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Rheological Characterization of Polymer Solutions and Melts with an Integral Constitutive Equation

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A full nonlinear regression program has been developed in order to determine the appropriate relaxation spectrum and set of material constants for a constitutive equation which can give the best fit to experimental data and predictions for a series of rheological material functions. The constitutive model used is an integral equation of the K-BKZ type suitable for polymer solutions and melts. Available experimental data for determination of the material parameters of the model were dynamic data (storage and loss modulus), steady shear flow data (shear viscosity and first normal stress difference), and steady elongational flow data (uniaxial, planar and biaxial elongational viscosities). The material parameters were determined by a nonlinear least-squares procedure based on the Levenberg-Marquardt method. The program was tested against experimental data of material functions for several polymer solutions and melts. A good fit was obtained between predictions and experimental data. Furthermore, predictions have also been made for unsteady (transient) material functions in shear and elongational flows using the parameters by best-fitting the model, and comparisons have been made with experimental data whenever available. In all cases, the predicted values were in good agreement with the experimental ones.

KEY WORDS Rheology, polymer melts, K-BKZ constitutive equation

INTRODUCTION

In recent years numerical simulations of polymer fluid flows using an integral constitutive equation of the K-BKZ type [1] have made considerable progress with remarkable achievements [2]. In these simulations it is necessary to know first the rheological behavior of the polymeric liquid by determining a discrete relaxation spectrum and other parameters appearing in the constitutive model. In general, these parameters are determined so as to fit available experimental data of some

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known rheological material functions. An accurate rheological characterization is thus very important to obtain reliable simulation results.

The original seminal paper by Papanastasiou *et al.* [1] addressed the issue of determining the parameters appearing in that model. A nonlinear regression analysis had then been used and it was shown how experimental data are best-fitted to obtain the material constants. In that work, it was pointed out that the regression problem is an especially difficult one, and that no unique solution is guaranteed. Since then several other researchers in the field have addressed the problem of determining the linear viscoelastic relaxation spectrum. A linear regression analysis has been used [3] for determining the relaxation times λ_k , and relaxation modulus coefficients a_k from linear viscoelastic data, such as small-amplitude stress relaxation or sinusoidal oscillation. This method is based on linear least-squares procedures, and the λ_k and a_k values are determined for a given number N of relaxation modes by fitting the model to experimental data. Another method to determine the relaxation spectrum is to employ a nonlinear regression analysis as proposed by Baumgaertel and Winter [4]. In this method the values of λ_k and a_k as well as N are determined as adjustable parameters, and a more accurate fitting can be obtained than that from linear regression. However, few details are given in ref. 4 regarding its successful accomplishment. Furthermore, that analysis does not address the determination of parameters associated with the nonlinear behavior of polymeric liquids in strong shear and elongation flows.

In the present study we have developed a full nonlinear regression program based on the Levenberg-Marquardt method in order to determine the nonlinear parameters of the K-BKZ model as well as the relaxation spectrum which can give the best fit to experimental data and predictions for a series of rheological material functions. This program was tested against experimental data of material functions in both steady and unsteady (transient) flows for several well-characterized polymer solutions and melts.

CONSTITUTIVE EQUATION AND MATERIAL FUNCTIONS

The constitutive equation for polymer solutions and melts used in this study is an integral model of the K-BKZ type proposed by Papanastasiou *et al.* [1] and is written as

$$\tau = 2\eta_{\text{solv}} D + \int_{-\infty}^t \sum_{k=1}^N \frac{a_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k}\right) H(I_{c^{-1}}, II_{c^{-1}}) C_t^{-1}(t') dt' \quad (1)$$

where τ is the stress tensor, λ_k and a_k are the relaxation times and relaxation modulus coefficients, N is the number of relaxation times, C_t^{-1} is the Finger strain tensor, and $I_{c^{-1}}$, $II_{c^{-1}}$ are its first and second invariants; η_{solv} is the solvent viscosity for the polymer solutions and D is the rate-of-deformation tensor. The first term in the right hand side of Equation (1) is omitted for polymer melts. H is the strain

memory function and we use the following equation proposed by Papanastasiou et al. [1]

$$H(I_{C^{-1}}, II_{C^{-1}}) = \frac{\alpha}{(\alpha - 3) + \beta I_{C^{-1}} + (1 - \beta) II_{C^{-1}}} \quad (2)$$

where α and β are nonlinear model constants to be determined from strong shear and elongational flow data, respectively.

