高分子溶融体に対する微分型・積分型粘弾性モデルの パラメーターの最適化とモデルの検討

—第1報：緩和スペクトルの自動最適化とせん断流動特性
からの非線形パラメーターの決定—

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Optimum Determination of Parameters in Differential and Integral Viscoelastic Models and Study on Reliability of the Models for Polymer Melts

—1. Automatic Optimization of a Relaxation Spectrum and Determination
of Nonlinear Parameters from Rheological Shear Data—

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We have developed a full nonlinear regression program to determine the relaxation spectrum and the nonlinear parameters for differential and integral viscoelastic models that will give the best fit to experimental rheological data. The least-squares procedure is based on the Levenberg-Marquardt method. The program for determining the optimum relaxation spectrum from dynamic linear viscoelastic data includes a function to automatically reset the initial guesses in the computation. The program was tested against experimental data for several polymer melts and a good fit was obtained. This new program was confirmed not only to be reliable but also to reduce the labor of manually resetting the initial guesses. The program for determining the nonlinear parameters was developed for the Phan Thien-Tanner (PTT), Larson, Giesekus and K-BKZ models and the determination from the experimental data of simple shear flow (shear viscosity and first normal stress difference) was performed for several polymer melts. The best-fit curves for all models were in good agreement with the experimental data within the range of experimental shear rate.

Key words : Material constant/Nonlinear regression/Relaxation spectrum/
Rheological property/Viscoelastic model

1. Introduction

In recent years, the technique of flow analysis for

polymeric materials has made considerable progress with remarkable achievements and the researchers are successively tackling to more complicated problems. Using the several constitutive models, the numerical analyses for the flow fields in which the viscoelastic characteristics of materials remarkably appear have been possible up to high deformation rate as seen in the industrial produc-

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tion. However, there are many cases in which the reliability of flow analysis is not sufficient because no constitutive model can quantitatively predict the complicated behavior of polymer fluid with adequate accuracy. Therefore, we need to select the most suitable model depending on the class of flow field.

In the flow analysis using a viscoelastic model, it is necessary to determine the material constants, a discrete relaxation spectrum and nonlinear parameters, so as to fit available experimental data of some known rheological properties. This determination is not easy because a lot of material constants exist as adjustable parameters, especially when several kinds of rheological properties should be given in consideration. An accurate rheological characterization is very important to obtain reliable simulation results.

Several researchers have addressed the issue of determining the material constants appearing in the model. A linear regression analysis¹⁾ has been used for determining the relaxation times and relaxation modulus coefficients from linear viscoelastic data, such as small-amplitude stress relaxation or sinusoidal oscillation. This method is based on linear least-squares procedures and the values of relaxation modulus coefficients are determined for a given number of relaxation modes and given values of relaxation times. Another method to determine the relaxation spectrum is to employ a nonlinear regression analysis as proposed by Baumgaertel and Winter²⁾. In this method, the values of both the relaxation times and modulus coefficients as well as the number of mode are determined as adjustable parameters, and a more accurate fitting can be obtained than that from linear regression analysis. Papanastasiou *et al.*³⁾ addressed the problem of determining the material constants by the linear and nonlinear regression analyses. In that work, it was pointed out that no unique solution was guaranteed. The authors^{4),5)} have extended this method to determine the relaxation spectrum as well as nonlinear parameters related to large deformation for the K-BKZ model. The authors found that unique solution could be guaranteed and a good fit was obtained between prediction and experimental data by using adequate initial guesses of material constants.

However, the regression analysis depends on the initial guesses of material constants and the reset of initial guesses is required until obtaining the reliable solution of material constants.

In the present study, we have modified the nonlinear regression program in order to determine the relaxation spectrum more easily in regard to the reset of initial guesses. And we have developed the program to determine the nonlinear parameters for the Phan Thien-Tanner (PTT), Larson, Giesekus and K-BKZ models and discussed the reliability and applicability of these constitutive models.

