

## 모세관 점도계에 의한 고밀도폴리에틸렌/저밀도폴리에틸렌 블렌드의 유변학적 물성

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### Rheological Properties of HDPE/LDPE Binary Blends by Capillary Rheometer

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**요 약** : 모세관 점도계를 이용하여 고밀도폴리에틸렌과 저밀도폴리에틸렌(LDPE) 블렌드의 유변학적 물성에 대해 연구하였다. 블렌드는 압출기를 이용하여 용융혼합하여 제조하였는데 분지도가 다른 두 가지 LDPE를 사용하였다. 두 가지 모세관(L/D=40, 80)을 이용한 모세관 점도계를 전단응력-속도에 대한 대수실험식으로부터 블렌드의 용융점도, 탄성회복변형을 전단속도 및 블렌드 조성의 함수로서 연구하였다. 또한, 용융점도와 탄성회복변형의 온도의존성을 편미분방정식의 chain rule에 의해 해석하고 실험과 비교 검토하였다.

**Abstract** : Rheological properties of high density polyethylene and low density polyethylene(LDPE) binary blends were investigated by using a capillary rheometer. Blends have been prepared by mixing the melts using a single screw in an extruder. Two types of LDPE, differing in degree of branching (mainly short-chain branches) were used for comparison. Melt viscosity and elastic recoverable strain were investigated as functions of shear rate(or shear stress) and blend ratio by capillary rheometer (L/D=40 and 80) measurements using the logarithmic empirical equation for the shear stress-strain relation. Temperature dependence of melt viscosity and elastic recoverable strain was analyzed by the chain rule of partial differential equation and compared with experimental results.

### INTRODUCTION

Polymer blends have been extensively investigated because of their commercial importances as well as their theoretical interests. Among the polymer blends attracting commercial interests are polyethylene(PE)-based ones.<sup>1-3</sup>

It has been reported the blends containing high density polyethylene(HDPE), low density polyethylene(LDPE), linear low density polyethylene(LL-

DPE) and/or ultrahigh molecular weight polyethylene(UHMWPE), and etc.<sup>4-7</sup> There are extensive literatures on the blends of HDPE and LDPE.<sup>8-11</sup> It was reported that LDPE provides flexibility, impact strength and toughness to the stiff HDPE.<sup>8,9</sup> Rheology of HDPE/LDPE blends with different molecular weight were studied using a capillary rheometer by Dobrescu.<sup>12</sup> Kammer and Socher studied HDPE/LDPE blends using a cone-and-plate rotational rheometer.<sup>13</sup> Few works have been

reported, however, on the blends of HDPE and LDPE having degree of different chain branching.

Object of this work is to investigate the rheological properties such as melt viscosity and elastic recoverable shear strain of the HDPE/LDPE blends and effects of different chain branching on the properties of the blends by using a capillary rheometer.

## EXPERIMENTAL

**Materials.** The characteristics of polyethylenes used in this study are summarized in Table 1. The HDPE and LDPE were all commercially available grades. The methyl contents in HDPE and LDPE were estimated from their IR spectra using the method suggested by Bryant and Vorter,<sup>14</sup> and Cross, et al.<sup>15</sup>

**Blend Preparation and Rheological Measurements.** Blends were prepared by melt-mixing in a 30 mm  $\phi$ -single screw extruder ( $L/D=28.8$ ). Temperature of two cylinders was set at 200°C and the die temperature was set at 210°C. Rheological properties were measured using a capillary rheometer (Instron Model 3211) in the shear rate range of 3.5~350.5  $\text{sec}^{-1}$  at 180, 190, and 200°C. Two capillaries of different dimensions were used for this study; Dimensions of lengths/diameters of the capillaries were 5.0925/0.1275 cm ( $L/D=40$ ) and 10.1735/0.1273 cm ( $L/D=80$ ), respectively.

## RESULTS AND DISCUSSION

Fig. 1 shows the viscosity variations with different HDPE compositions for HDPE/LDPE blends.