As rheological experimental data necessary for the determination of material parameters, we have used a series of data available in the literature for well-characterized polymer solutions and melts. These are dynamic data (the storage modulus G' and loss modulus G''), shear flow data (the shear viscosity η_s and the first normal stress difference N_1) and elongational data (the uniaxial η_E , planar η_p and biaxial η_B elongational viscosities). The linear viscoelastic storage and loss modulus G' and G'' can be expressed as follows at a frequency ω :

$$G'(\omega) = \sum_{k=1}^N a_k \frac{(\omega\lambda_k)^2}{1 + (\omega\lambda_k)^2} \quad (3)$$

$$G''(\omega) = \sum_{k=1}^N a_k \frac{\omega\lambda_k}{1 + (\omega\lambda_k)^2} \quad (4)$$

These functions are independent of the strain memory function, that is, the type of constitutive model, and only λ_k and a_k values can be determined from these data.

However, material functions are dependent on the strain memory function H under large deformations. In *shear flow*, Equation (2) can be rewritten as follows:

$$H(I_{C^{-1}}, II_{C^{-1}}) = \frac{\alpha}{\alpha + \gamma^2} \quad (5)$$

where γ is the shear strain. The material functions in shear flow are dependent on α but not β . In the three kinds of elongational flows mentioned above, Equation (2) can be represented as follows, respectively:

Uniaxial elongation:

$$H(I_{C^{-1}}, II_{C^{-1}}) = \frac{\alpha}{(\alpha - 3) + \beta(e^{2\varepsilon} + 2e^{-\varepsilon}) + (1 - \beta)(e^{-2\varepsilon} + 2e^{\varepsilon})} \quad (6)$$

Planar elongation:

$$H(I_{C^{-1}}, II_{C^{-1}}) = \frac{\alpha}{(\alpha - 3) + e^{2\varepsilon} + e^{-2\varepsilon} + 1} \quad (7)$$

Biaxial elongation:

$$H(I_{C^{-1}}, II_{C^{-1}}) = \frac{\alpha}{(\alpha - 3) + \beta(2e^{2\varepsilon} + e^{-4\varepsilon}) + (1 - \beta)(2e^{-2\varepsilon} + e^{4\varepsilon})} \quad (8)$$

where ε is the elongational strain. H is dependent on both α and β in uniaxial and biaxial elongations but only on α in planar elongation.

Considerable success in modeling the material functions in shear and elongational flows of typical polymeric fluids has been achieved with the K-BKZ model described above [1]. It has often proved insufficient, however, to characterize accurately several polymer melts and solutions with only α and β as the nonlinear model parameters. Luo and Tanners [5] used multiple β_k in order to better fit elongational data of an LDPE melt. Therefore we have used the model in its most general form with multiple nonlinear parameters, α_k and β_k , corresponding to each relaxation mode for these materials. Under these conditions, H in this model can be expressed as:

$$H(I_{C^{-1}}, II_{C^{-1}}) = \frac{\alpha_k}{(\alpha_k - 3) + \beta_k I_{C^{-1}} + (1 - \beta_k) II_{C^{-1}}} \quad (9)$$

PROCEDURE OF NONLINEAR REGRESSION

A full nonlinear regression analysis is used to determine the material parameters of the constitutive model so as to minimize the error between the predicted values of material functions (with the parameters to be determined) and the experimental data in an average sense. To do this, rheological material functions used for the determination of material parameters are the storage and loss modulus, G' , G'' , the shear viscosity η_s , the first normal stress difference N_1 and the uniaxial η_E , planar η_p and biaxial η_B elongational viscosities. The adjustable parameters are N , λ_k and a_k , α (or α_k) and β (or β_k), that is,

$$\sum_{i=1}^M \left(\frac{[F_i(N, \lambda_k, a_k, \alpha, \beta)]_{pre} - [F_i]_{exp}}{[F_i]_{exp}} \right)^2 = \min \quad (10)$$

where F_i denotes the material functions, G' , G'' , η_s , N_1 , η_E , η_p and η_B while M is the number of experimental data. The subscripts *pre* and *exp* represent the predicted and experimental values, respectively.

