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CHARACTERIZATIONS ON THE THIXOTROPY-LOOP TESTS USING UCM MODEL WITH A RATE-TYPE KINETIC EQUATION*

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Abstract The theoretical characterizations on the triangular-form thixotropy-loop tests of an LDPE melt (PE-FSB-23D022/Q200) were conducted in the present paper by using a new thixotropy model, which is constituted by the upper convected Maxwell model and a rate-type kinetic equation. The new thixotropic Maxwell model can partially describe well three reported thixotropy-loop experiments by comparison with the previous calculations of the variant form of the thixotropy-type Huang model. It is noted that the stress deviations between the experiments and the predictions of the new thixotropic Maxwell model are much slighter than those deviations obtained by using the variant Huang model at the same condition, although both models include five parameters. The constitution of the new thixotropic Maxwell model is more reasonable than that of the variant Huang model.

Keywords: Thixotropy-loop tests; Theoretical characterization; Thixotropy models.

INTRODUCTION

Many constitutive equations usually used to describe the relationship between the stress and the rate of strain or the strain for non-Newtonian fluid have been proposed in the past six decades[1]. All the constitutive equations ultimately have to be tested against experimental data to validate their capability, and the rheometric experiments and the benchmark flow problems are the two approaches commonly used for this purpose. The former method is a basic and simple method, which has been employed by Tanner[2] to evaluate the abilities of Oldroyd-B model, PTT model, Giesekus model and KBKZ model, *etc.* In the present paper, the rheometric-experiments method was adopted to test the effects of two constitutive models on characterizing the time-dependent viscoelasticity.

The characterization on the time-dependent viscoelasticity for polymer solution and melt is still an important topic in the field of rheology[3, 4], because the time-dependent viscoelastic property of polymer liquids indeed has an apparent influence on some industries' processes, such as painting, coating and polymer processing. Recently, the triangular thixotropy-loop tests[5] of an LDPE (PE-FSB-23D022/Q200) melt were carried out and characterized by using a simple time-dependent thixotropy equation, which was proposed by Fang *et al.*[6] on the basis of the well-known thixotropy equation of Huang[7]. The thixotropy equation given by Fang *et al.* is a simple summation of viscous term, elastic term and thixotropy term, which can be used to describe the thixotropy-loop tests well in the regions of the shear-rate up and the shear-rate down. Later, the authors[8] have attempted to use the traditional KBKZ-type viscoelastic model to describe the reported triangular thixotropy-loop tests, and the results showed that KBKZ model seems not well in some descriptions of the tests. So, it needs to add the thixotropy effect in the traditional viscoelastic model in order to improve the characterization on the thixotropic time-dependent viscoelastic behavior of polymer melts.

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In the recent reviews on the theoretical characterization of thixotropy phenomenon, given by Barnes[3] in 1997 and Mujumdar *et al.*[4] in 2002, there were a few thixotropy constitutive equations available for characterizing the thixotropic behaviors of viscoelastic fluid, in which the thixotropy model based on the viscoelastic Maxwell model has attracted more attention. In the present paper, the Maxwell model combined with a rate-type kinetic equation was proposed to describe the reported thixotropy-loop tests, and at the same time, the predictions on the thixotropy-loop tests by the new viscoelastic thixotropic model given here will be compared with the results predicted by the model given by Fang *et al.* The common features of both models include two points. One is that both models contain the same number of parameters, and another is that both models adopt the rate-type kinetic equation. The main difference of the two models is at the understanding on the thixotropy phenomenon of viscoelastic fluid. So, the subject of the paper is to examine the effect of the formation of theoretical equation on the characterization of thixotropy-loop behaviors of viscoelastic fluid, especially the effect of the combination of Maxwell model and rate-type kinetic equation.

