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INFLUENCE OF MOLECULAR WEIGHT DISTRIBUTION ON ELONGATIONAL FLOW OF POLYETHYLENE

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Synopsis

An experimental investigation of elongational viscosity of polyethylene has been carried out using an isothermal elongational rheometer at constant strain rate. Elongational viscosity data are presented for a series of four high-density polyethylene samples having various molecular weight distributions. In the small strain region, linear viscoelastic behavior was observed for all samples, and the steady state was only observed for the sample with narrowest distribution. The non-linearity behavior strongly depended on the distribution of molecular weight and its intensity decreased with broadening the molecular weight distribution. These non-linear response data were compared to predictions from constitutive equation, specifically the Bogue and White model. The molecular weight distribution dependence of elongational viscosity was explained in terms of adjustable parameter a : the value of a increased with broadening the molecular weight distribution. Temperature dependence of elongational viscosity was small for broad distribution sample.

INTRODUCTION

The elongational viscosity of polymer melt increases with time at constant strain rate experiment. The increase occurs in two stages. The elongational viscosity first increases slowly independent of strain rate (linear region). The linear region appears at small strain. In the second state there is a rapid increase in the elongational viscosity from arbitrary time determined by the constant critical strain (non-linear region). The non-linear region appears at large strain and is shown as the deviation from the linear curve to the larger values. The critical strain (ϵ_c), at which the non-linear region begins, is independent of strain rate. The non-linearity parameter (λ_n), which is defined as division of the elongational viscosity values obtained experimentally (λ) by the values of linear parts at the same time (λ_l), is also independent of strain rate.^{2,3)}

The previous paper⁴⁾ reported on the elongational viscosity of a series of polypropylenes wide variety in molecular weight and similar in molecular weight distribution (MWD). Both the critical strain and the non-linearity parameter are also independent of molecular weight. The present paper is an attempt to clarify the MWD dependence of the non-linearity behavior of the elongational viscosity.

EXPERIMENTAL

The studied polymers are commercialized polyethylenes; linear high-density materials of melt index from 0.033 to 1.02 and having different molecular weight distribution. These samples were supplied by Idemitsu Petrochemical Company. Overall MWD curves are presented in Figure 1 for samples PE-A, B, C, and D. These normalized chromatograms were obtained using a gel permeation chromatograph of Walters Ltd. The

Fig. 1. Gel permeation chromatogram of materials studied.

sample: (----), PE-A; (— — —), PE-B;
(——), PE-C; (-----), PE-D

molecular characteristics of samples are summarized in Table I. As may be seen from Table I, the differences in MWD, which is indicated as the ratio of weight average molecular weight ($\bar{M}_w$) to number average molecular weight ($\bar{M}_n$), may be attributed mainly to the values in weight average molecular weight. The weight average molecular weight increases and the number average molecular weight decreases slightly with increasing MWD.

The rod shaped sample was prepared by extruding and taking up without extension force and was used in the elongational experiments. The diameter of the rods was about 4mm and length was about 100cm.

The experimental details for the measurement of elongational force and filament diameter were the same as those reported in previous study.¹⁾ A rod shaped sample was floated on the bath fluid of silicone oil and was melted at a constant temperature for 20min. The molten sample was pulled between two sets of rotating clamps, being driven at a constant rotational speed. The space between the clamps was kept constant. Force was

measured by a leaf spring and a differential transducer and corrected by calculating the rheological elongational force. The sample diameters during elongational experiments were measured directly by a microscope photographic technique.

Elongational strain is defined after Hencky

$$r = \ln \frac{l}{l_0} \quad (1)$$

where l_0 and l are the initial and the instantaneous length of the sample. Then the rod diameter at constant strain rate is given by

$$\ln d = \ln d_0 - \frac{\dot{\epsilon}}{2} t \quad (2)$$

where d_0 and d are the initial and the instantaneous diameter of the sample. An example of the typical attenuation of diameter to start up is shown in Figure 2, where $\ln d$ is plotted versus time for four samples. In Figure 2, linear relationships are observed and it means the constant strain rate

Fig. 2. Variation of sample diameter with time at a strain rate of 0.004sec^{-1} at 160°C for various polyethylene samples.

sample: ($\blacktriangle$), PE-A; ($\triangle$), PE-B;
($\bullet$), PE-C; ($\circ$), PE-D

Table I. Physical properties and molecular weights of high density polyethylene.