TABLE I

Determination of material parameters for fitting experimental data of a S-PDMS (polydimethylsiloxane) melt given by Papanastasiou *et al.*[1]. ($\alpha = 2.78$, $\beta = 0.99$)

k	1	2	3	4	5	6
λ_k (s)	9.19×10^{-4}	1.46×10^{-2}	1.40×10^{-1}	$1.51 \times 10^{+0}$	$1.46 \times 10^{+1}$	$1.60 \times 10^{+2}$
a_k (Pa.s)	$1.17 \times 10^{+5}$	$5.93 \times 10^{+4}$	$2.68 \times 10^{+4}$	$6.91 \times 10^{+3}$	$7.93 \times 10^{+2}$	$6.84 \times 10^{+1}$

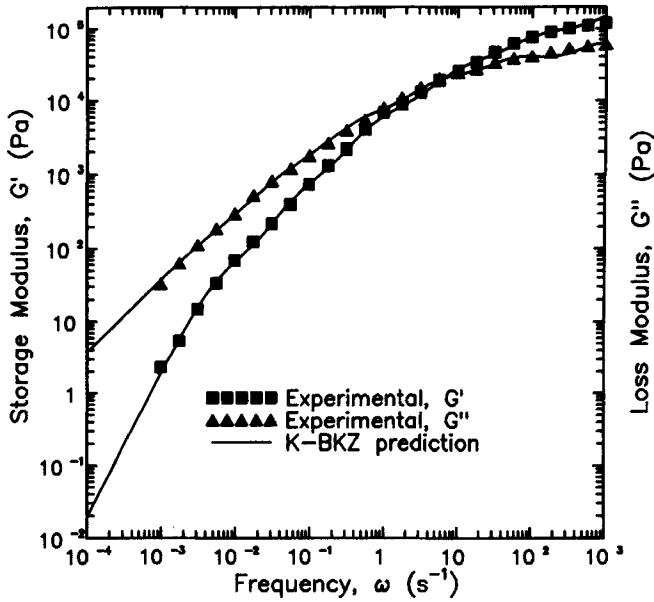


FIGURE 1 Prediction of storage and loss modulus for a S-PDMS (polydimethylsiloxane) melt. Experimental data are given by Papanastasiou et al.[1]. Material parameters are given in Table I.

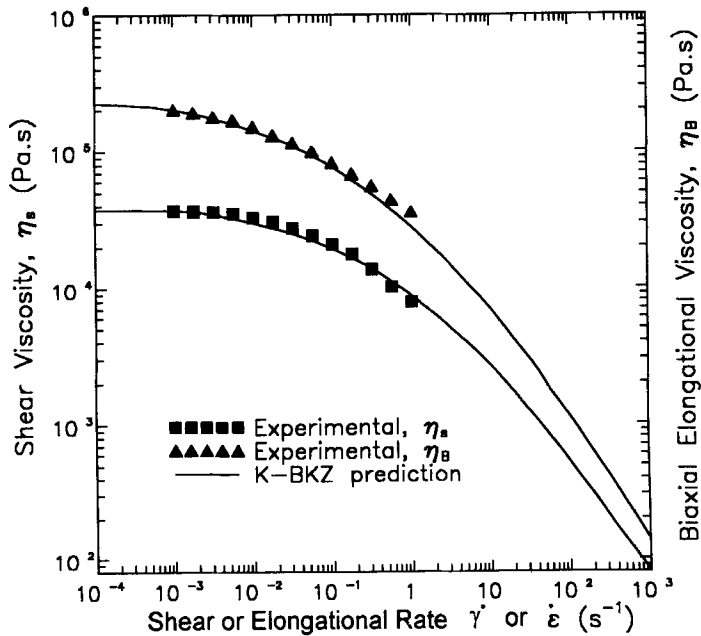


FIGURE 2 Prediction of steady shear and biaxial elongational viscosities for a S-PDMS (polydimethylsiloxane) melt. Experimental data are given by Papanastasiou et al.[1]. Material parameters are given in Table I.