In this figure, apparent melt viscosity of polymers was determined by using a logarithmic parabola type of modified power-law equations (1) and (2).<sup>16</sup>

$$\log \tau_w = a + b \log \dot{\gamma}_{aw} + c(\log \dot{\gamma}_{aw})^2 \quad (1)$$

$$\tau_w = K' \dot{\gamma}_{aw}^{n'} \quad (2)$$

where  $a$ ,  $b$  and  $c$  are experimentally determined constants by linear regression from the measured shear stress at wall,  $\tau_w$  and apparent shear rate at wall,  $\dot{\gamma}_{aw}$ .

In equation (2),  $n'$ , the Rabinowitch-corrected power law index, is the slope of the  $\log \tau_w$  vs.  $\log \dot{\gamma}_{aw}$  plot, i. e.

$$n' = \frac{d \log \tau_w}{d \log \dot{\gamma}_{aw}} \quad (3)$$

The intercept of the  $\log \tau_w$  vs.  $\log \dot{\gamma}_{aw}$  plot gives the consistency factor,  $K'$ . Then, differentiation of equation (1) gives  $n'$  as follows

$$n' = b + 2c(\log \dot{\gamma}_{aw}) \quad (4)$$

It is well known that the use of the Rabinowitch correction for the true shear rate at wall,  $\dot{\gamma}_w (\dot{\gamma}_{aw}^{3n'+1}/(4n'))$  in equation (2) gives further the power law.<sup>17</sup>

$$\tau_w = K \dot{\gamma}_w^n \quad (5)$$

in which

$$n = n' \\ K = K' (4n' / (3n' + 1))^{n'} \quad (6)$$

Once flow curves are constructed, one can then calculate the melt viscosity,  $\eta$ , for power-law relationship from the definition.

Table 1. Characteristics of Materials

Polymers	Melt index (g/10 min)	Density (g/cm <sup>3</sup> )	Amount of methyl groups per 1,000 carbon atoms	Molecular weight		Sources
				M <sub>n</sub>	M <sub>w</sub>	
HDPE	0.89 <sup>a</sup>	0.960	2.0	13,100	100,200	Kor. Petro.
LDPE-A	4.00 <sup>a</sup>	0.920	14.9	11,800	81,000	Hanyang
LDPE-B	0.80 <sup>a</sup>	0.923	17.6	93,000	115,000	Hanyang

<sup>a</sup>) measured at 190°C

$$\eta = \tau_w / \dot{\gamma}_w = K \dot{\gamma}_w^{n-1} \quad (7)$$

In this calculation, however, the entrance and the exit corrections for the true wall shear stress have not been made.

It is seen that the HDPE/LDPE blends show typical sigmoidal deviation behavior from their additive values over the entire compositions, implying that the two blends are incompatible over the entire compositions. Careful inspection of Fig. 1 indicates that the melt viscosities of HDPE/LDPE-A blends are higher than those of HDPE/LDPE-B blends over all the composition ranges. The result is in accordance with the general trend that the viscosity of LDPE having lower degree of branching is higher than that of LDPE having longer degree of branching.<sup>18,19</sup>

In general, however, the overall minima and maxima behavior with different shear rates in the viscosity-composition plot are attributed to the change of morphology, caused by the change of the domain size and shape, and interfacial energy in a molten state depending on the shear rates.<sup>20,21</sup> For reference, the dotted additive-rule line in Fig. 1 was drawn following the Hayashida<sup>22</sup> equation (8)

$$1/\eta_b = w_1/\eta_1 + w_2/\eta_2 \quad (8)$$

where  $w_i$  is the weight fraction of  $i$  component in the blend,  $\eta_i$  and  $\eta_b$  are the melt viscosities of  $i$  component and blend, respectively.

Fig. 2 shows the flow behavior indices against HDPE compositions at various temperatures. Power-law relationship was observed in the shear rate range studied. Values of the exponent  $n'$  or the Rabinowitch-corrected flow behavior index of the power-law equation were calculated from equation (4). It is seen that the flow behavior indices slightly increased with HDPE composition regardless of temperature and the increase in flow behavior index was more clearly seen in the blend of HDPE with LDPE-A.

