硬質 PVC의 發泡押出 Ⅲ.
基本 및 發泡配合의 流性學的 性質

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Foam Extrusion of Rigid PVC. III. The Rheological Properties of Unexpanded and Expandable Formulations

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Abstract: To assess the processability of rigid polyvinylchloride (PVC) foam extrusion, the rheological properties of unexpanded and expandable formulations were measured by means of capillary rheometer. The power law index of unexpanded formulation was 0.050 at 160°C and 0.062 at 170°C. The power law index of expandable formulations was increased with increasing the usage level of chemical blowing agent and temperature. The pressure profile of expandable formulation deviated from straight line in the vicinity of die exit, which was more prominent with azodicarbonamide (ADCA) than with sodium bicarbonate (SBC). Inclusion of chemical blowing agent gave substantial viscosity reduction, which was also more noticeable with ADCA than with SBC.

INTRODUCTION

To comprehend the bubble dynamics in a foam extrusion, it is essential to measure the rheological properties of the polymeric materials containing gaseous products. However, it was impossible until a closed type rheometer came into use. From the early 1970's some rheological measurements for the foam process have been carried out by use of slit and capillary rheometers. It is generally accepted that inclusion of gaseous products reduces both wall normal stress and viscosity, which may be ascribed to the bubble growth[1-4]. Although the bubble dynamics is surely to depend on the en-

vironment most rheological measurements have been performed only on the low viscosity systems. Nowadays, however, lots of foams are manufactured in the form of structural foam which deals with highly viscous polymer phase. As already discussed in Part I of this series[5], the decomposition mode of chemical blowing agent is very crucial to foaming process if the medium has high viscosity.

To assess the effect of decomposition mode of chemical blowing agent on the bubble growth in the medium with high viscosity, the rheological ties of rigid polyvinylchloloride (PVC) foam extrusion were measured.

EXPERIMENTS

Materials and Formulations

The materials and formulations are described in Part I of this series[5].

Apparatus and Experimental Procedure

Compounding: The compounding procedure is described in Part I of this series[5].

Measurement of Rheological properties: Specially designed equipments were attatched to the exit of a 1-in-single screw extruder to measure the rheological properties.

The overall apparatus is schematically illustrated in Figure 1, and the detailed layouts of each section are given in Figure 2.

A tapered reservoir with an entrance angle of 60° was adopted to eliminate the dead space, in which a local thermal degradation may be initiated. The capillary die composed of three pieces had a diameter of 4mm to give any desired die L/D ratio by combined use of them. A reservoir with a diameter of 48mm was used to exclude the effect of reservoir geometry on the viscoelastic properties of the polymer[6].

A band heater and two lined-ribbon-heaters were used to control the temperature of the reservoir and die sections. The thermocouple and temperature controller used were iron-constantan type and WIC/RKC series-45/C. Both of the reservoir and die sections were highly insulated to prevent heat loss, and the temperature was controlled to within ±1°C by an on-off electrical heating system.

The pressure transducer and amplifier system applied were strain gauge type melt pressure transducer (Dynisco Co., USA) and SCM 600 (Dynisco Co., USA), respectively. Pressure transducers were calibrated to give outputs repeatable to within ±1% of the measured value at the pressures of 690,000 Pa and greater. A microcomputer system was employed for the continuous measurement of the pressure at the wall. After the adjustment of extrusion temperature, a preliminary extrusion was carried out to get a steady state. The pressure at the wall, i.e., the radial normal stress at wall, was measured with pressure transducers located along the capil-

lary wall. The electrical outputs in millivolts were amplified with SCM 600 to voltages and they were digitized by 8-bit A/D converter. The wall pressure measurement was performed 5 times a second for 40 seconds and their average was taken by a microcomputer to minimize the error by mechanical fluctuations. The wall normal stress distribution in axial direction, so called "pressure profile," was determined from the pressure measurement after the deviation of the slope of the profile became less than 0.5%. This procedure was repeated every two minute 12 times, and the run with the least standard deviation was chosen.