MATHEMATICAL MODEL

Marrucci and co-workers[9] (1973) introduced a thixotropy model formed by a combination of the Maxwell model and a stress-type kinetic equation, and then, such stress-type kinetic equation has been used and introduced in the viscoelastic-thixotropy equations[3, 4, 10, 11] based on the Maxwell model. In fact, the rate-type kinetic equation were also often used in the thixotropy theories[3, 4] for viscous system. The stress-type kinetic equation means that the change of the structural variable is related with the change of first or second invariant of stress, while the rate-type kinetic equation means that the change of the structural variable is related with the change of shear rate. In the works of describing the thixotropic behavior of viscoelastic fluid, there is a little application[4, 6] for the rate-type kinetic equation. So, the author gives a try here by using a new combination of the Maxwell model and a rate-type kinetic equation to characterize the time-dependent thixotropy loop test, in which the kinetic equation is selected in terms of the introduction of Barnes[3] on the description of thixotropy. The new thixotropy equation is written as follows:

$$\lambda \overset{\nabla}{\boldsymbol{\tau}} + \boldsymbol{\tau} = 2\eta \boldsymbol{d} \tag{1a}$$

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = k_1(1-\xi) - k_2\xi\dot{\gamma}^m \tag{1b}$$

in which

$$\overset{\nabla}{\boldsymbol{\tau}} = \frac{\partial \boldsymbol{\tau}}{\partial t} + \boldsymbol{v}\cdot\nabla\boldsymbol{\tau} - \nabla^{\mathrm{T}}\boldsymbol{v}\cdot\boldsymbol{\tau} - \boldsymbol{\tau}\cdot\nabla\boldsymbol{v} \tag{2}$$

$$\eta = \lambda \cdot G \tag{3}$$

$$\lambda = \lambda_0 \xi^{1.4} \tag{4}$$

$$G = G_0 \xi \tag{5}$$

$$\boldsymbol{d} = \frac{1}{2}\left[\nabla \boldsymbol{v} + \nabla^{\mathrm{T}} \boldsymbol{v}\right] \tag{6}$$

where $\boldsymbol{\tau}$ is the viscoelastic extra stress tensor, $\overset{\nabla}{\boldsymbol{\tau}}$ is the upper convected derivative of stress tensor, λ and G are the relaxation time and the relaxation modulus, respectively, η is the shear viscosity, ξ is a scalar structural variable, λ_0 and G_0 are the equilibrium values of λ and G, respectively, k_1, k_2, and m are also the parameters of the new thixotropic Maxwell model, $\boldsymbol{d}$ is the rate of deformation tensor, $\boldsymbol{v}$ is the velocity vector, $\nabla\boldsymbol{v}$ is the velocity gradient tensor, $\nabla^{\mathrm{T}}\boldsymbol{v}$ is the transpose of the velocity gradient tensor. The forms of Eqs. (4) and (5) were used in the works of Marrucci *et al.*[9, 10] and also introduced in the review of Barnes[3].

Both λ and G are the functions of the structural variable ξ, which result in the change of viscoelastic stress with the structural variable. Equation (1b) is the so-called kinetic equation depending on the shear rate. The first term on the righthand side of Eq. (1b) represents the process of structural build-up due to the Brownian motion (by constant k_1), while the second term indicates the structural breakdown process due to the shear rate (by constants k_2 and m). Barnes[3] once introduced a general rate-type kinetic equation in the indirect microstructural theories describing the thixotropy phenomenon, and the difference between the general rate-type kinetic equation and the used kinetic equation is at the power of $(1-\xi)$, which is allowed to be non-unitary values for the general rate-type kinetic equation. The used kinetic equation is a special case of the general rate-type kinetic model, as introduced by Barnes[3]. The new Maxwell-type thixotropy model (named simply as MK model here) contains five parameters, *i.e.* k_1, k_2, m, λ_0 and G_0.

The thixotropic constitutive equation given by Fang *et al.*[5, 6] is as follows:

$$\tau_{12} = \eta\dot{\gamma} + G_{12}\gamma + \beta\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{7}$$

where τ_{12} is the shear stress, $\dot{\gamma}$ is the shear rate, G_{12} is the elastic modulus, γ is the elastic deformation, β is the thixotropic coefficient, ξ is the molecular arrangement parameter of the fluid defined in the original paper[7], which can also be explained as the structure parameter reflecting the changing of microstructure according to the indirect microstructural approach[3, 4]. ξ satisfies the following equation,

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -C_1\xi\dot{\gamma}^n \tag{8}$$

where C_1 and n are the constants.