The shear rate-temperature superposition principle provides the temperature-independent viscoelasticity.<sup>23</sup>

$$\eta(T) = a_T \eta(T_g) \quad (9)$$

where the shift factor  $a_T$  is calculated by the WLF equation (10) or Arrhenius equation (10)

$$\log a_T(T) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (10)$$

$$a_T(T) = A \exp(E_a/RT) \quad (11)$$

where  $E_a$  is the flow activation energy,  $R$  is the gas

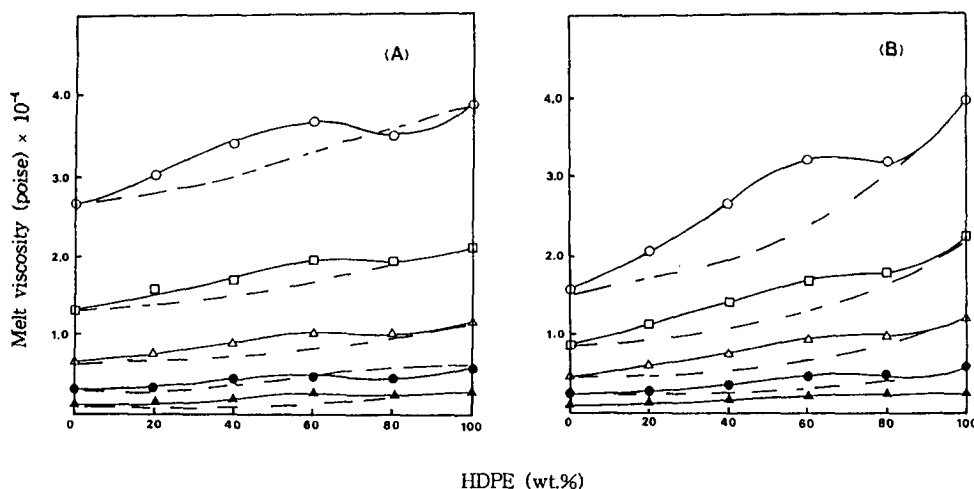


Fig. 1. Viscosity variations with different compositions of (A) HDPE/LDPE-A and (B) HDPE/LDPE-B blends at 190°C. (shear rate : (○) 3.50, (□) 11.67, (△) 35.02, (●) 116.73, (▲) 350.18 sec<sup>-1</sup>)

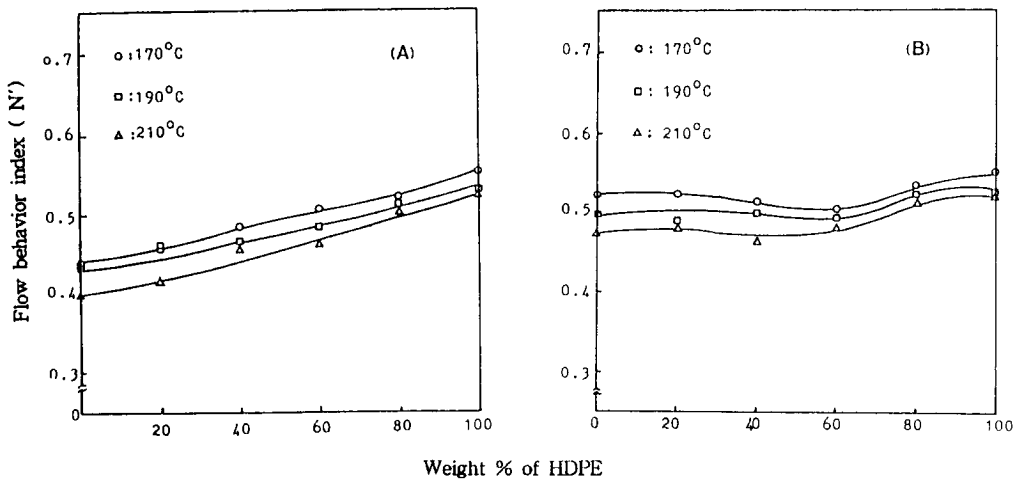


Fig. 2. Effect of HDPE compositions on flow behavior index for (A) HDPE/LDPE-A and (B) HDPE/LDPE-B blends at  $\dot{\gamma} = 35 \text{ sec}^{-1}$ .

constant, and  $A$  is  $\exp(-E_a/R T_R)$ . ( $T_R$  is any reference temperature).