RESULTS AND DISCUSSION

The shear rates were restricted to the values below 400 s^{-1} to avoid complications from shear-induced heating, and the temperatures were limited below 170°C to exclude the possibility of thermal degradation.

Rheological Properties of Unexpanded Formulation

Since the physical properties of base resin will have a significant influence on the bubble dynamics, the steady shear flow properties of unexpanded
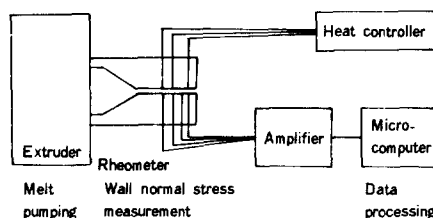

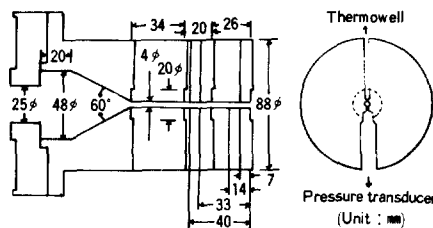**Fig. 1.** Experimental apparatus for rheological measurement.

Fig. 2. Detailed layouts of the reservoir and die sections.

formulation were measured with a capillary rheometer.

Typical pressure profiles at 160°C are given in Figure 3. Two points are notable in the figure. One is the large entrance pressure drop and the other is the positive pressure at the die exit. These are the characteristic features of viscoelastic fluids[7,8].

From the measurements of pressure profile and volumetric flow rate (Q), the wall shear stress (τ_w) and wall shear rate ($\dot{\gamma}_w$) are calculated from the equations

$$\tau_w = (-\partial P/\partial z)\, R/2$$

$$\dot{\gamma}_w = \left(\frac{3n+1}{4n}\right)\frac{32Q}{\pi R^3} = \left(\frac{3n+1}{4n}\right)\dot{\gamma}_a$$

where ($-\partial P/\partial z$) is the pressure gradient in the fully developed region, R is the capillary radius, and n is the power law index defined by

$$n = \frac{d\ln \tau_w}{d\ln \dot{\gamma}_a}$$

Plots of shear stress versus shear rate at 160°C and 170°C are shown in Figure 4.
The power law index of the unexpanded formulation determined from the flow curves was 0.050 at 160°C and 0.062 at 170°C. The unusually small values of power law index may be ascribed to the fact that the fluid is not a melt state in the temperature range tested. An investigation of thermal transitions by DSC and TGA also indicated that the unexpanded formulation did not show any melting peak in the temperature range of 160°C to 170°C as shown in Figure 5. Viscosity (η) and first normal stress difference (N_1) are calculated from the following expressions:

$$\eta = \tau_w/\dot{\gamma}_w$$

$$N_1 = \tau_{11} - \tau_{22} = P_{exit} + \tau_w\frac{d\,P_{exit}}{d\,\tau_w}$$

where τ_{ij} represents the components of the deviatoric stresses.

Figure 6 represents viscosity and first normal stress difference against shear rate at 160°C and 170°C.

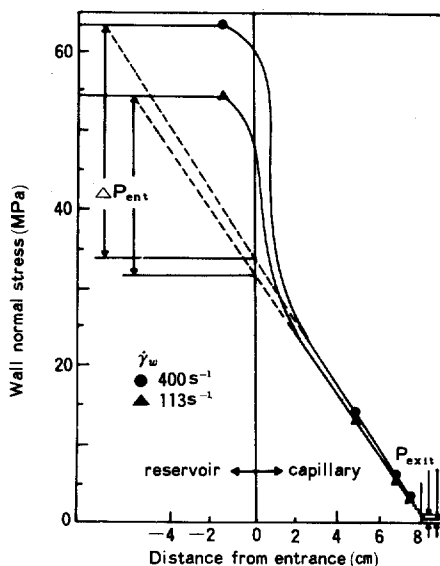Both viscosity and first normal stress difference were decreased as the temperature was increased,

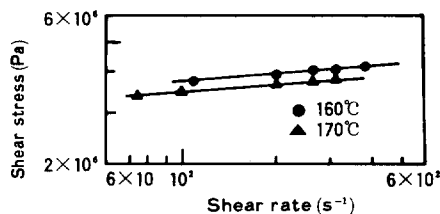**Fig. 3.** Typical pressure profiles of P-base in a capillary die with L/D ratio 20 at 160°C.

