용융 폴리스티렌의 유성학적 특성 측정

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Measurements of the Rheological Properties of Molten Polystyrenes

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Abstract: To examine the processability of four commercial grades of the domestic polystyrenes (GP125, GP/150, HI425 and HI425E) in the vicinity of the actual processing conditions, the steady shear flow properties such as viscosity (η), first normal stress difference (N_1) and second normal stress difference (N_2) were measured by use of a capillary type instrument. And the dynamic properties were investigated by a parallel plate type instrument. All grades of polystyrenes showed a non-Newtonian flow properties over the range of shear rates investigated. In general, high impact (HI) grades showed slightly higher melt viscosities than general purpose (GP) grades. The viscosity data also suggested that the use of the melt index as a parameter for the polymer fluidity gave us an errorneous conclusion to evaluate the actual polymer processing. An inspection of N_1 and N_2 revealed that GP grades showed higher melt elasticity than HI grades, and the ratio of $-N_2/N_1$ lay between 0.14 and 0.72 for the four grades of polystyrenes tested. Comparison of capillary rheometer data with the dynamic data yielded a close analogy. That is, the shapes of viscosity curves and the dynamic viscosity curves were similar and in the same range. However, the shapes of N_1 curves and the dynamic storage modulus curves showed some discrepancy at the high range of shear rates of frequencies, due probably to different deformation history and mode between steady shear and dynamic flows.

1. INTRODUCTION

A better understanding of the viscoelastic properties of polymer melts is very important for many reasons. For instance, it helps one to formulate the mixed polymer systems which would best provide a particular set of physical properties desired in the final products, because the viscoelastic properties are intimately related to processing conditions as molding temperature and extrusion rate. Thus, accurate determination of these properties will help one to design the right kind of processing equipment and to manufacture the product with the desired properties.

In measuring the rheological properties of viscoelastic fluids, there are two basic types of apparatus which may be used for determining those

properties; the rotational type and the capillary type.

In recent years, some efforts have been made on modifying the rotational type instrument. However, use of the rotational type instrument for polymer melts is limited to rather low shear rates. It is because that the polymer melt in a rotational instrument start to exhibit flow instability at a certain value of shear rate, commonly referred to as "secondary flow", or "radial flow"[1].

On the other hand, the capillary type apparatus has no such limitation and therefore it is suitable for determining rheological properties for polymer melts, in particular at high shear rates which may be the closer range to the actual processings. However, the capillary type requires a relatively large amount of sample for testing.

The objectives of the present study were to determine the rheological properties of polystryrene melts, which are being produced by Han Nam Chemical Company, by the use of capillary rheometer. Measurements are also carried out by the use of Rheometrics Dynamic Spectrometer for comparison purpose. The melt index is also discussed with the melt viscosity measured at various temperatures.

2. EXPERIMENTS

2-1. Materials

The polymers used for this study were two kinds of general purpose(GP) polystyrenes and two high impact(HI) polystyrenes which have the code names as GP125, GP150, HI425 and HI425E. Table 1 shows the general characteristics of polymers investigated. Molecular para-

meters for the four samples were obtained by gel permeation chromatographic analysis with Waters Model 150-C ALC/GPC using tetrahydrofuran as solvent at 35°C. The melt index was measured with the method specified by ASTM D1238. To obtain the glass transition temperature (Tg) of four polystyrenes, a differential scanning calorimeter (DSC, Perkin-Elmer, U.S.A.) was used.

2-2. Apparatus

The capillary die used in the study was made of stainless-steel 316. Fig. 1 shows the detailed layouts of the two basic dies and Table 2 gives the dimensions of the die used. The entrance to the capillary is flat (180°). To avoid the any noticeable influence of entrance effects[2], a capillary die having an L/D ratio of 23.09 was chosen. The capillary die section is attached to a reservoir section using D_R/D of 21.74 with 50mm in diameter to avoid the effects of reservoir diameter on the rheological properties[2]. In controlling the temperature accurately, the band heater was used to reservoir section and two line ribbon-heaters to capillary die. Thermocouples used were iron-constantan type. To prevent heat loss of the die face, a disc type insulating material was attached to bottom of the die, and the entire system was heavily insulated. The pressure at the wall (i.e., the total radial normal stress) of capillary die was measured with Dynisco melt pressure transducers (strain gauge type). Their electrical outputs, in millivolts, were amplified with SCM 600 (Dynisco Co.) to voltage and it is digitized by 8-bit A/D converter, and read on a microcomputer. One inch single-screw extruder (Jung Ang Machinary Co.) was used to extrude polymer melts. The heating