	MI	d_{23}	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-6}$	$\bar{M}_{z+1} \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$
PE-A	1.02	0.954	2.7	1.9	2.1	5.9	6.9
PE-B	0.3	0.951	1.8	3.1	4.1	9.9	17.0
PE-C	0.05	0.955	1.5	3.8	2.7	4.9	25.0
PE-D	0.033	0.953	1.4	6.0	9.8	24.9	43.0

experiments are established. The maximum error in strain rate is of the order of $\pm 3\%$ for the samples in present study. The constant strain rate can be maintained in the narrow MWD samples (PE-A and B) for long time interval compared with that of broad MWD ones (PE-C and D).

RESULTS AND DISCUSSION

Elongational viscosity data as a function of time are shown in Figure 3 for four high-density polyethylene samples. Comparing the results of this figure with the MWD data of Table I, we see that time dependence of the linear parts are larger for the broad MWD. Broadening the MWD increases the ratio of the $\lambda(100)/\lambda(1)$ from 2 (PE-A) to 15 (PE-D), where $\lambda(100)$ and $\lambda(1)$ are the viscosity values of linear parts at 100sec and 1sec, respectively.

The linear parts of elongational viscosity can be successfully expressed in terms of the constitutive

Fig. 3. Variation of elongational viscosity with time at 160°C at constant strain rate of 0.04sec^{-1} (black mark) and 0.004sec^{-1} (open mark).

sample: (▲, △), PE-A; (■, □), PE-B;
(●, ○), PE-C; (▼, ▽), PE-D

models.²⁾ One of these constitutive models is the Bogue and White model,^{5,6)} the elongational viscosity of the model is expressed as

$$\lambda(t) = \sum_{i=1}^N G_i (e^{ut} - e^{vt}) + \sum_{i=1}^N \frac{G_i}{\tau_{ie}} + \sum_{i=1}^N \frac{G_i}{\tau_{ie}} \{ (u^{-1} e^{ut} - v^{-1} e^{vt}) - (u^{-1} - v^{-1}) \}$$

$$u = -\tau_{ie}^{-1} + 2\dot{\gamma}, \quad v = -\tau_{ie}^{-1} - \dot{\gamma}, \quad \tau_{ie} = \frac{\tau_i}{1 + \sqrt{3} a \tau_i \dot{\gamma}} \quad (3)$$

where τ_i and G_i are constants to fit the linear parts of the elongational viscosity-time curve, τ_{ie} is called the effective time constant. A feature of this model is that the adjustable fitting parameter a is contained. The Lodge model⁷⁾ is equal to the this model in which a is zero.⁵⁾ The adjustable parameters to fit the linear parts, τ_i and G_i , are estimated for the data from 0.32 to 200sec in the experiment at $\dot{\gamma} = 0.004\text{sec}^{-1}$. The results of the least squares data fitting are shown by the solid line in Figure 3. The values of estimated parameters are given in Table II. The value of G_i of PE-A is rapidly decreased at longer time constant. The long time constant is considered to be associated with high molecular weight species. The PE-A shows the smaller fraction at higher molecular weight ($>10^6$) in Figure 1. The rapid decrease in G_i at longer time constant of PE-A is related to the smaller fraction of higher molecular weight.

It can be also seen as the dominant feature of Figure 3 that the increase in elongational viscosity at longer time region of the narrow MWD samples (PE-A and PE-B) is more rapid than that of the broad ones (PE-C and PE-D). That is, non-linear intensity of elongational viscosity is larger for narrow MWD samples than for broad ones. The dependence of non-linearity behavior on molecular weight distribution would be compatible with the observation of Münstedt⁸⁾ on a series of rather

Table II. Constants of τ_i and G_i of high-density polyethylene.