Fig. 4. Flow curves of P-base at 160°C and 170°C by a capillary die with L/D 20.
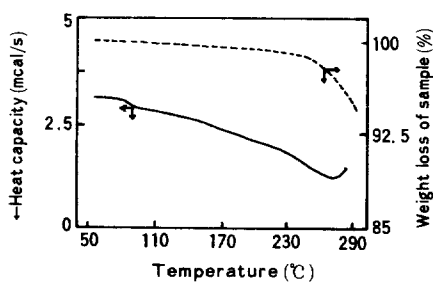

Fig. 5. Thermal properties of P-base.

and an increase of shear rate decreased viscosity but increased first normal stress difference as expected.

The unusual shear sensitive viscosity reduction may be obliged to the effective shear induced orientation of polymer chains. That is, PVC has a strong
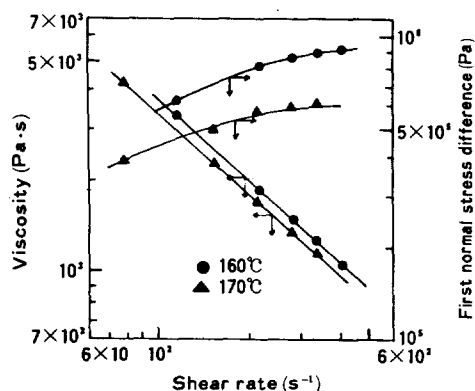
326

Fig. 6. Variations of viscosity and first normal stress difference with shear rate for P-base at 160°C and 170°C by a capillary die with L/D 20.
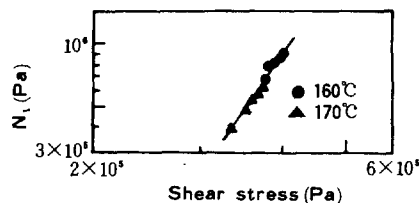

Fig. 7. First normal stress difference (N_1) versus shear stress for P-base at 160°C and 170°C by a capillary die with L/D 20.

polar groups in the chain and is extruded at relatively low temperatures, so the strong intermolecular force and the low chain mobility will have favorable effect on shear induced chain orientation. Furthermore, the low molecular weight processing additives such as thermal stabilizers and lubricant may also make the molecular chain slippage easier. Therefore, the extent of disentanglement and orientation of the polymer chains may be rapidly increased with the increase of external shear force, which may lead to unusual shear sensitive viscosity behavior.

Using an Instron Viscometer, Collins and Krier[9] also observed similar viscosity behavior for a rigid PVC at low temperatures.

Figure 7 shows plots of first normal stress difference versus shear stress instead of shear rate. It is worth noting in the figure that plots of first normal stress difference against shear stress on the logarithmic scale gave almost a straight line independent of temperature. Such elastic parameters

as recoverable shear strain (S_R) and steady-state elastic compliance (Je) are also calculated from the following expressions and the results are given in Table. 1.

$$S_R = N_1 / 2 \, \tau_w$$
$$J_e = N_1 / \tau_w{}^2$$

Three elastic parameters obtained at two temperatures, 160°C and 170°C, also exhibited a good proportionality to the shear stress without temperature effect. Although there is no sound theoretical basis, it is interesting to see, on the experimental bases, that the temperature effect can be eliminated by a substitution of shear stress for shear rate in most elastic parameters[10-14].
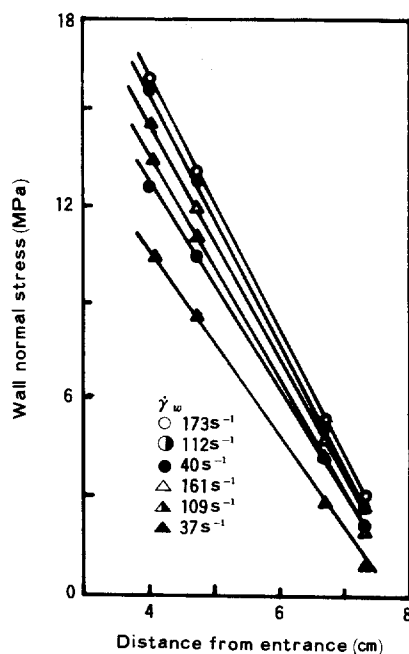
Rhelogical Properties of Expandable Formulations