Table 1. General Characteristics of Polystyrenes Investigated

Sample code	Density (g/cm^3)	Melt index	Molecular weight			Tg °C
			M_n	M_w	M_w/M_n	
GP125	1.05	8.0	152000	290000	1.908	94
GP150	1.05	2.5	175000	340000	1.943	101
HI425	1.04	6.5	128000	247000	1.930	93
HI425E	1.04	3.0	160000	275000	1.718	98
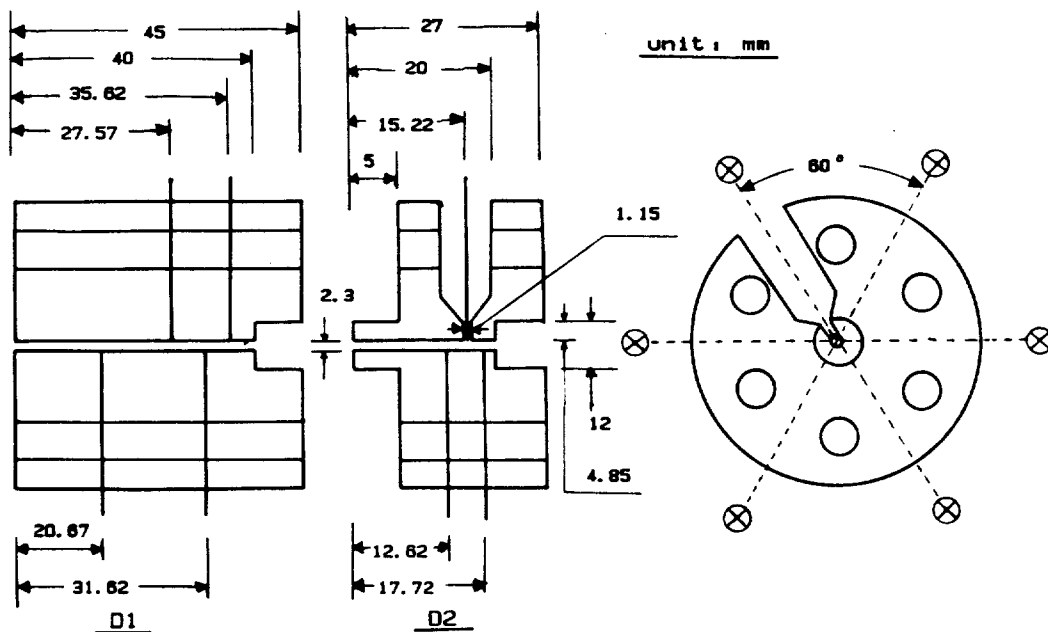
Fig. 1. Schematic diagram of capillary die.

Table 2. Capillary Rheometer Geometry

Copillary rheometer geometry	
Length of die L. mm	60
Capillary diameter D. mm	2.3
Capillary length to diameter L/D	26.09
Length of reservoir L_R. mm	110
Reservoir diameter D_R. mm	50
Reservoir to Cap. diameter ratio D_R/D	21.74
Location of pressure transducers from die inlet. mm	
Transducer A	35.62
Transducer B	52.62
Transducer C	55.22
Transducer D	57.72

bands were applied to five regions with temperature controllers. Screw rpm could be varied from 0 to 70. Measuring the dynamic rheological properties (complex modulus and complex viscosity), a commercial parallel plate apparatus, Rheometrics Dynamic Spectrometer (RDS-7700: Rheometrics Inc., U.S.A.) was used.

2-3. Experimental Procedure

After the adjustment of temperature by the heat controller, a preliminary extrusion was carried out to get the steady state. The exit pressure, gauge pressure and slope of the normal stress distribution profile were obtained from the wall normal stress distribution curve. The curve was measured at the capillary wall every two minutes from the moment that the deviation of the slope variation of the curve became less than 0.5% at various processing conditions. Shear rate variation was 6 or 7 points in the range of 20 to 1100 sec^{-1} and temperatures were 200°C, 220°C and 240°C. Mass flow rate measurements were made by collecting the extrudates at each shear rate for ten minutes.