τ_i	0.1	1	10	100	1000
PE-A	4.1×10^5	7.8×10^4	3.2×10^3	2.6×10^2	4.5×10^1
PE-B	2.7×10^5	1.1×10^5	4.4×10^4	9.9×10^3	2.3×10^3
PE-C	2.9×10^5	3.2×10^5	1.2×10^5	3.4×10^4	1.5×10^4
PE-D	3.7×10^6	3.3×10^6	1.9×10^6	5.6×10^5	2.1×10^4

narrow distribution polystyrenes. However, these results contrast with the data of Minoshima et al.,⁹⁾ which show that the non-linearity of broader distribution results in more rapid increment than that of narrow distribution samples. The apparent inconsistency seems to be due to an experimental technique of Minoshima et al., because there is no assurance of constant strain rate in their elongational experiments.⁹⁾

It is interesting to further consider that the non-linearity behavior strongly depends on the MWD. It has been pointed out previously that the melt elastic properties of shear flow are highly sensitive to polydispersity.¹⁰⁾ The modulus of elasticity, at which the recoverable strain is constant, decrease with broadening the molecular weight distribution.¹¹⁾ The steady-state compliance is also highly sensitive to polydispersity, and increases with broadening the MWD.^{12,13)} On the other hand, the non-linearity intensities of elongational viscosity have been dependent on the polydispersity, not on molecular weight⁴⁾ (Figure 3). The similarity between the non-linearity of elongational viscosity and the elasticity of shear flow is obvious. Then, the non-linearity behavior of elongational viscosity increases with increasing the elastic property of polymer molecules.

Figures 4 and 5 show the plot of the non-linearity parameter (λ_n) against the strain for four high density polyethylenes at 160°C. Where the non-linearity parameter was defined as $\lambda_n = (\text{elongational viscosity obtained experimentally}) / (\text{elongational viscosity of superposed linear viscoelastic data at same time})$. The non-linearity parameters predicted from the Lodge model are also shown in same figures. Experimental data show almost linear relationship in each sample and the critical strain can be obtained as about 0.7, as reported in the previous paper.³⁾ The slope of the straight line or the intensity of the non-linearity parameter of elongational viscosity is very sensitive to MWD (Figures 4 and 5), although it was independent on molecular weight for samples having similar distribution.⁴⁾ Broadening the MWD decreases the intensity of the non-linearity in elongational viscosity. While, the non-linearity parameter from the Lodge model increases with broadening the MWD. In particular, the PE-A having the small relaxation intensity at

Fig. 4. Plots of non-linearity parameter versus elongational strain at 160°C at strain rate of 0.04sec^{-1} for high density polyethylene of experimental data (plots) and the values predicted from the Lodge model (lines). sample: (▲, —), PE-A; (△, ---), PE-B; (●, -·-), PE-C; (○, ···), PE-D

Fig. 5. Plots of non-linearity parameter versus elongational strain at 160°C at strain rate of 0.004sec^{-1} for high density polyethylene of experimental data (plots) and the values predicted from the Lodge model (lines). Symbols as in Figure 4.

longer time constant (Table II) shows much smaller non-linearity parameter of elongational viscosity than others, and its value is almost equal to the experimental value in the case of $\dot{\gamma} = 0.004 \text{sec}^{-1}$. The discrepancies between the experimental data and the model predicted values increase with broadening the MWD.

The Bogue and White model is convenient to represent the MWD dependence of the non-linearity of elongational viscosity, because the adjustable parameter, a , to fit the non-linear parts of data is used in this experiment. One evaluates the model parameter a to fit the non-linearity parameter λ_n . The results for a are summarized in Table III. The model predictions and the comparison with data have also been shown in Figures 6 and 7. The agreement between the model prediction and the data is good. The values of a increased with broadening the MWD. The strain rate dependence of a is also observed, the value of a being increased with strain rate for polyethylene with narrow MWD. The constant a for polyethylene with broad MWD is large and independent on strain rate.

The essential idea of the Bogue and White model is that the effective time constants are dependent on the average second invariant of the strain rate tensor. The adjustable parameter is the coefficient meaning the intensity of strain rate dependence. At a constant a , higher strain rate causes smaller relaxation times, and the shift of relaxation time by strain rate variation is proportional to the magnitude of the relaxation time. The relaxation spectrum is shown as the solid line for two polyethylene samples having different MWD in Figure 8. A discrete rather than a continuous spectrum was actually used and the five spikes in this figure show the five elements of a discrete spectrum corresponding to the relaxation time $\tau_i = 0.1, 1,$

Table III. List of adjustable parameter a of the Bogue and White model.

$\dot{\gamma}$	0.004	0.04
PE-A	0.0	0.3
PE-B	0.5	0.6
PE-C	0.8	0.8
PE-D	0.8	0.8

Fig. 6. Plots of non-linearity parameter versus elongational strain at 160°C at strain rate of 0.04sec^{-1} for high density polyethylene of experimental data (plots) and the values predicted from the Bogue and White model (lines). Symbols as in Figure 4.