Pressure profiles of three formulations (P-base, P-A (0.75) and P-S (0.75) are given in Figures 8, 9 and 10.

Observation of pressure profiles shows several important facts. Firstly, two expandable formulations (P-A (0.75) and P-S (0.75)) gave lower values of wall normal stress and wall shear stress than unexpanded formulation (P-base). Secondly, although pressure profiles of unexpanded formulation were linear over the measured distance of die, two expandable formulations showed deviated pressure profiles from straight line in the vicinity of die exit particularly at high temperatures and low shear rates. Thirdly, azodicarbonamide (ADCA) gave larger reduction in both wall normal stress and wall shear stress and exhibited greater deviation from the linearity than sodium bicarbonate (SBC).

Since the rheological implications of such a deviation around die exit may be a phase separation by microbubble growth, the extent of deviation will be dependent on the blowing pressure of chemical blowing agent. Therefore, the third fact may be closely related to the decomposition mode of chemical blowing agent and the physical properties of evolved gases. ADCA decomposes explosively at a specific temperature and evolves relatively inert gases, while the decomposition of SBC is pressure-dependent and yields gases with some solubility to

Table 1. Some Elastic Parameters of P-base at 160°C and 170°C

Processing temp. (°C)	Shear stress (MPa)	Exit press. (MPa)	Recoverable shear strain	Elastic compliance (MP^{-1})
170	0.336	0.325	0.585	1.74
	0.345	0.432	0.729	2.17
	0.352	0.496	0.807	2.28
	0.363	0.502	0.795	2.19
	0.367	0.525	0.804	2.19
160	0.376	0.501	0.823	2.20
	0.379	0.695	1.099	2.87
	0.385	0.730	1.131	2.90
	0.395	0.739	1.118	2.83
	0.400	0.770	1.148	2.89
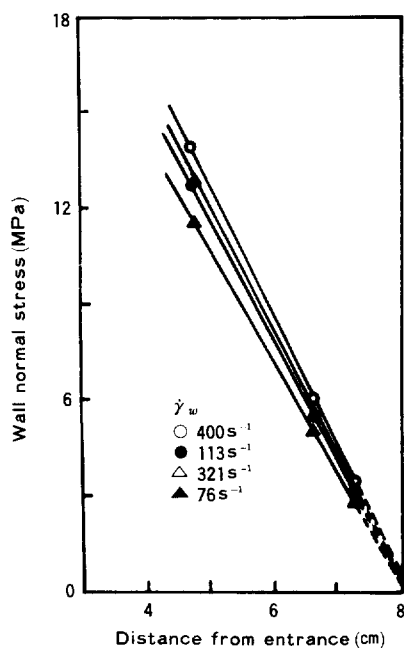
Fig. 8. Pressure profiles of P-base (circles for 160°C and triangless for 170°C).

Fig. 9. Pressure profiles of P-S (0.75) (circles for 160°C and tringles for 170°C).

PVC [15-19]. Therefore, ADCA exerts higher blowing pressure than SBC. In consequence, ADCA gave greater reduction in wall normal stress and greater deviation in the pressure profiles.