The following equations were used to calculate the shear rate $\dot{\gamma}_w$, shear stress τ_w, the viscosity η and normal stress differences, N_1, N_2;

$$\dot{\gamma}_w = \frac{\dot{\gamma}_a}{4}\left(3 + \frac{d\ln\dot{\gamma}_a}{d\ln\tau_w}\right) \tag{1}$$

$$\tau_w = \left(-\frac{\partial P}{\partial Z}\right)\frac{R}{2} \tag{2}$$

$$\eta = \tau_w/\dot{\gamma}_w \tag{3}$$

$$N_1 = \tau_{11} - \tau_{22} = P_{exit} + \tau_w\frac{d P_{exit}}{d\tau_w} \tag{4}$$

$$N_2 = \tau_{22} - \tau_{33} = -\tau_w \frac{d\,P_{exit}}{d\,\tau_w} \qquad (5)$$

3. RESULTS AND DISCUSSION

3-1. Capillary Pressure Drop

Fig. 2 represents the typical pressure profiles of GP125 at several shear rates, which shows a good linearity with the axial distance of the capillary within the range of pressure measured. From the pressure profile, the positive pressure at the die exit, so called the "exit pressure", was obtained by an extrapolation. From the constancy of the pressure gradient, the true wall shear stress, τ_w, was calculated by Eq. 2. It can be seen from Fig. 2 that, for a given material, the pressure gradient $\dfrac{-\partial P}{\partial Z}$ is increased with the increase of shear rate. Other polystyrene samples showed similar behavior in the pressure gradients. It should be noted that when Eq. 2 is used no end correction is necessary.

3-2. Flow Curve

Figs. 3 and 4 show the plots of shear stress versus shear rate, i.e., the flow curve, for GP150 and HI425E at 200°C, 220°C and 250°C, respectively. Both figures show non-Newtonian flow behavior, that is, there is no proportionality between shear stress (τ_w) and shear rate ($\dot{\gamma}_w$)—curved line instead of straight. Further, the concave-downward curves indicate that two polymers exhibit the pseudoplasticity. Similar trends were observed with the other two polystyrenes.

3-3. Viscosity

Figs. 5 to 7 compare the viscosity of the four polystyrenes at three different temperatures. All grades of polymer melts showed the pseudoplasticity (shear thinning effect) as shown in the flow curve. This pseudoplasticity may be attributable to disentanglement and orientation of the polymer chains at higher shear rates[3]. It can be seen from Figs. 5 to 7 that the viscosity profiles measured by a capillary rheometer give contradictory results to those given by melt index. Accor-
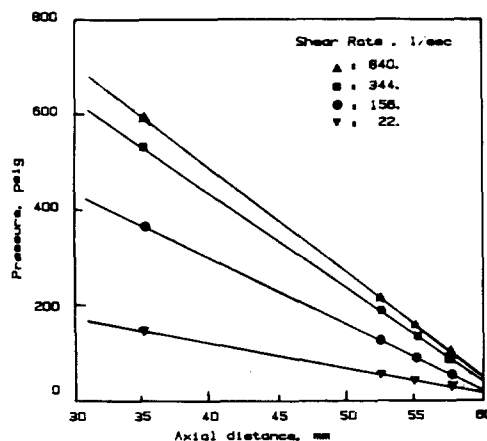

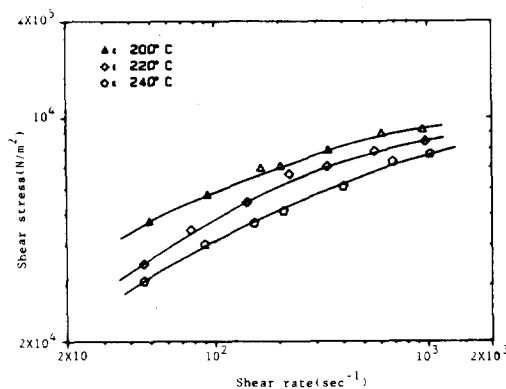**Fig. 2.** Axial pressure profiles of GP125 melt at 200°C.

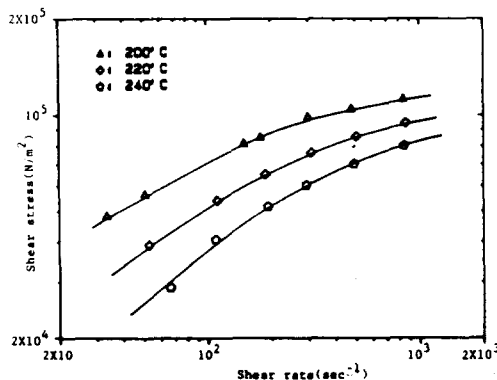**Fig. 3.** Flow curves for GP150 at three temperatures.

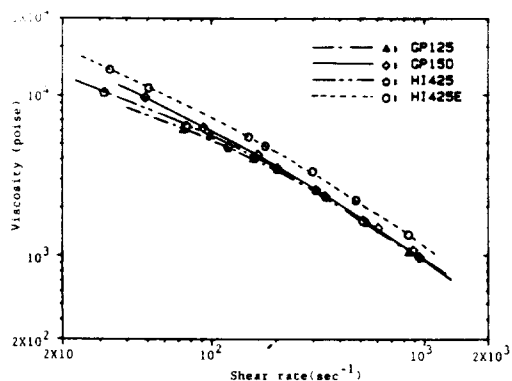**Fig. 4.** Flow curves for HI425E at three temperatures.