Fig. 3 shows the relative viscosity ( $\eta/\eta_R$ ) as a function of  $a_T \dot{\gamma}_w$  for HDPE/LDPE-B blends. In this figure, the shift factor was calculated by the Arrhenius equation (11) using  $T_R$  as  $200^\circ\text{C}$ . One can see that the HDPE/LDPE-B blends follows the shear rate-temperature superposition principle well. Similar result was obtained for HDPE/LDPE-A blends.

In general, it may be thought that the temperature dependency of melt viscosity measured at constant shear rate is smaller than that at constant shear stress from the following chain rule of partial differential equations.

$$(\partial\eta/\partial T)_\dot{\gamma} = (\partial\eta/\partial T)_{\tau_{12}} \times [1 + (\partial \ln \eta / \partial \ln \dot{\gamma})_T] \quad (12)$$

In the pseudoplastic flow system,

$$(\partial \ln \eta / \partial \ln \dot{\gamma})_T < 0 \quad (13)$$

Thus, the following relationship is valid

$$|(\partial\eta/\partial T)_\dot{\gamma}| < |(\partial\eta/\partial T)_{\tau_{12}}| \quad (14)$$

Equation (14) implies that it is more reasonable to express the melt viscosity as function of shear rate than as a function of shear stress to minimize the temperature dependency of melt viscosity.

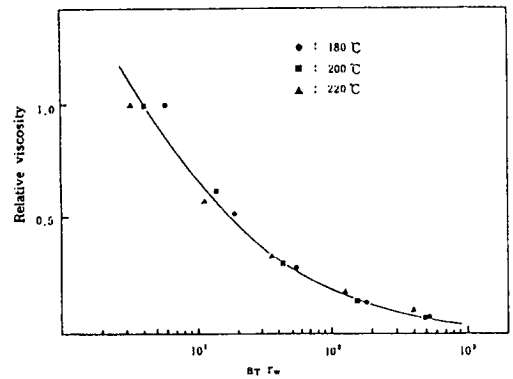


Fig. 3. Relative viscosity  $\eta/\eta_R$  vs.  $a_T \dot{\gamma}_w$  for low-density polyethylene B.

Melt elasticity of the blends was analyzed using the elastic recoverable shear strain  $S_R$ , defined as the equation (15).<sup>23-26</sup>

$$S_R = (\tau_{11} - \tau_{22}) / 2\tau_w = (\phi_{12} / 2\eta) \dot{\gamma}_w \quad (15)$$

The shear stress,  $\tau_{12}$ , and the first normal stress difference,  $\tau_{11} - \tau_{22}$ , are related with the viscosity,  $\eta$ , and the first normal stress difference coefficient,  $\phi_{12}$ , respectively.

$$\tau_{12} = \eta(\dot{\gamma}_w) \dot{\gamma}_w \quad (16)$$

$$\tau_{11} - \tau_{22} = \phi_{12}(\dot{\gamma}_w) \dot{\gamma}_w^2 \quad (17)$$

$S_R$  can be estimated experimentally from the die swell ratio ( $B = D_{ext}/D$ ) by using Bagley and Duffey equation (18).<sup>7</sup>

$$S_R = (\bar{B}^4 - \bar{B}^2)^{1/2} \quad (18)$$

$D_{ext}$  and  $D$  denote the diameter of extrudate and capillary die, respectively.  $B$  was measured ten times and averaged.

Then, the shift factor  $a_T$  can be also calculated by the equations (11) and (16).

$$S_R(T) = a_T S_R(T_R) \quad (19)$$

The first normal stress differences are plotted against shear rates in Fig. 4 for the HDPE/LDPE blends. Fig. 5 shows the first normal stress difference plotted against shear stress. One can see that the first normal stress difference increases with increasing shear stress or shear rate for the blends of HDPE with LDPE-A or LDPE-B. The melt elasticity in terms of the first normal stress difference increased with increasing HDPE compositions. This trend is more clearly appeared in the plot of the first normal stress difference coefficient against shear rate (Fig. 4). The  $\phi_{12}$  against shear rate of homopolymers are illustrated in Fig. 6. The  $\phi_{12}$  increased in the order of HDPE > LDPE-A > LDPE-B. This means that the melt elas-

ticity of polyethylene is higher as the degree of branching is lower. It has known that the presence of long chain branching in a polymer tends to give rise to lower viscosity and high elasticity when it was highly deformed.<sup>19</sup>

