture, and ΔP_{ent}, is characteristic of PVC, and such remarkable effects have not been observed for other resins. The larger die swell at the higher extrusion temperature is also a characteristic of PVC. Such characteristics of PVC were assumed to originate from the transition from the particle flow to the uniform molecular flow caused by the advanced gelation. In extrusion processing, because the melt fracture drops the product value, it must always be prevented, and because too much die swell drops the dimensional precision of product, it must be adjusted to an appropriate level. Because the gelation (milling) of PVC strongly affects its flow processabilities, as mentioned previously, sufficient control is necessary in addition to the consideration of its effect on the product properties.

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