The power law indices of expandable formulations at 160°C and 170°C are given in Table 2. On the whole, the formulation including ADCA gave larger power law index than the formulation including SBC at the same usage level. The increase of power law index by addition of chemical blowing agent may be ascribed to the lubricating or plasticizing effect of dissolved or nucleated microbubbles[20]. That is, the microbubble may increase chain mobility by a lubrication action, which may

Table 2. Power-Law Index of Expandable Formulations at 160℃ and 170℃

Temp. (°C)	P-S (.5)	P-S (.75)	P-S (1)	P-A (.5)	P-A (.75)	P-A (1)
160	0.14	0.14	0.15	0.19	0.20	0.22
170	0.16	0.16	0.17	0.24	0.26	0.29
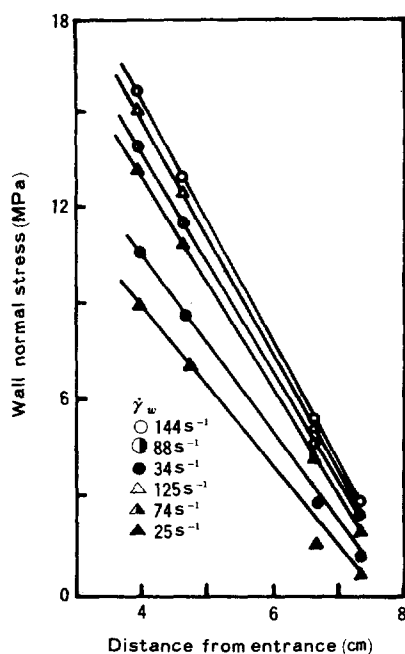
Fig. 10. Pressure profiles of P-A (0.75) (circles for 160°C and triangles for 170°C).

result in a pseudo-melt flow. In accordance with such an assumption of lubrication, the power law index seemed to be increased as the usage level of chemical blowing agent and temperature were increased.

As the curvature in a pressure profile means that the usual assumption of fully developed flow in the capillary die is violated, only the linear portion of pressure profile was used in determining the viscosities of the gas charged polymer system. This implies that the results are valid only for the situation where evolved gases are largely dissolved in the polymer phase. In fact, the true viscosity of the mixture can be obtained only in high shear rates in which no deviation from the straight line over the measured distance of die takes place.

Plots of viscosity versus shear rate of various formulations are shown in Figures 11 and 12.

Two facts are worth mentioning in the viscosity curves. Firstly, addition of chemical blowing agent brought about viscosity reduction, and the extent of viscosity reduction was increased with the increases of temperature and usage level of chemical blowing agent. Secondly, of the two chemical blowing agents, ADCA gave greater viscosity reduction than SBC.

The viscosity reduction by addition of chemical blowing agent may also be interpreted by the lubricating effect of microbubble[20]. The increase of extent of viscosity reduction with temperature and usage level of chemical blowing agent may be attributed to formation of separate phase by microbubble growth, which may be obliged to increased blowing pressure and reduced viscosity. Therefore, the greater viscosity reduction by ADCA can be ascribed to higher blowing pressures. That is, since ADCA exerts higher blowing pressure than SBC, it will give more nucleated microbubble seeds which may impart a lubrication effect to the system.

The extent of viscosity reduction by chemical blowing agent was decreased with the increase of shear rate because an increase of external pressure will suppress the microbubble growth in the die[21,22]. As a result, all the viscosity data fell on a single viscosity curve above the shear rate of around 100 s^{-1} because the external pressure may be much greater than the critical blowing pressure of two chemical blowing agents.