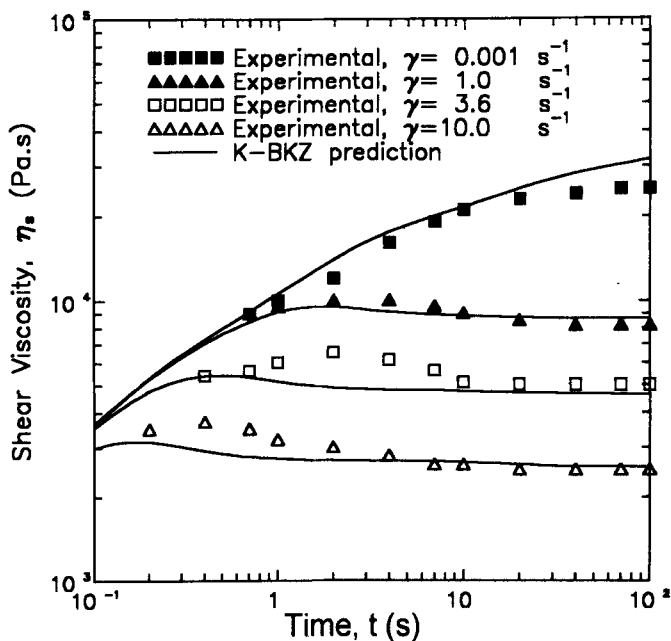


FIGURE 3 Prediction of unsteady shear viscosity after start-up of shearing under constant shear rate for a S-PDMS (polydimethylsiloxane) melt. Experimental data are given by Papanastasiou *et al.*[1]. Material parameters are given in Table I.

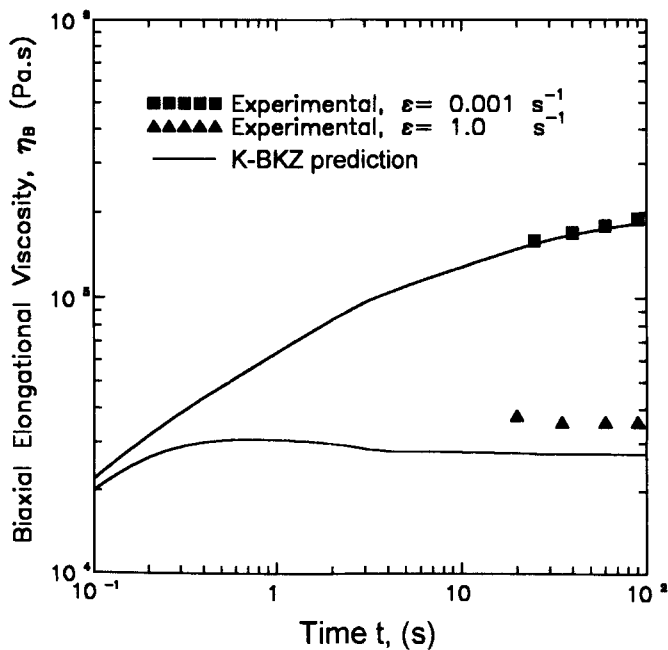


FIGURE 4 Prediction of unsteady biaxial elongational viscosity after start-up of elongation under constant elongational rate for a S-PDMS (polydimethylsiloxane) melt. Experimental data are given by Papanastasiou *et al.*[1]. Material parameters are given in Table I.

The procedure is as follows: the initial guesses of λ_k are chosen for each of eight decades from 10^{-4} to 10^{+3} s (say $N = 8$). When dynamic data are available, we find the a_k values by a linear regression analysis. The so-found a_k values are then used together with the λ_k values as initial guesses for a full nonlinear regression analysis. If there are no dynamic data available, we assume the initial guesses of all parameters except N . Then Equation (10) is solved by a least-squares procedure based on the Levenberg-Marquardt method, [6] and the values of λ_k , a_k , α (or α_k) and β (or β_k) are obtained. When the available data do not cover the whole range corresponding to the initial guesses of λ_k or the material does not have a relaxation spectrum over the range of the initial guesses, we may omit the corresponding relaxation modes (decrease N) and solve Equation (10) again.

In this study, we developed two kinds of programs to solve Equation (1). One program determines simultaneously all parameters except for N . The other program works as follows: the λ_k and a_k values are determined from dynamic data first. Next α (or α_k) is determined from shear flow data using the so-found λ_k and a_k (fixed) and finally β (or β_k) is determined from elongational flow data. The solutions by the nonlinear regression analysis are strongly dependent on the initial guesses. If we use the K-BKZ model with multiple α_k and β_k by the first program (i.e., simultaneous determination), we have to set $4N$ initial guesses. The second program of a step-by-step procedure is more suitable for those cases.

RESULTS AND DISCUSSION

The programs developed for the nonlinear regression analysis were tested against experimental data for several polymer melts and solutions.