2. Constitutive Equations of Viscoelastic Models

The viscoelastic models for polymer melts discussed in this study are the Phan Thien-Tanner (PTT)⁶⁾, Larson⁷⁾ and Giesekus⁸⁾ models as a differential type, and the K-BKZ⁹⁾ model with the strain memory function of the PSM³⁾ or Wagner¹⁰⁾ type as an integral type. These models can predict the rheological properties of polymer melts relatively well with multiple relaxation times. These equations are written as

$$\tau = \sum_{k=1}^N \tau_k, \left[\exp\left(\frac{\varepsilon}{G_k} \text{tr}(\tau_k)\right) \right] \tau_k + \lambda_k \left[\frac{\varepsilon}{2} \dot{\tau}_k + \left(1 - \frac{\varepsilon}{2}\right) \nabla \tau_k \right] = 2\lambda_k G_k D \quad (\text{PTT}) \quad (1)$$

$$\tau = \sum_{k=1}^N \tau_k, \quad \tau_k + \lambda_k \nabla \tau_k + \frac{2}{3} \frac{\zeta \lambda_k}{G_k} \times D : \tau_k (\tau_k + G_k \delta) = 2\lambda_k G_k D \quad (\text{Larson}) \quad (2)$$

$$\tau = \sum_{k=1}^N \tau_k, \quad \tau_k + \lambda_k \nabla \tau_k + \frac{\alpha}{G_k} \tau_k^2 = 2\lambda_k G_k D \quad (\text{Giesekus}) \quad (3)$$

$$\tau = \frac{1}{1-\theta} \int_{-\infty}^t \sum_{k=1}^N \frac{G_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k}\right) \times h(I_{Ct'}, I_{Ct}) [C_t^{-1}(t') + \theta C_t(t')] dt' \quad (\text{K-BKZ}) \quad (4)$$

PSM type

$$h(I_{Ct'}, I_{Ct}) = \frac{\alpha}{\alpha + \beta I_{Ct'}(t') + (1-\beta) I_{Ct}(t') - 3} \quad (5)$$

Wagner type

$$h(I_{Ct'}, I_{Ct}) = \exp\left[-\alpha \sqrt{\beta I_{Ct'}(t') + (1-\beta) I_{Ct}(t') - 3}\right] \quad (6)$$

where τ is the extra stress tensor of fluid, τ_k the tensor in the k -th mode, C_t^{-1} the Finger strain

tensor, C_t the Cauchy strain tensor, $I_{C_t^{-1}}$ and I_{C_t} the first invariant of C_t^{-1} and C_t , respectively. D is the rate-of-deformation tensor and δ the unit tensor.

λ_k is the relaxation time, G_k is the relaxation modulus coefficient and N is the number of relaxation mode. A set of λ_k and G_k ($k=1\sim N$) is called a relaxation spectrum. The relaxation spectrum is related to both linear and nonlinear viscoelasticity. On the other hand nonlinear parameters, ε and ξ (PTT), ζ (Larson), α (Giesekus), α , β and θ (K-BKZ) are related to the nonlinear viscoelasticity (i. e. large deformation).

$\overset{\nabla}{\tau}_k$ and $\overset{\Delta}{\tau}_k$ are the upper-convected and lower-convected time derivatives of τ_k , respectively, represented as

$$\overset{\nabla}{\tau}_k = \frac{\partial \tau_k}{\partial t} + v \cdot \nabla \tau_k - (\nabla v)^t \cdot \tau_k - \tau_k \cdot \nabla v \quad (7)$$

$$\overset{\Delta}{\tau}_k = \frac{\partial \tau_k}{\partial t} + v \cdot \nabla \tau_k + \nabla v \cdot \tau_k + \tau_k \cdot (\nabla v)^t \quad (8)$$

where ∇v and $(\nabla v)^t$ are the velocity gradient tensor and its transpose tensor, respectively.

3. Procedure of Nonlinear Regression

A full nonlinear regression analysis is used to determine the material constants of the constitutive model so as to minimize the error between the predicted values of rheological properties and the experimental data in an average sense, that is

$$\sum_{i=1}^M \left[\frac{\{F_i(X)\}_{\text{pre}} - \{F_i\}_{\text{exp}}}{\{F_i\}_{\text{exp}}} \right]^2 = \min \quad (9)$$

where F_i denotes a rheological property, for example, storage and loss modulus, shear viscosity, etc. while M is the number of experimental data. The subscripts "pre" and "exp" represent the predicted and experimental values, respectively. X denotes the adjustable parameters which are a set of material constants, i.e. N , λ_k , G_k ($k=1\sim N$) and nonlinear parameters in each model. The technique of least-squares procedure is based on the Levenberg-Marquardt method¹¹⁾.