Fig. 5. Viscosity versus shear rate for four poly-
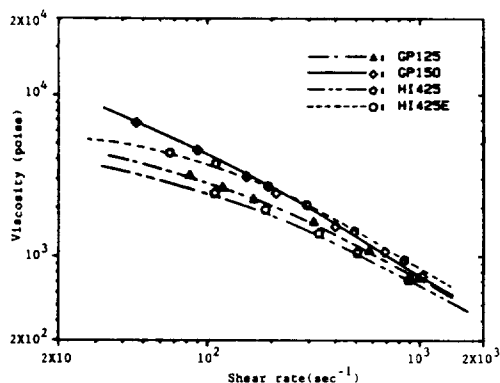styrenes at 200°C.

Fig. 6. Viscosity versus shear rate for four poly-
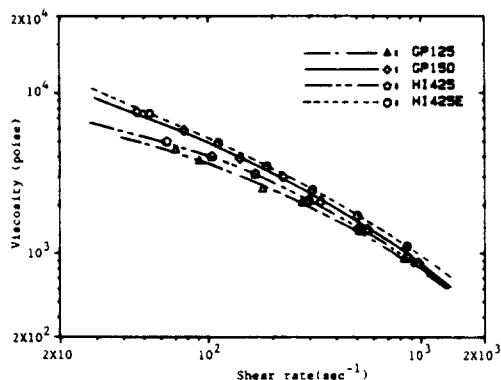styrenes at 220°C.

Fig. 7. Viscosity versus shear rate for four poly-
styrenes at 240°C.

ding to melt index GP125 has the best fluidity and
followed by HI425, HI425E and GP150 in order.
However, GP125 has the best fluidity and follow-
ed by HI425, GP150 and HI425E at 200°C and
220°C over the measured shear rate range.
Moreover, a careful observation of these figures
reveals that there are cross-over and reversal bet-
ween the different polystyrene grades in the
viscosity profiles. For example, a very distinct
viscosity reversal between GP125 and HI425 can
be seen in Fig. 6 to Fig. 7. And cross-over bet-
ween GP150 and HI425E can be observed in Fig.
7. In other words, at 240°C, HI425E has the bet-
ter flow properties than GP150 up to the shear
rate of 190 sec^{-1}, and above the shear rate of 190
sec^{-1}, however, GP150 shows the better fluidity
than HI425E. Therefore, it is very important to in-
spect the utility of the melt index critically at this
point as an industrial measure of polymer pro-
cessability. In general, melt index is measured at a
relatively low shear rate and compares the viscosi-
ty at different shear rates. On the other hand, the
most polymers are processed at relatively high
shear rates

Fig. 8 is a plot of viscosities measured with
capillary and compares with the melt index, which
shows that all four polystrenes exhibit very little
differences in viscosities even though they have a
big differences in the MI. It should be noted that
the Mooney—Rabinowitsch correction[4,5] is used
to calculate the shear rate from the MI.

In Table 3, GP150 (the lowest MI) gives lower
viscosities than HI425E (MI = 3.0) at 100 sec^{-1} at
200°C and 220°C. At 1000 sec^{-1} 200°C, the
viscosity of GP150 is even lower than that of
HI425 (MI = 6.5). The order of MI from Table 3
has nothing to do with the viscositites of
polystyrenes measured at 220°C and 240°C. Thus
the melt index shall have little value to the real
processing performed at the different temperature
from the MI temperature (200°C).

In spite of lower molecular weights, HI grades
(blends of polystyrene with butadiene rubber par-
ticles) give higher melt viscosity than GP grades
(polystyrene homopolymers). This can be at-