In terms of Eqs. (7) and (8), the following equation is obtained,

$$\tau_{12} = \eta\dot{\gamma} + G_{12}\int_0^t \dot{\gamma}\,\mathrm{d}t + C_1 B\dot{\gamma}^n \exp\left(-C_1\int_0^t \dot{\gamma}^n\,\mathrm{d}t\right) \tag{9}$$

where η, G_{12}, B, C_1 and n are the five parameters of the model of Fang *et al.*, and the five parameters were obtained in the previous papers[5, 6] by using an optimization method to fit the thixotropy loop experiments.

The basic characteristic of the Huang model[7] is that the effect of thixotropy is an independent characteristic of fluid, parallel to the viscous property of fluid. The model given by Fang *et al.*[6] adopts the same idea, and so, we refer to their model as the variant of Huang model (named simply as VHuang model here). In addition, the difference between the MK model and the VHuang model on the kinetic equation is that MK model includes both the breakdown and the buildup process of structure, while VHuang model only contains the breakdown process according to the thixotropy theory[3, 4].

THEORETICAL DESCRIPTIONS ON THIXOTROPY LOOP TESTS

The thixotropy loop test is a kind of typical experimental technique usually used to study the time-dependent viscous or viscoelastic characteristic. In the triangular-form thixotropy loop mode, the shear rate rises linearly from zero to the maximum and then drops linearly to zero, which is expressed as follows:

$$\dot{\gamma} = a_0 t \qquad 0 \le t \le t_0 \tag{10a}$$

$$\dot{\gamma} = a_0(2t_0 - t) \qquad t_0 \le t \le 2t_0 \tag{10b}$$

where t is a time variable, t_0 is a time interval for the raising time of shear rate from zero to the maximum, and also equals to the falling time of shear rate, a_0 is a constant change rate of shear rate, which is defined as

$$a_0 = \frac{\dot{\gamma}_0}{t_0} \tag{11}$$

where $\dot{\gamma}_0$ is the maximum shear rate. Figure 1 shows the schematic of the triangular-type thixotropy loop mode.

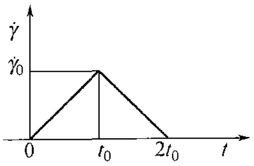

Fig. 1 Schematic of the triangular-type thixotropy loop test

For the transient simple shear flow, the new thixotropic Maxwell model (MK model) can be expressed as the following scalar equations:

$$\frac{\partial \tau_{11}}{\partial t} - 2\tau_{12}\dot{\gamma} + \frac{\tau_{11}}{\lambda_0 \xi^{1.4}} = 0 \tag{12a}$$

$$\frac{\partial \tau_{12}}{\partial t} - \tau_{22}\dot{\gamma} + \frac{\tau_{12}}{\lambda_0 \xi^{1.4}} = G_0 \xi \dot{\gamma} \tag{12b}$$

$$\frac{\partial \tau_{22}}{\partial t} + \frac{\tau_{22}}{\lambda_0 \xi^{1.4}} = 0 \tag{12c}$$

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = k_1(1-\xi) - k_2 \xi \dot{\gamma}^m \tag{12d}$$

with the initial condition,

$$t = 0, \qquad \tau_{11} = \tau_{12} = \tau_{22} = 0, \qquad \xi = 1 \tag{12e}$$

The stresses in Eq. (12) can be solved numerically by using the fourth order Runge–Kutta method in terms of the given flow process, *i.e.* Eq. (10), and then the nonlinear programming method can be employed to obtain the values of parameters of the MK model by fitting the thixotropy loop test.

Three triangular thixotropy loop tests at the maximum shear rate of 5 s^{-1} for the LDPE melt (PE-FSB-23D022/Q200) at 150°C have been given recently[5] with the time interval t_0 of 1, 10 and 100 s, respectively, together with the description of the VHuang model. The values of the parameters in the MK model obtained here by fitting the thixotropy loop tests are listed in Table 1, while the values of the parameters in the VHuang model are listed in Table 2, which were reported in the previous paper[5] by fitting the same three tests. The expressions of stresses of the VHuang equation for the triangular thixotropy loop test can be found in the references[5, 6]. In Tables 1 and 2, the symbols of r5-t1 denote the thixotropy loop tests with the maximum shear rate of 5 s^{-1} and t_0 = 1 s, and the other two symbols r5-t10 and r5-t100 mean that the time interval t_0 of the two tests are equal to 10 and 100 s, respectively.