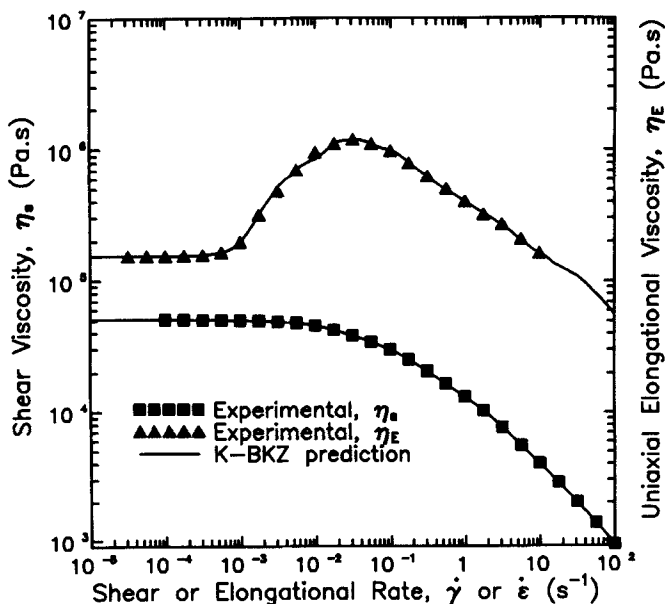


FIGURE 5 Prediction of steady shear and uniaxial elongational viscosities for a low-density polyethylene (LDPE-IUPAC A) melt. Experimental data are given by Meissner [7]. Material parameters are given in Table II.

TABLE II

Determination of material parameters for fitting experimental data of a low-density polyethylene (LDPE-IUPAC A) melt given by Meissner [7]

k	1	2	3	4	5	6	7	8
λ_k (s)	1.00×10^{-4}	1.00×10^{-3}	1.00×10^{-2}	1.00×10^{-1}	$1.00 \times 10^{+0}$	$1.00 \times 10^{+1}$	$1.00 \times 10^{+2}$	$1.00 \times 10^{+3}$
a_k (Pa.s)	$1.29 \times 10^{+5}$	$9.48 \times 10^{+4}$	$5.86 \times 10^{+4}$	$2.67 \times 10^{+4}$	$9.80 \times 10^{+3}$	$1.89 \times 10^{+3}$	$1.80 \times 10^{+2}$	$1.00 \times 10^{+0}$
α_k	14.4	14.4	14.4	14.4	14.4	14.4	14.4	14.4
β_k	0.200	0.200	0.200	0.056	0.130	0.134	0.030	0.002

Polymer Melts

First we investigated data for a polydimethylsiloxane (S-PDMS) melt. The material parameters were determined using the experimental data for the storage and loss modulus, the steady shear viscosity, and the steady biaxial elongational viscosity given by Papanastasiou et al. [1]. Equation (2) was used as the strain memory function. The results by the two different procedure regression programs, that is, the simultaneous and the step-by-step determination programs, were almost identical with each other. The material parameters so determined are given in Table I. Figures 1 and 2 show the comparison of storage and loss modulus, and steady shear and biaxial elongational viscosities between the experimental data and the predicted values with these parameters, respectively. The predicted values show a remarkable agreement with the experimental data for all cases. We have also predicted unsteady (transient) material functions using these parameters. Figure 3 shows the time dependence of unsteady shear viscosity after start-up of shearing under a constant shear rate, while Figure 4 shows unsteady biaxial elongational viscosity after start-up of elongation under a constant elongational rate. Both results agree very well with the experimental data. From these results the reliability of our nonlinear regression program was confirmed.

Figure 5 shows the experimental data of steady shear and uniaxial elongational viscosities for low-density polyethylene (IUPAC-LDPE A) melt given by Meissner [7] and the predictions obtained by the nonlinear regression. We used the set of relaxation spectrum obtained by Laun, [8] and determined the nonlinear model parameters from those experimental data. A sufficiently good fit to the experimental data for the uniaxial elongational viscosity, which showed strongly strain-thick-