Table 3. Comparison of Viscosity from Melt Index & Viscosity Profiles

Melt index data				Viscosity (poise) from capillary data					
Sample code	MI	$\dot{\gamma}_w$ (sec^{-1})	Viscosity (poise)	200°C $\dot{\gamma}_w$ (sec^{-1})10^2	10^3	220°C 10^2	10^3	240°C 10^2	10^3
GP125	8.0	19.6	22900	5400	800	3420	796	2820	695
GP150	2.5	8.2	54700	6143	915	4680	845	4200	746
HI425	6.5	17.7	25400	5473	952	3960	810	2480	640
HI425E	3.0	8.9	50400	8259	1147	4980	956	3500	810
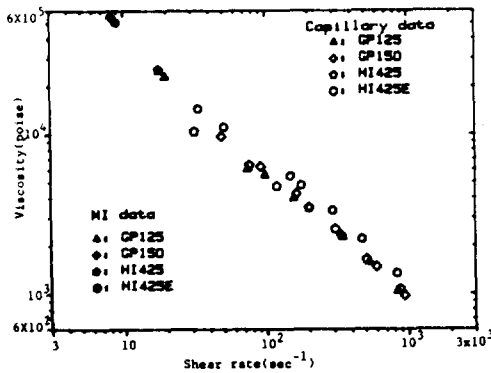
Fig. 8. Comparison of viscosity from capillary with melt index for four polystyrenes at 200°C.
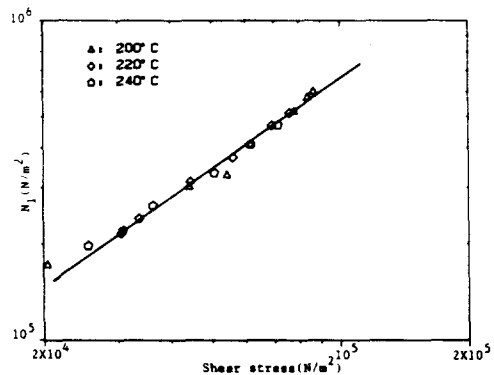
Fig. 10. First normal stress difference versus shear stress for GP125 at three temperatures.
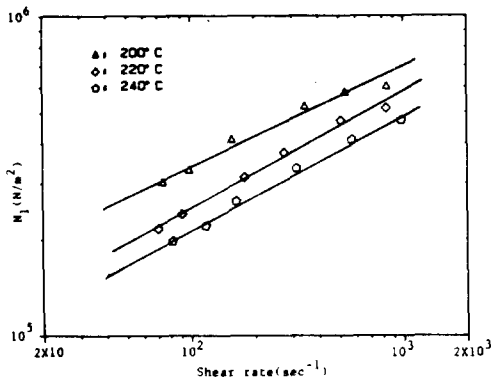
Fig. 9. First normal stress difference versus shear rate for GP125 at three temperatures.

tributed to the fact that the rubber phase may act as a filler[6].

3-4. First Normal Stress Difference

Fig. 9 is a plot of the first normal stress difference (N_1) with the shear rate for GP125 at 200°C, 200°C and 240°C. As seen in this figure, N_1 is increased with the increase of shear rate. Similar results can be found with other three polystyrenes. However, the plot of N_1 versus shear rate shows high temperature dependence, which may cause inconvenience to assess the elastic properties of polymer melts at different processing temperatures. Plot of N_1 versus shear stress instead of shear rate, however, can exclude the effect of temperature as shown in Fig. 10. This figure can also be used to evaluate the magnitude of elasiticity directly. One can see that N_1 is increased as the shear stress increases, in good agreements with other experimental results by dynamic test[7-9] and die swell tests[10-12]. It is also seen that the log-log plot of N_1 versus shear stress appears to be a straight line independent of temperature, from which the consistancy(a) and the index(b) can be obtained by considering the polystyrene melts as a power-law type fluid in the

shear stress region measured[13,14]. Values of a and b which were evaluated using a power-law type Eq. 6 by a regression method are listed in Table 4.

$$N_1 = a(\tau_w)^b \qquad (6)$$

Fig. 11 shows that the N_1 versus shear stress curves for four polymers, which includes all data obtained at three temperatures. From Fig. 11, it is seen that GP grades are more elastic than HI grades. As the stress is increased, however, difference in N_1 between these two grades is increased further. For the same species, polystyrenes in this case, the higher molecular weight and the broader molecular weight distribution ($\overline{M}_w/\overline{M}_n$) give the higher elasticity[15,16.] Making allowance for structural factors for the HI grades which contain 6 to 7 wt% of butadiene rubber with average diameter of 4 to 5 μ, the rubber particles may act to the system as a filler[6]. This kind of grade gives lower elasticity than the general grade[17-19].

3-5. Second Normal Stress Difference

Having been discussed about the magnitude and sign of the second noraml stress difference(N_2), nowadays, it is a well accepted fact that N_2 proves to be negative in sign and its magnitude is always less than that of N_1[1,18,20]. It is also used as a parameter for determining the fluid elasticity together with N_1. As is the case with N_1, plots of-N_2 with the shear rate at three different temperatures do not represent the elasticity comparison. In Fig. 12.-N_2 versus shear stress of four polymers investigated are shown. Substituting shear rate to shear stress, the same plot exercised to N_1, also excludes the effect of temperature as shown in Fig. 12. It is also seen that fairly good linear curve can be constructed, allowing us to use the power-law type empirical equation can be made.

$$-N_2 = a'(\tau_w)^b \qquad (7)$$

where a' and b' are constants representing characteristics of the polymers. And values are listed in Table 4.