Comparison of Figs. 4 and 5 exhibits that the melt elasticity of the blends is independent the blend compositions shear stress, but depended upon the compositions with different shear rate. The result can be explained by the chain rule of partial differential equations similar as the equations of (12)~(1310) for the melt viscosity. Let

$$N_1 = \tau_{11} - \tau_{22} \quad (20)$$

The chain rule of partial differential equations gives

$$\left(\frac{\partial N_1}{\partial C}\right)_{\tau_{12}} = \left(\frac{\partial N_1}{\partial C}\right)_{\dot{\gamma}} - \left(\frac{\partial N_1}{\partial \dot{\gamma}}\right)_{\tau_{12}} \times \left[ \frac{\partial \tau_{12}}{\partial C} \dot{\gamma} / \left(\frac{\partial \tau_{12}}{\partial \dot{\gamma}}\right)_C \right] \quad (21)$$

$$\text{or } \left(\frac{\partial N_1}{\partial C}\right)_{\tau_{22}} = \left(\frac{\partial N_1}{\partial C}\right)_{\dot{\gamma}} \left[ 1 - \left(\frac{\partial \tau_{12}}{\partial C}\right)_{\dot{\gamma}} \left(\frac{\partial N_1}{\partial \tau_{12}}\right)_C \right] \quad (22)$$

where  $C$  is composition of HDPE in a HDPE/LDPE blend.

Since

$$\left(\frac{\partial \tau_{12}}{\partial N_1}\right)_{\dot{\gamma}} > 0 \text{ and } \left(\frac{\partial N_1}{\partial \tau_{12}}\right)_C > 0 \quad (23)$$

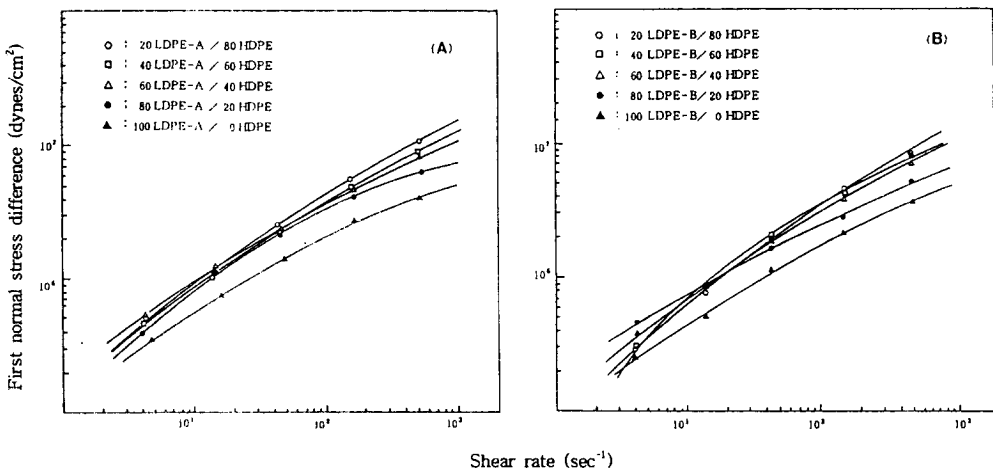


Fig. 4. First normal stress difference vs. shear rate for (A) HDPE/LDPE-A and (B) HDPE/LDPE-B blends at 180°C.