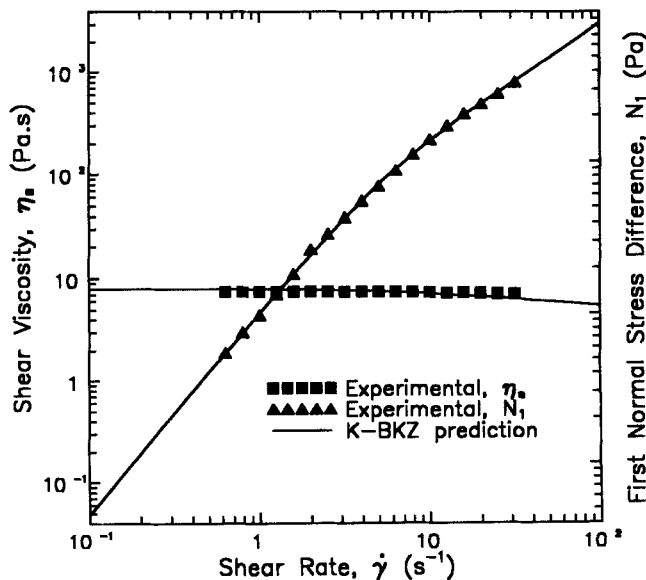


FIGURE 6 Prediction of steady shear viscosity and first normal stress difference for a glucose/separan solution (0.02 wt% separan/3.8 wt% water in glucose). Experimental data are given by Chhabra et al.[9]. Material parameters are given in Table III.

TABLE III
 Determination of material parameters for fitting experimental data of a glucose/separan solution (0.02 wt% separan/3.8 wt% water in glucose)*

k	1	2	3	4
$\lambda_k (s)$	1.02×10^{-2}	9.78×10^{-2}	$1.01 \times 10^{+0}$	$4.47 \times 10^{+0}$
$a_k (Pa.s)$	$4.22 \times 10^{+2}$	$1.71 \times 10^{+1}$	$1.89 \times 10^{+0}$	1.51×10^{-2}

* Given by Chhabra et al.[9] ($\eta_{\text{gov}} = 0 \text{ Pa.s}$, $\alpha = 516.0$)

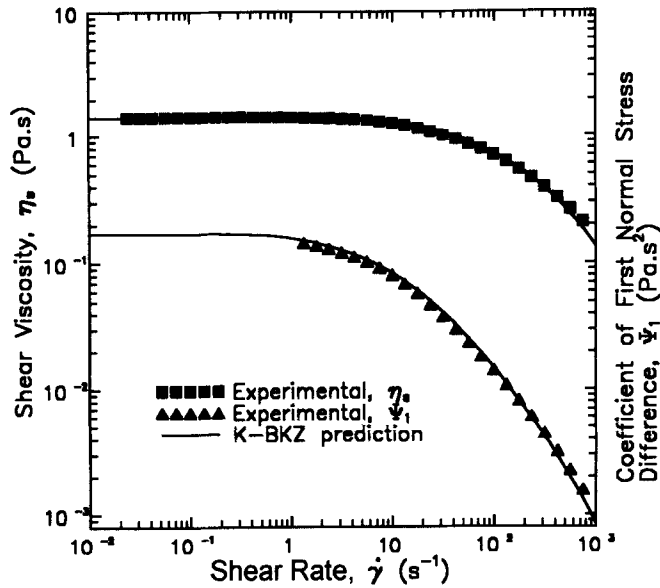


FIGURE 7 Prediction of steady shear viscosity and first normal stress coefficient for a PIB/C14 (5.0 wt% polyisobutylene/tetradecane) solution. Experimental data are given by Quinzani et al. [10]. Material parameters are given in Table IV.

ening behavior, could not be achieved with the strain memory function of Equation (2). Therefore, we have used multiple α_k and β_k [i.e., Equation (9)]. The determined material parameters are shown in Table II. The predictions by the K-BKZ model with multiple α_k and β_k succeed very well as shown in Figure 5. It is thus seen that this model is useful and practical for polymer melts, such as LDPE with the most complex and highly elastic behavior.

Polymer Solutions

Figure 6 shows the results for a glucose/separan solution (0.02 wt% separan/3.8 wt% water in glucose). The relaxation spectrum parameters and nonlinear model parameters α were determined from experimental data of steady shear viscosity and first normal stress difference given by Chhabra et al. [9]. The parameter β cannot be determined because these material functions are independent of β . The determined parameters are given in Table III.

Figure 7 shows the results for a PIB/C14 (5.0 wt% polyisobutylene/tetradecane) solution. The material parameters except for β were determined from experimental data of steady shear viscosity and first normal stress coefficient given by Quinzani et al. [10]. We have used the values given in the literature [10] for the relaxation spectrum, which were obtained from dynamic data, and have thus determined the value of α . The determined parameters are given in Table IV. The predictions by the K-BKZ model with the strain memory function of Equation (2) are sufficient to obtain a good fit for the above polymer solutions whose material functions change monotonically.