In this study, the relaxation spectrum is determined from the dynamic data of linear viscoelasticity, the storage modulus, G' and loss modulus, G'' . The procedure of determination is as follows :

① Initial guesses are chosen for each of nine decades from 10^{-4} to 10^{+4} s for λ_k and from 10^3 to 10^9 Pa for G_k (say $N=9$). We can obtain the reasonable

solutions with the other sets of initial G_k when initial G_k values are set to decrease as λ_k values increase. The reasonable solution can not be obtain when initial G_k values are set to be constant for all relaxation modes.

② Eq. (9) is solved and the values of λ_k and G_k are obtained.

③ The smallest or largest relaxation time (λ_1 or λ_N) becomes negative or diverges when the available data don't cover the whole range corresponding to the initial guesses of λ_k or the objective material does not have a relaxation spectrum over the range of the initial guesses. The same result occur for the corresponding relaxation modulus coefficient (G_1 or G_N). In this case, we omitted the corresponding relaxation modes in the initial guesses one by one and solved Eq. (9) again. As the repeat to reset the initial guesses by a trial and error until obtaining the suitable solution required much labor, we developed a new program adding the procedure of automatic reset of initial guesses in the computing. In this study, when the values of λ_1 , λ_N , G_1 or G_N become to be negative or larger than 10^{15} s (or Pa) in each iteration, the corresponding relaxation mode is automatically omitted and initial guesses are reset as $N=8$ ($\lambda_k=10^{-3}\sim 10^4$ s or $10^{-4}\sim 10^3$, $G_k=10^7\sim 10^9$ Pa or $10^8\sim 10^{11}$) in the program. The relaxation modes decrease one by one until all values of the λ_k and G_k values become reasonable. The converging solution is independent of the threshold value of large λ_k or G_k in reset process because λ_k or G_k diverge to the infinite in this case. When the physically reasonable results can be obtained, the determination procedure is achieved.

Nonlinear parameters, ε and ξ (PTT), ζ (Larson), α (Giesekus), α (K-BKZ) are determined from the shear flow data, shear viscosity, η_s and the first normal stress difference, N_1 . In this case, initial values are set suitable values. The reasonable solution can be obtained using any initial value of nonlinear parameter if the value is not unrealistic for polymer melts. In this study, initial values are set as 10 of α in the PSM type, 0.2 of α in the Wagner type, 0.1 of ε and 0.1 of ξ in the PTT, 0.25 of ζ in the Larson and 0.5 of α in the Giesekus models. Then Eq. (9) is solved and real values of nonlinear parameters are obtained.

β in the K-BKZ model is independent of the simple shear flow and therefore can not be determined from these data. θ in the K-BKZ model depends on the ratio between the second and first normal stress differences, N_2/N_1 . As there are few available and reliable data of N_2 , we set the value of θ at 1/9 which indicates $N_2/N_1 = -0.1$.

4. Results and Discussion

4.1 Optimization of relaxation spectrum

We show the result of determination of a relaxation spectrum from the dynamic data of linear

viscoelasticity by the developed nonlinear regression program. The experimental data of storage and loss modulus for a high density polyethylene (HDPE) melt at 190°C given by Otsuki *et al.*¹²⁾ are shown in Fig.1 as symbols. The relaxation spectrum determined from these data with manual reset by a trial and error of initial guesses is listed in Table 1 and the predictions of storage and loss modulus using these values in Table 1 are represented in Fig.1 as solid curves. The predicted values showed a remarkable agreement with experimental ones within the range of experimental frequency.

Fig.1 Determination of a relaxation spectrum by fitting to the dynamic data of linear viscoelasticity for a HDPE melt at 190°C by the nonlinear regression with the manual reset of initial guesses. Experimental data are given by Otsuki *et al.*¹²⁾. Determined values are listed in Table 1

Fig.2 Determination of a relaxation spectrum by fitting to the experimental data of dynamic viscoelasticity for a HDPE melt at 190°C by the nonlinear regression with the automatic reset of initial guesses. Experimental data are given by Otsuki *et al.*¹²⁾. Determined values are listed in Table 2

Table 1 Determined relaxation spectrum for a HDPE melt at 190°C by the nonlinear regression with the manual reset of initial guesses. Best-fit curves are shown in Fig.1

k	1	2	3	4	5	6
λ_k (s)	7.1×10^{-3}	4.7×10^{-2}	3.4×10^{-1}	1.4×10^0	1.5×10^1	2.5×10^2
G_k (Pa)	1.3×10^5	4.0×10^4	1.9×10^4	6.3×10^3	2.0×10^3	8.6×10^2