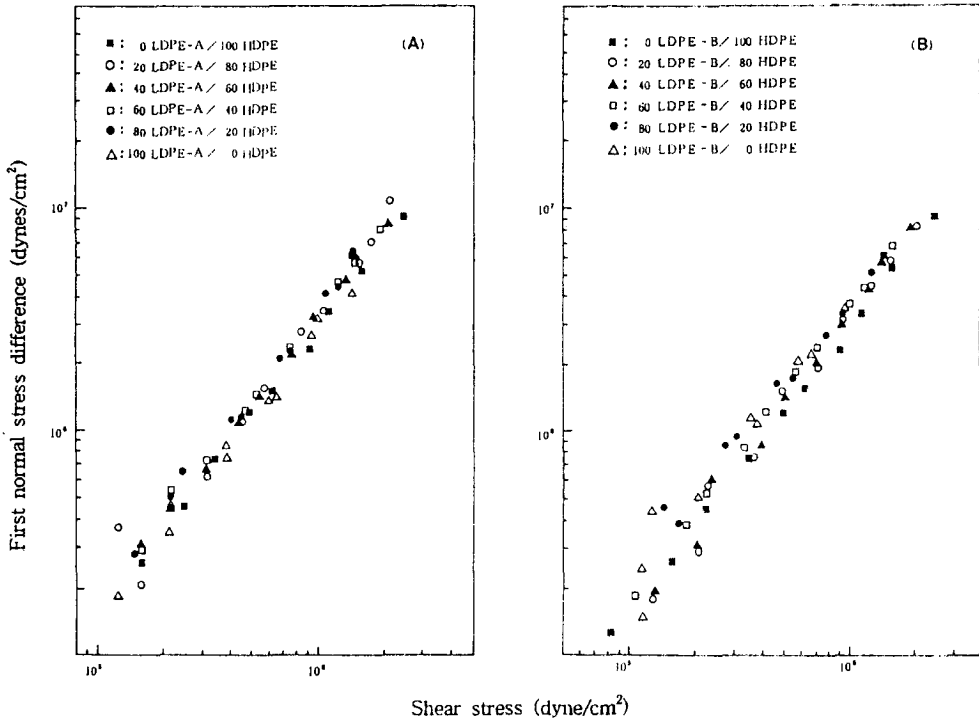


Fig. 5. First normal stress difference vs. shear stress for (A) HDPE/LDPE-A and (B) HDPE/LDPE-B blends at 180°C and 220°C.

for the present system, the following relationship holds,

$$(\partial N_1 / \partial C)_{\tau_{12}} < (\partial N_1 / \partial C)_{\dot{\gamma}} (> 0) \quad (24)$$

Thus, the results of Figs. 4 and 5 are not surprising since the composition dependence of the first normal stress at constant shear stress is smaller than that at constant shear rate, as seen in equation (24).

Fig. 7 shows the plot of first normal stress difference coefficient against the blend compositions for both HDPE/LDPE blends. Dependence of melt elasticity on the blend compositions are larger at lower shear rate for both HDPE/LDPE blends, and the melt elasticities of HDPE/LDPE-A blends are higher than those of HDPE/LDPE-B blends at the same HDPE composition in the blends.

Meanwhile, temperature dependency of elastic recoverable shear strain can be derived from the chain rule of partial differential equations,

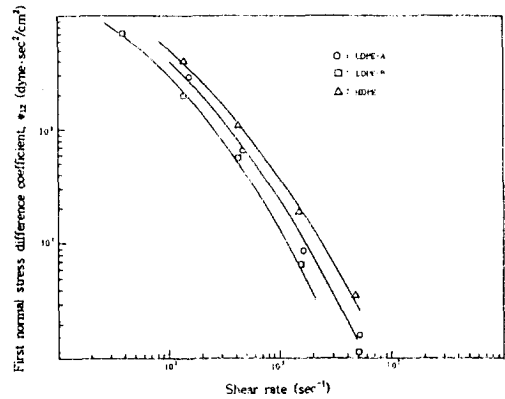


Fig. 6. Shear rate dependence of melt elasticity.

$$\left(\frac{\partial S_R}{\partial T}\right)_{\tau_{12}} = \left(\frac{\partial S_R}{\partial T}\right)_{\dot{\gamma}} \left[ 1 - \left(\frac{\partial \tau_{12}}{\partial S_R}\right)_{\dot{\gamma}} \left(\frac{\partial S_R}{\partial \tau_{12}}\right)_T \right] \quad (25)$$

Since  $(\partial \tau_{12} / \partial S_R)_{\dot{\gamma}}$  is negative and  $(\partial S_R / \partial \tau_{12})_T$  is positive for the present system, the temperature dependency of  $S_R$  evaluated at constant shear st-