It is interesting to have that values of the index

Table 4. Characteristic Constants of N_1 and N_2 for four Polystyrenes in Eq'ns (6) and (7)

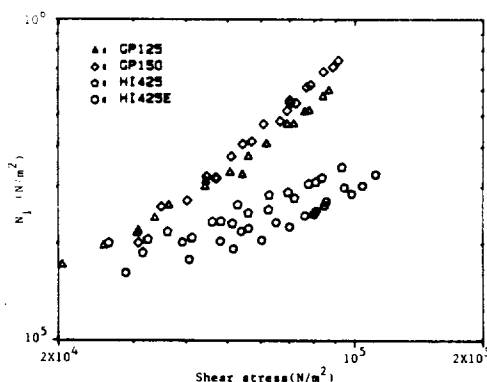| Sample code	a	b	a'	b'
GP125	2.164	0.882	1.104	1.023
GP150	1.619	1.183	1.417	1.041
HI425	2.650	0.465	0.163	1.044
HI425E	2.416	0.492	0.174	1.057

Fig. 11. First normal stress difference versus shear stress for four polystyrenes at three temperatures.
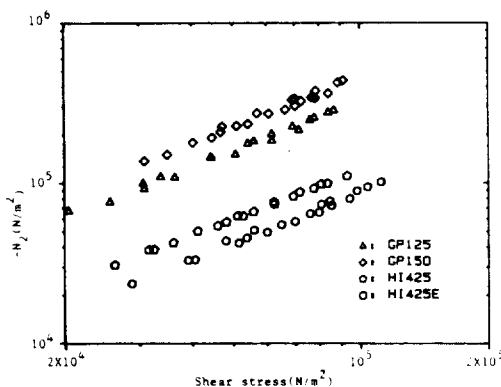

Fig. 12. Second normal stress difference versus shear stress for four polystyrenes at three temperatures.

b' in $-N_2$ are almost same for four polystyrenes. As already seen in Table 4, however, those for N_1 are different for the general purpose grade (0.88 - 1.18) and for the high impact grade

(0.47−0.49).

As in the case of first normal stress difference, the value of second normal stress difference,-N_2, was increased as shear stress increases, and the order of magnitude is same as with first normal stress difference.

To assess the magnitude of N_2, one often uses the ratio of two normal stress differences, $\phi = -N_2/N_1$. Reported experimental values of ϕ range from 0.0 (the Weissenberg hypothesis value[21]) to about 0.4[22]. However, values as high as about 0.6 have also been reported[1].

Fig. 13 shows the ratio of the two normal stress difference $-N_2/N_1$ for four polymers. It can be seen that value of $-N_2/N_1$ for two GP grades are from 0.38 to 0.72 and those for two HI grades are from 0.14 to 0.32.

3-6 Comparison of Steady-shear Flow Data with Dynamic Flow Data

When one define the complex viscosity η^* and the complex modulus G^* as

$$\eta^* = \eta' - i\eta'' \tag{8}$$

$$G^* = G' + iG'' \tag{9}$$

the real parts, η' and G', can be measured with any rotational type dynamic equipment. Of course, η^* and G^* are interrelated by Eq. (10)

$$\eta^* = \frac{G^*}{iw} \tag{10}$$

from which one can calculate η'' and G'' easily.

Comparison of capillary rheometer data with Rheometrics Dynamic Spectrometer data is given in Figs. 14 to 21. As can be seen in Figs. 14 to 17, the shear viscosity curves and the dynamic viscosity curves coincide very well over the range
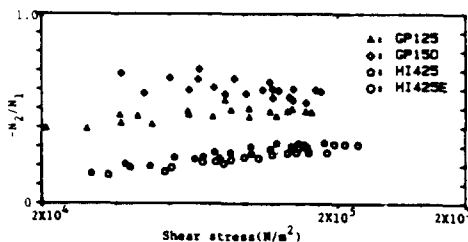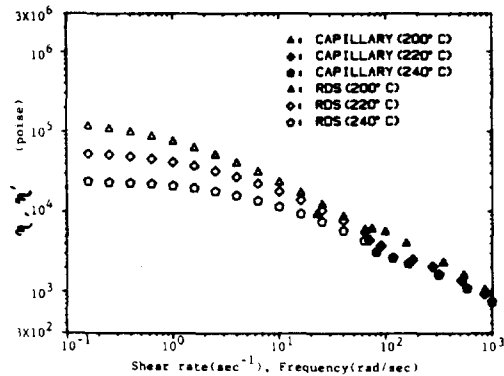