CONCLUSIONS

1. The power law index of unexpanded polyvinylchloride (PVC) formulation was 0.050 at 160°C and 0.062 at 170°C. The power law index of expandable
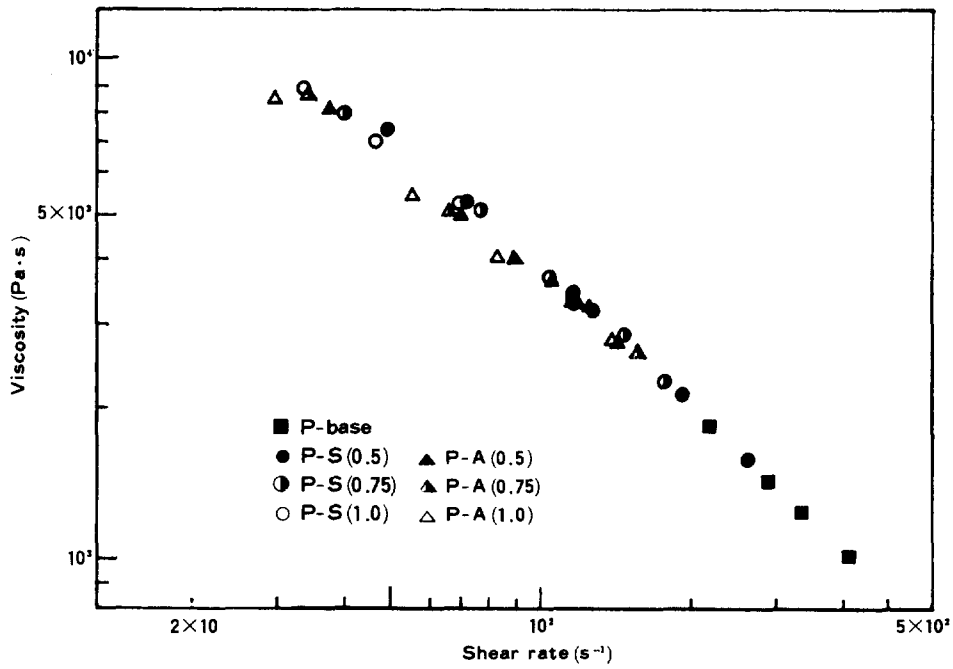
Fig. 11. Viscosity versus shear rate for various formulations at 160°C.
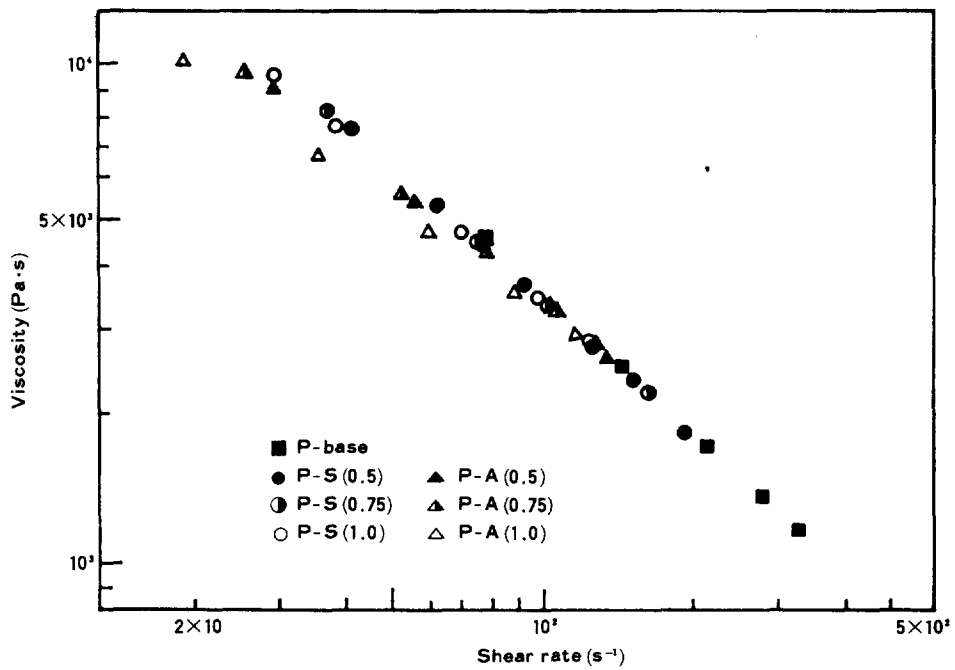

Fig. 12. Viscosity versus shear rate for various formulations at 170°C.

PVC formulation was increased as the usage level of chemical blowing agent and temperature were increased.

2. The unexpanded PVC formulation gave a straight pressure profile over the measured distance of die. The pressure profile of expandable PVC formulation, however, deviated from straight line in the vicinity of die exit, which was more prominent with azodicarbonamide (ADCA) than with sodium bicarbonate (SBC).

3. Inclusion of chemical blowing agent gave substantial viscosity reduction. Of the two chemical blowing agents tested, ADCA gave greater viscosity reduction than SBC.

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