Table 1. Values of parameters of MK model obtained by fitting the three thixotropy loop tests of the LDPE (Q200)

Symbol of test	Parameters				
	λ_0 (s)	G_0 (Pa)	k_1	k_2 (s^m)	m
r5-t1	1.814	27468.3	0.679	0.720	0.382
r5-t10	1.671	15030.7	0.477	0.172	0.560
r5-t100	2.093	23758.7	1.916	1.714	0.369

Table 2. Values of parameters of VHuang model obtained by fitting the three thixotropy loop tests of the LDPE (Q200)

Symbol of test	Parameters				
	η (Pa • s)	C_1 (s^{n-1})	B (Pa • s)	G_{12} (Pa)	n
r5-t1	4626.9	0	-	3450.313	-
r5-t10	5144.5	7.644×10^{-2}	48371.9	146.255	1.700
r5-t100	4162.8	1.235×10^{-2}	800039.2	9.997	0.843

In Figs. 2–4, the theoretical descriptions of the three thixotropy loop tests by using the new thixotropic Maxwell model (MK model) are shown, together with the experimental data and the fitted curves of VHuang model reported in the previous paper. The arrows in the three figures are used to indicate the evolution process of shearing. We can see from the three figures that the fitted results of MK model show good agreement with the thixotropy-loop tests with the short- and the medium-time shearing process, but show some deviation with the long-time shear test.

Figure 2 presents the experimental and the calculated results of the thixotropy loop test with the maximum shear rate of 5 s^{-1} and t_0 = 1 s, in which the apparent feature of the experiment, *i.e.* the maximum shear stress appears at the rate-down region and not at the maximum shear rate, can be described well by MK model, but cannot be described by VHuang model. Such experimental characteristic is consistent with the stress overshoot behavior of viscoelastic fluid at high shear rate in start-up experiment. So, the constitution of MK model is more suitable than that of VHuang model for characterizing the stress overshoot phenomenon of the viscoelastic LDPE melt.

The calculations of both MK model and VHuang model in Fig. 3 agree well with the thixotropy-loop test with the characteristic time interval t_0 of 10 s. However, for the test with the longest time interval of 100 s shown in Fig. 4, it can be seen that there is an apparent deviation between the experiment and the calculation for MK model, and we cannot obtain better parameters for the MK model to describe the test precisely. In Fig. 4, the experimental stress in the rate-up region at high shear rate is much higher than the stress value in the rate-down region, while the calculated results of MK model in both the rate-up and the rate-down region are almost the same. The fitted result of VHuang model approaches the experimental data more apparently than that of MK model. So, the VHuang model is superior to the MK model in describing the long-time shearing loop.

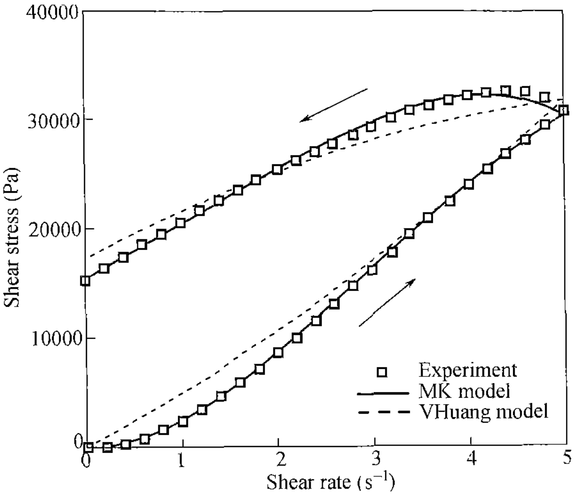

Fig. 2 Description on the thixotropy loop test with $\dot{\gamma}_0$ = 5 s^{-1}, t_0 = 1 s obtained by using MK model, together with the results of VHuang model