Fig. 7. Plots of non-linearity parameter versus elongational strain at 160°C at strain rate of 0.004sec^{-1} for high density polyethylene of experimental data (plots) and the values predicted from the Bogue and White model (lines). Symbols as in Figure 4.

Fig. 8. Discrete spectra in the constitutive model for PE-A (a) and PE-D (b).

Solid lines are the results from the Lodge model ($a=0$). Broken lines are the case of $\dot{\gamma}=0.004\text{sec}^{-1}$ and dotted lines the case of $\dot{\gamma}=0.04\text{sec}^{-1}$.

10, 100 and 1000sec. The broken and dotted lines in Figure 8 indicate the results of strain rate of 0.004 and 0.04sec^{-1} , respectively. The consequences at $\dot{\gamma}=0.004\text{sec}^{-1}$ (broken lines) for PE-A are consistent to solid line, since the parameter a equals to zero by the Lodge model. For the case at $\dot{\gamma}=0.04\text{sec}^{-1}$ of PE-A, the maximum time constant (1000sec) decreases to 46sec. The maximum time constant of PE-D is 18sec and is smaller than that of PE-A. The polyethylene having the broadest MWD, PE-D, shows the highest sensitivity to strain rate. The small time constants do not depend on strain rate, however the long time constant alone depends on strain rate. As MWD broadens, the decrease of the longer time constant with strain rate becomes to be noteworthy.

The elongational viscosity-time curves of PE-C with a strain rate of 0.04sec^{-1} at four temperatures are shown in Figure 9. It can be seen that the elongational viscosity decreases by a factor of 1.6–2.0 over the temperature range from 140°C to 200°C . These observations for high-density polyethylene are similar with those for polypropylene¹⁾ and low-density polyethylene.³⁾ Es-

Fig. 9. Variation of elongational viscosity of PE-C with time at strain rate of 0.04sec^{-1} for various temperatures.

temperature ($^{\circ}\text{C}$): ($\circ$), 140; ($\bullet$), 160; ($\triangle$), 180; ($\blacktriangle$), 200

pecially at longer time region, however, the temperature dependence of the polymer is smaller than that of the other polymers, of which the viscosity values decrease by a factor of 20 over similar temperature range. These small temperature dependence of elongational viscosity for high-density polyethylene may be characterized by broad MWD. It is also significant to note in Figure 9 that non-linearity behavior of elongational viscosity is similar to each datum at different temperature. It means that the temperature dependence of the non-linearity parameter is small. Therefore, the adjustable parameter of the Bogue and White model is insensitive to temperature.

CONCLUSION

It has been shown that the elongational viscosity of high-density polyethylene melts depends on the MWD. The linear parts of elongational viscosity increased with increasing weight average molecular weight. On the other hand, the non-linear parts of elongational viscosity decreased with broadening molecular weight distribution regardless of molecular weight. The non-linearity parameter λ_n decreases with broadening the MWD. This tendency is opposite result predicted by the

Lodge model. Qualitative understanding was obtained by considering the analysis of the Bogue and White model. The MWD dependences of non-linearity behavior are explained in terms of the adjustable parameter a of the Bogue and White model: the parameter increases with broadening the MWD. Temperature dependence of adjustable parameter a is small for high-density polyethylene having broad MWD.

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ポリエチレンの伸長流動におよぼす分子量分布の影響

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溶融体の一定ひずみ速度下での伸長粘度を等温伸長レオメータによって測定した。使用した試料は分子量分布の大きく異なる高密度ポリエチレンである。これらすべての試料の伸長粘度-時間関係は、短時間側、すなわち低ひずみ域で、線形粘弾性に従う挙動が観測された。また定常状態は最も分子量分布がせまい試料にのみ認められた。伸長粘度の非線形性は分子量分布に強く依存し、しかもその強さは分子量分布がひろがるにつれて減少し

た。このような非線形性のデータを構成方程式から予測される値と比較した。その結果、伸長粘度の非線形性の分子量依存性はBogue-Whiteモデルでうまく説明できた。すなわち、このモデルのパラメータ a は分子量分布が広がるにつれて増加すると考えられる。また分子量分布の広い試料の伸長粘度は温度依存性が小さいことが明らかにされた。