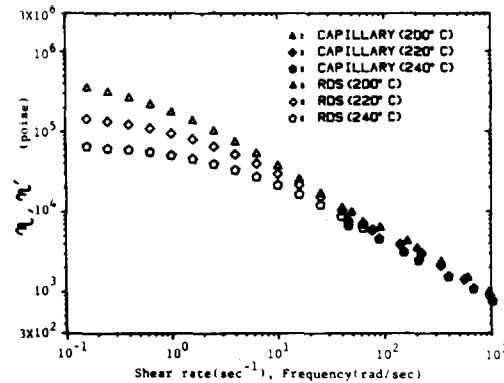**Fig. 14.** Viscosity versus shear rate for GP125 at three temperatures.

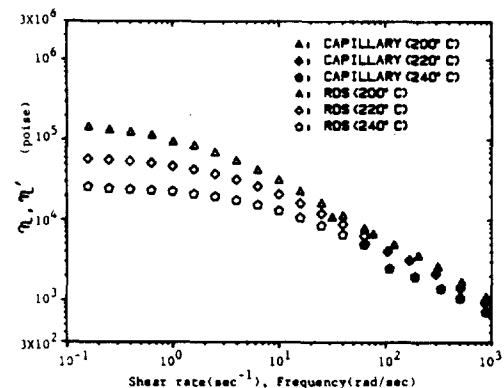**Fig. 15.** Viscosity versus shear rate for GP150 at three temperatures.

Fig. 16. Viscosity versus shear rate for HI425 at three temperatures.

Fig. 13. $-N_2$ to N_1 ratio versus shear stress for four polystyrenes at various temperatures.

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of shear rates and frequencies investigated at three different temperatures. However, curves for N_1 and G' are not in the same lines as shown in Figs. 18 to 21. This discrepancy on the elastic behavior may imply that there are further works to be done to measure the elasticity accurately. In other words, the method to measure the viscosity is a well-established and fairly accurate one in spite of different modes of deformation history and different measuring instruments employed. However, the method to measure the elastic behavior is still improving and there is no absolute method for accurate determination of the elasticity both theoretically and experimentally[23]. Two
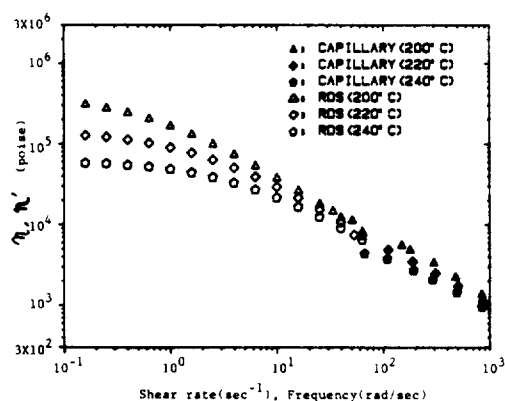

Fig. 19. First normal stress difference versus shear rate for GP150 at three temperatures.

Fig. 17. Viscosity versus shear rate for HI425E at three temperatures.

Fig. 20. First normal stress difference versus shear rate for HI425 at three temperatures.
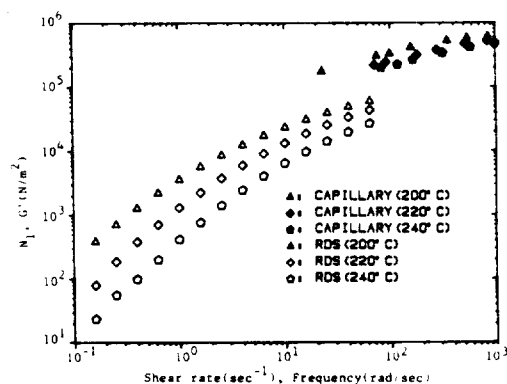