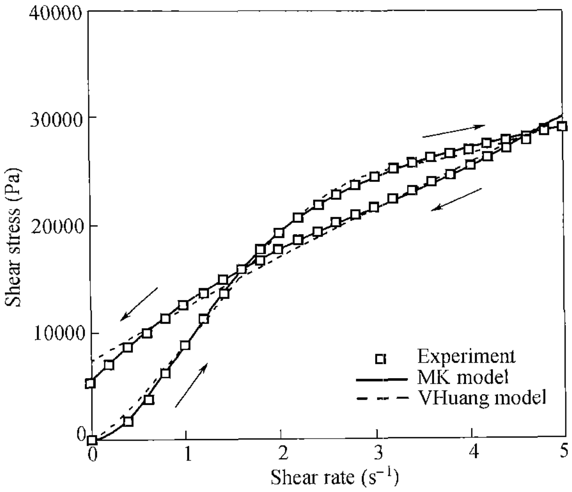

Fig. 3 Description on the thixotropy loop test with $\dot{\gamma}_0$ = 5 s^{-1}, t_0 = 10 s obtained by using MK model, together with the results of VHuang model

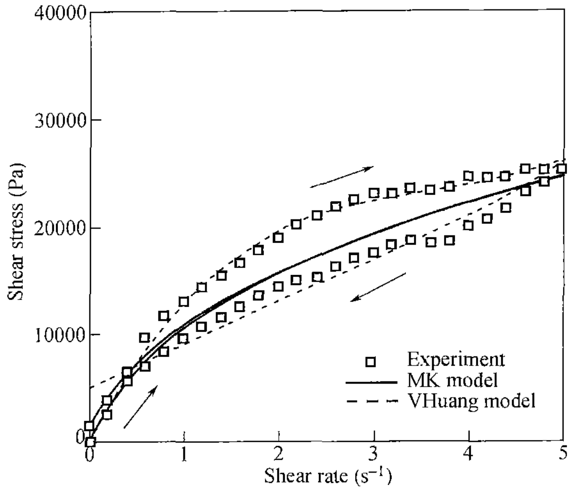

Fig. 4 Description on the thixotropy loop test with $\dot{\gamma}_0 = 5$ s^{-1}, $t_0 = 100$ s obtained by using MK model, together with the results of VHuang model

From Tables 1 and 2, we can notice that each test corresponds to a group of parameters, different with another test's parameters for both models, which can be explained as the presence of some dependence of the models' parameters on the particular flow conditions and at the same time brings an availability problem of the used model. For many sophisticated non-Newtonian flow problems in polymer industry, it is needed to predict them through the theoretical model in order to understand the flow process and adjust the technology. We sometimes cannot predict the whole flow process precisely using the given rheological model for the particular material, but we hope that the theoretical model could be available for more cases, at least qualitatively. So, it is natural to check the prediction capability of the theoretical model. In the following section, we will examine the predictions of the two used models in order to illustrate qualitatively the effects of the constitution of the theoretical models on their prediction capabilities on viscoelasticity.

DISCUSSION ON THE CAPABILITY OF PREDICTION OF THE TWO MODELS

To check the capability of prediction of the two models, the following method was adopted. For a given experiment, the parameters obtained by fitting the other two thixotropy loop tests were used to predict it. Both models employed the same procedure. In Figs. 5–7, the predicted results of the two models are shown simultaneously for the thixotropy loop experiments of r5-t1, r5-t10 and r5-t100, respectively. It is obvious that the prediction of MK model given here is more close to the experimental data than that of VHuang model.

In Fig. 5, the predicted-1 curve for the thixotropy loop experiments with the maximum shear rate of 5 s^{-1} and $t_0 = 1$ s was calculated with the parameters obtained by fitting the thixotropy loop tests with the maximum shear rate of 5 s^{-1} and $t_0 = 10$ s, and the predicted-2 curve was calculated with the parameters obtained by fitting the thixotropy loop tests with the maximum shear rate of 5 s^{-1} and $t_0 = 100$ s. The MK model can predict both the stress overshoot phenomenon of the test and the residual stress qualitatively, while the VHuang model cannot predict these basic characteristics of the test. In addition, the predicted stresses by VHuang model at the higher shear rates are much larger than the experimental data when compared with the results of MK model.