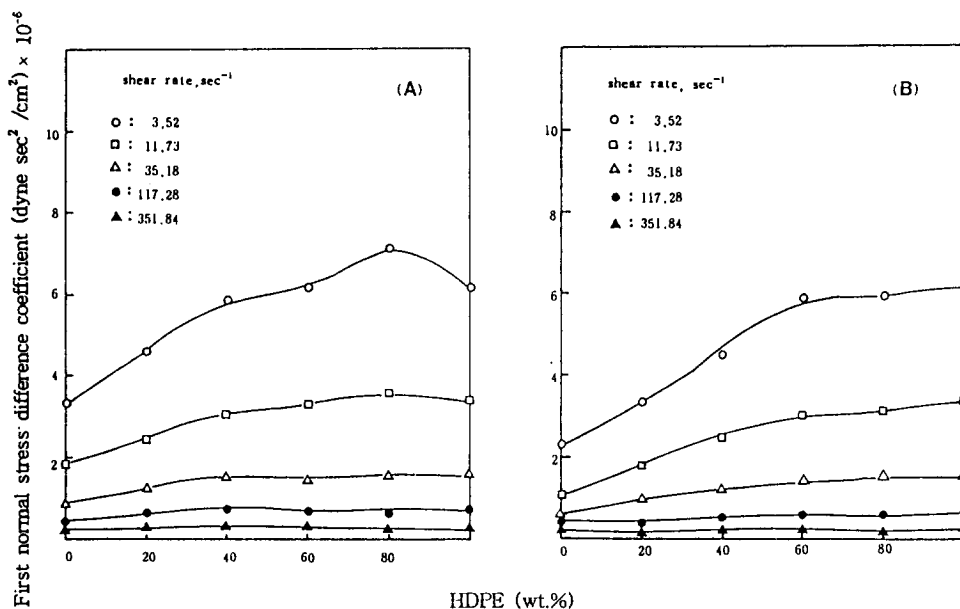


Fig. 7. First normal stress difference coefficient variations with different compositions of (A) HDPE/LDPE-A and (B) HDPE/LDPE-B blends at 220°C.

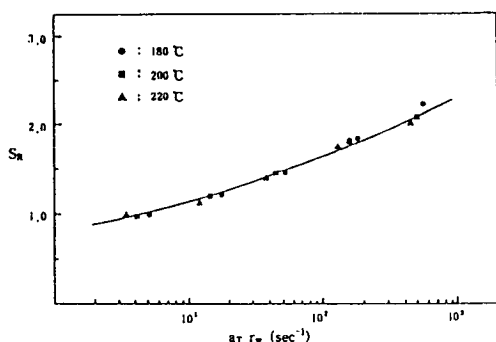


Fig. 8. 200°C Master curves of  $S_R$  vs.  $\log a_T r_w$  for 60 HDPE/40 LDPE-A blends obtained by superposition using generalized shear rate-temperature shift factor.

ress will be larger than that evaluated at constant shear rate. Hence,

$$(\partial S_R / \partial T)_{\dot{\gamma}} < (\partial S_R / \partial T)_{\tau_{12}} \quad (26)$$

Equation (22) also suggests that it is desirable to express the melt elasticity as a function of shear rate than as a function of shear stress to minimize its temperature dependency.

Fig. 8 shows a Arrhenius plot of  $S_R$  against shift factor  $a_T$ . It is clearly seen that the elastic recoverable shear strain also corresponds to the shear rate-temperature superposition principle within our experimental range. In this plot,  $T_R$  was set at 200°C.

## CONCLUSIONS

Composition dependency of rheological properties of HDPE/LDPE blends has been investigated using a capillary rheometer and the effect of degree of branching in LDPE was discussed.

Rheological measurements showed that both the melt viscosity and the melt elasticity of the blends containing the LDPE with low degree of branching were larger than those with high degree of branching. It was found that the viscosity and melt elasticity in terms of the die swell ratio of HDPE/LDPE blends observed the Arrhenius type of shear rate-temperature superposition principle well. It was analyzed from the chain rule of partial differential equations that to express both the melt

viscosity and melt elasticity as a function of shear rate than as a function of shear stress is more reasonable to minimize their temperature dependency.

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