Table 2 Determined relaxation spectrum for a HDPE melt at 190°C by the nonlinear regression with the automatic reset of initial guesses. Best-fit curves are shown in Fig.2

k	1	2	3	4	5	6
λ_k (s)	7.3×10^{-3}	5.0×10^{-2}	3.2×10^{-1}	2.4×10^0	1.5×10^1	1.4×10^2
G_k (Pa)	1.3×10^5	3.9×10^4	1.9×10^4	6.6×10^3	2.0×10^3	8.6×10^2

Table 2 shows the determined values of relaxation spectrum by a new program of automatic reset of initial guesses and Fig.2 shows the predictions of storage and loss modulus. The good fit is obtained similar to the result by the previous program. The automatic reset program could save the labor of manual reset and the reliability of our new program was confirmed.

Figure 3 and Table 3 show the result for a low density polyethylene melt (LDPE IUPAC A) at 150°C. The experimental data are given by Meissner¹⁴⁾. Figure 4 and Table 4 show the result for a

low density polyethylene melt (LDPE Melt I) at 150°C. The experimental data are given by Laun¹⁵⁾. The intervals of discrete relaxation times as initial guesses were set closely in comparison with the case for the HDPE melt (The intervals of initial relaxation time can be set arbitrarily). Sufficient optimization of the relaxation spectrum was achieved in both melts.

4.2 Determination of nonlinear parameters from shear flow data

The developed program for determination of nonlinear parameters was tested against experimen-

Fig. 3 Determination of a relaxation spectrum by fitting to the dynamic data of linear viscoelasticity for a LDPE melt (IUPAC A) at 150°C by the nonlinear regression with the automatic reset of initial guesses. Experimental data are given by Meissner¹⁴⁾. Determined values are listed in Table 3

Fig. 4 Determination of a relaxation spectrum by fitting to the dynamic data of linear viscoelasticity for a LDPE melt (Melt I) at 150°C by the nonlinear regression with the automatic reset of initial guesses. Experimental data are given by Laun¹⁵⁾. Determined values are listed in Table 4

Table 3 Determined relaxation spectrum for a LDPE IUPAC A melt at 150°C by the nonlinear regression with the automatic reset of initial guesses. Best-fit curves are shown in Fig.3

k	1	2	3	4	5	6	7	8
λ_k (s)	1.31×10^{-3}	1.64×10^{-2}	6.05×10^{-2}	3.26×10^{-1}	2.85×10^0	2.45×10^1	1.2×10^2	1.0×10^3
G_k (Pa)	2.12×10^5	3.95×10^4	1.62×10^4	1.62×10^4	4.81×10^3	8.0×10^2	1.0×10^2	2.3×10^0

Table 4 Determined relaxation spectrum for a LDPE Melt I at 150°C by the nonlinear regression with the automatic reset of initial guesses. Best-fit curves are shown in Fig.4

k	1	2	3	4	5	6	7	8
λ_k (s)	3.62×10^{-4}	3.46×10^{-3}	3.02×10^{-2}	2.83×10^{-1}	2.17×10^0	1.59×10^1	1.24×10^2	1.32×10^2
G_k (Pa)	1.49×10^5	7.83×10^4	3.89×10^4	1.73×10^4	5.95×10^3	1.06×10^3	1.03×10^2	1.17×10^1

tal data of rheological properties in simple shear flow for several polymer melts.

Figure 5 shows the result for the HDPE melt described above. The nonlinear parameters in the PTT, Larson, Giesekus and K-BKZ of the PSM and Wagner types models were determined from the experimental data¹²⁾ of shear viscosity and first normal stress difference with the relaxation spectrum determined from the dynamic data. The best-fit curves for all models were in good agreement with the experimental data within the range of experimental shear rate. The first normal stress differences for the PTT, Larson and K-BKZ models at high shear rate beyond the experimental region coincided with one another while that for the Giesekus model is estimated larger than other three models.

The result for a LDPE IUPAC A melt is shown in Fig. 6. The Experimental data of η_s and N_1 are referred in the literature¹³⁾ (original data are given by Meissner¹⁴⁾). All models could predict well in the

range of the experimental data but the Giesekus model inclined to be larger than other models in high shear rate for the first normal stress difference.

Figure 7 shows the result for a LDPE Melt I. The experimental data¹⁵⁾ were measured at various different temperatures and the master curves were obtained by the time-temperature shifting. Therefore, the first normal stress difference at high shear rate region was obtained. It was found from Fig. 7 that the all models could predict the experimental data but the Giesekus model slightly underpredicted in the range of experimental data and overestimated the first normal stress difference from other models in high shear rate as a LDPE IUPAC A melt.