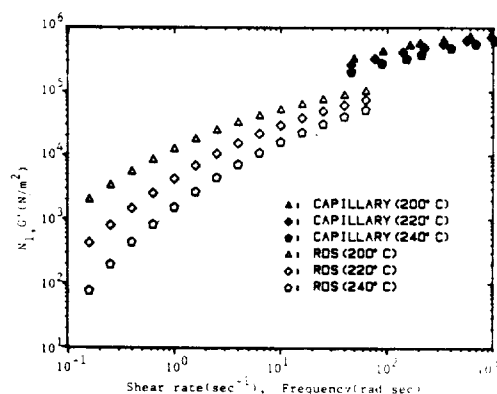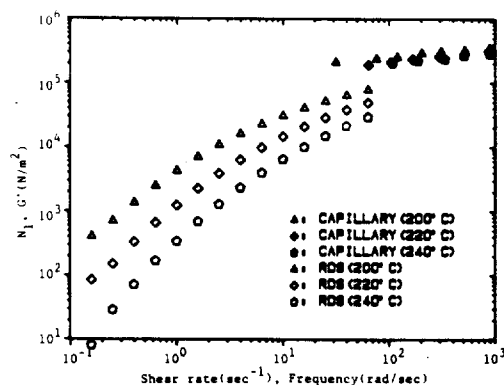**Fig. 18.** First normal stress difference versus shear rate for GP125 at three temperatures.
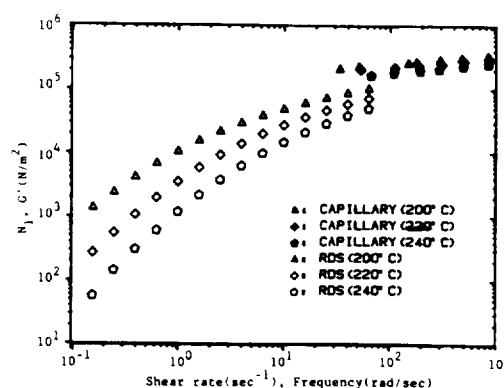

Fig. 21. First normal stress difference versus shear rate for HI425E at three temperatures.

different modes of deformation, steady and dynamic, may also result in different assessment of the elastic behavior. Further, the steady measurement may include the effect of elongational flow which occurs at the entrance of capillary from the reservoir due to the flat entry. Exact magnitude of this elongational effect on the elasticity should be investigated in the future. One other point to be mentioned on Figs. 18 to 21 is analogy between the steady and dynamic measurements. At very low deformation range, i.e., very low shear rate or frequency, the following analogies are prevailed for the viscosity and elasticity[24].

$$\lim_{w \to 0} \eta'(w) = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma}) \qquad (11)$$

$$\lim_{w \to 0} \frac{G'(w)}{w^2} = \lim_{\dot{\gamma} \to 0} \frac{\tau_{11} - \tau_{22}}{2\dot{\gamma}^2} \qquad (12)$$

As demonstrated in Figs. 14 to 17, the viscosity analogy seems to prevail to fairly high shear rate range. However, the elasticity analogy in terms of first normal stress difference N_1 and storage modulus G' seems to be poor in the range of shear rates or frequencies investigated, i.e., over 30 sec⁻¹ or rad/sec. Thus, the elasticity analogy may be limited to the low deformation range only. For the elasticity, existence of the similar analogy in the high deformation range is not known theoretically or experimentally yet.

4. CONCLUSION

The rheological properties of four commercial polystyrenes, two general purpose and two high impact grades, were measured by a capillary rheometer. The rheometer was constructed in the laboratory by use of an extruder, transducers and dies. the study reveals the following conclusions.

1) Based on the theoretical development the measurement of radial total stress in the fully developed region enables us to calculate both viscosity and elasticity. Viscosity was obtained from the pressure gradient and elasticity from the

exit pressure, the extrapolated value of the radial total stress to the die exit.

2) The melt index which is essentially a single-point viscosity at a given shear stress was not suitable to use for the fluidity. Two main reasons for this are the range of shear rate for MI too low (below 60 sec⁻¹ in this study) to compare with the actual processing condition (more than a few hundred sec⁻¹) and the processing temperature not limited to a fixed temperature. It was demonstrated that, even though the MI values for four polystyrenes were different, their viscosities from MI seemed to fall on same viscosity line when plotted with shear rate. It indicates that all four show similar fluidity at 200°C.

3) The elastic behavior was characterized by two normal stress differences, N_1 and $-N_2$. The first normal stress difference N_1 also showed dependence on shear rate and temperature as in the case of viscosity. However, plotting N_1 against shear stress instead of shear rate, one could get temperature independent curve, from which a direct comparison of elasticity was possible. Two general purpose polystyrenes showed higher elasticity than two high impact grades.

4) The second normal stress difference N_2 was negative in sign and had the value in 0.14 – 0.72 range of N_1. Two general purpose polystyrenes gave the values of $-N_2/N_1$ in 0.14 – 0.32 range while two high impact grades in 0.38 – 0.72 range, indicating that the magnitude of $-N_2$ for the general purpose grades was higher than that of the high impact grades.

5) Comparison of the steady date with the dynamic measurement showed that two measuring techniques gave equally good assessment of viscosity over the range of shear rates or frequencies tested. But there are some discrepancy on the elastic behavior. The elastic analogy may be limited to the low deformation range only. Further, the elongational flow effect in the entrance region of capillary on first normal stress difference may not be negligible to compare two measuring techniques directly.

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