However, some polymer solutions show a more complex flow behavior. Figure 8 shows the steady shear viscosity and first normal stress coefficient for a PIB/PB/C14

TABLE IV
 Determination of material parameters for fitting experimental data of a PIB/C14 (5.0 wt% polyisobutylene/tetradecane) solution*

k	1	2	3	4
$\lambda_k(\text{s})$	5.90×10^{-3}	3.89×10^{-2}	1.40×10^{-1}	6.86×10^{-1}
$a_k(\text{Pa}\cdot\text{s})$	$9.92 \times 10^{+1}$	$1.46 \times 10^{+1}$	$1.67 \times 10^{+0}$	5.84×10^{-2}

* Given by Quinzani et al.[10] ($\eta_{\text{poly}} = 0.002 \text{ Pa}\cdot\text{s}$, $\alpha = 13.3$)

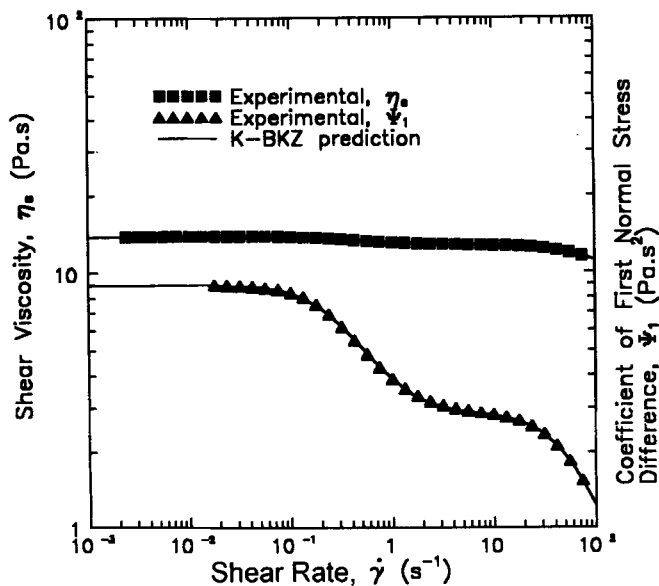


FIGURE 8 Prediction of steady shear viscosity and first normal stress coefficient for a PIB/PB/C14 (0.31 wt% polyisobutylene/polybutene/tetradecane) solution. Experimental data are given by Quinzani et al.[10]. Material parameters are given in Table V.

(0.31 wt% polyisobutylene/polybutene/tetradecane) solution. Experimental data are given by Quinzani et al. [10]. The first normal stress coefficient shows two plateaus in the low and mid-shear rate regions. The K-BKZ model with the strain memory function of Equation (2) cannot predict complex material functions. We have determined a set of multiple nonlinear parameters α_k in Equation (9) using the relaxation spectrum given in the literature [10]. The list of these parameters and predictions of material functions are shown in Table V and Figure 8. The predictions agree well with the experimental data despite such a complex behavior.

CONCLUSIONS

We have developed a full nonlinear regression program based on the Levenberg-Marquardt method in order to determine the appropriate set of material parameters of the K-BKZ model for polymer melts and solutions which can give the best fit to experimental data and predict a series of rheological material functions. This program was tested against experimental data of material functions in both steady and unsteady (transient) states for several polymer melts and solutions. The predictions of material functions using the determined material parameters by the nonlinear regression analysis agreed well with the experimental data. We have also found that the K-BKZ model with multiple nonlinear model parameters was useful and practical for both polymer melts and solutions which exhibit a rather complex character (lack of monotonicity) of their material functions.

TABLE V

Determination of material parameters for fitting experimental data for a PIB/PB/C14 (0.31 wt% polyisobutylene/polybutene/tetradecane) solution*

k	1	2	3	4
λ_k (s)	9.80×10^{-3}	1.09×10^{-1}	7.36×10^{-1}	$2.76 \times 10^{+0}$
a_k (Pa.s)	$1.24 \times 10^{+2}$	$1.52 \times 10^{+1}$	$2.27 \times 10^{+0}$	4.02×10^{-1}
α_k	$1.89 \times 10^{+1}$	$5.87 \times 10^{+2}$	$2.42 \times 10^{+4}$	$6.34 \times 10^{+0}$

* Given by Quinzani et al.[10] ($\eta_{\text{sol}} = 8.118$ Pa.s)

Acknowledgments

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