The reason why the Giesekus model shows these results is that this model has originally developed as the model with a single relaxation time. Its first normal stress difference in a single mode continues to increase in proportion to the square root of shear rate at higher region of shear rate. The first normal stress difference obtained from superposition of those in all modes has the possibility of overestimation at high shear rate when this model is used as

Fig. 5 Determination of nonlinear parameters by fitting to the experimental data of steady shear flow for a HDPE melt at 190°C. $\epsilon=0.568$ (initial value is 0.1) and $\xi=0.181$ (initial value is 0.1) in the PTT model, $\zeta=0.671$ (initial value is 0.25) in the Larson model, $\alpha=0.901$ (initial value is 0.5) in the Giesekus model and $\alpha=4.913$ (initial value is 10) of PSM type, $\alpha=0.274$ (initial value is 0.2) of Wagner type in the K-BKZ model. Experimental data are given by Otsuki *et al*¹²⁾. Relaxation spectrum are listed in Table 2

Fig. 6 Determination of nonlinear parameters by fitting to the experimental data of steady shear flow for a LDPE melt (IUPAC A) at 150°C. $\epsilon=0.171$ and $\xi=0.092$ in the PTT model, $\zeta=0.304$ in the Larson model, $\alpha=0.394$ in the Giesekus model and $\alpha=11.22$ of PSM type, $\alpha=0.201$ of Wagner type in the K-BKZ model. Experimental data are given by Meissner¹³⁾. Relaxation spectrum are listed in Table 3

Fig.7 Determination of nonlinear parameters by fitting to the experimental data of steady shear flow for a LDPE melt (Melt I) at 150°C. $\varepsilon=0.172$ and $\xi=0.100$ in the PTT model, $\zeta=0.301$ in the Larson model, $\alpha=0.625$ in the Giesekus model and $\alpha=10.79$ of PSM type, $\alpha=0.180$ of Wagner type in the K-BKZ model. Experimental data are given by Laun¹⁵⁾. Relaxation spectrum are listed in Table 4

the multiple relaxation modes.

As the shear viscosity and first normal stress difference for most of typical polymer melts show the characteristics as seen in Figs.5, 6 and 7 (i.e. shear-thinning properties of shear viscosity and first normal stress coefficient), all models would predict the rheological properties of steady shear flow for polymer melts.

5. Conclusions

We have developed a full nonlinear regression program in order to determine the material constants for differential and integral viscoelastic models from experimental data of some rheological properties based on the Levenberg-Marquardt method. The program for determining the optimum relaxation spectrum from dynamic data of linear viscoelasticity including the function of automatic reset of initial guesses was confirmed not only to be reliable but also to be able to save the much labor of manual reset of initial guesses. The program for determining the nonlinear parameters for the Phan Thien-Tanner (PTT), Larson, Giesekus and K-BKZ models was tested against experimental shear

data for several polymer melts. The best-fit curves for all models were in good agreement with the experimental ones but the first normal stress difference of the Giesekus model was inclined to be larger than other models at high shear rate. This nonlinear regression program is easy to extend for determination of other kinds of rheological properties and the study on determination from the data of both shear and elongational properties is desirable.

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和文要旨

レオロジー特性の実験データにモデル式を最適フィットさせることで、緩和スペクトルと微分型および積分型粘弾性モデルの非線形パラメーターを決定する完全非線形回帰プログラムを開発した。最小2乗解法はLevenberg-Marquardt法に基づいている。線形粘弾性の動的データから最適な緩和スペクトルを決定するプログラムには、初期値の再設定を計算中に自動で行う機能が含まれている。このプログラムをいくつかの高分子溶融体の実験データに対して適用したところ、

よいフィッティングが得られた。この新しいプログラムは、その信頼性が確かめられたと同時に手入力による初期値の再設定の煩雑さを軽減することが確認された。また、非線形パラメーターを決定するプログラムを Phan Thien-Tanner (PTT), Larson, Giesekus

および K-BKZ モデルに対して開発し、せん断流動特性（せん断粘度および第一法線応力差）の実験値からのパラメーターの決定をいくつかの高分子溶融体に対して行った。すべてのモデルで、その最適フィット曲線は実験のせん断速度範囲で実験値によく一致した。