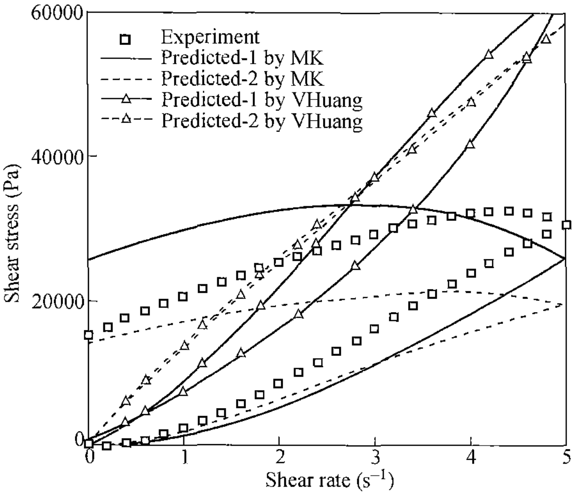

Fig. 5 Prediction on the thixotropy loop test with $\dot{\gamma}_0$ = 5 s^{-1}, t_0 = 1 s

Predicted-1 is obtained with the parameters fitting the loop test with t_0 = 10 s;
Predicted-2 is obtained with the parameters fitting the loop test with t_0 = 100 s

In Fig. 6, the predicted-1 curve for the thixotropy loop tests with t_0 of 10 s is calculated with the parameters obtained by fitting the thixotropy loop tests with t_0 = 1 s, and the predicted-2 curve is calculated with the parameters obtained by fitting the thixotropy loop tests with t_0 = 100 s. We can see from Fig. 6 that part of the predicted-1 curve obtained by VHuang model is too large to be shown in the figure, and even for the predicted-2 curve, the stress deviation between the experiment and the prediction of MK model is much less than that between the experiment and the VHuang's prediction. So, the prediction of MK model for the thixotropy loop tests with t_0 =10 s is also superior to that of VHuang model.

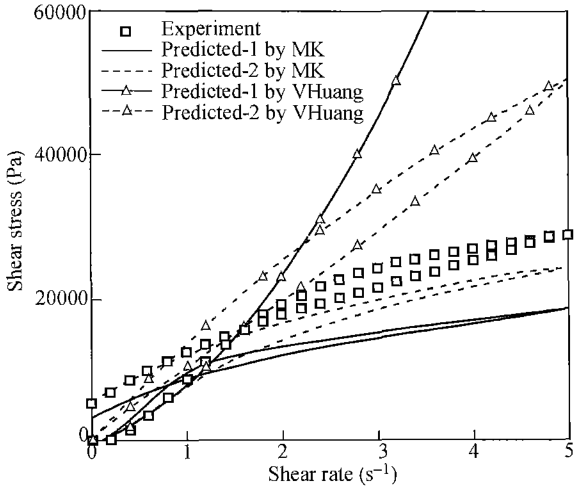

Fig. 6 Prediction on the thixotropy loop test with $\dot{\gamma}_0$ = 5 s^{-1}, t_0 = 10 s

Predicted-1 is obtained with the parameters fitting the loop test with t_0 = 1 s;
Predicted-2 is obtained with the parameters fitting the loop test with t_0 = 100 s

As for the predictions on the thixotropy loop tests with t_0 of 100 s, shown in Fig. 7, we can see that the deviation between the experimental and the VHuang's calculation are much more significant. The predictions of MK model show the superposition of the stress in the rate-down region with that in the rate-up region, similar to the fitted result and approaching the experimental data. However, such stress superposition also indicates that the given thixotropic Maxwell model seems not capable for the better characterization on the long-time shearing loop of viscoelastic fluid, although this model can give the prediction closer to the experiment.

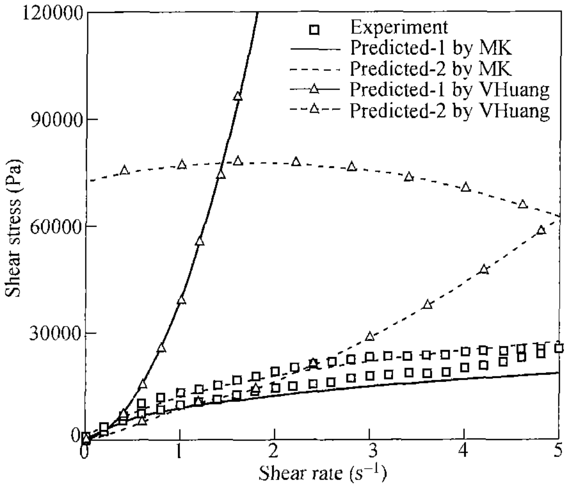

Fig. 7 Prediction on the thixotropy loop test with $\dot{\gamma}_0 = 5\ \mathrm{s}^{-1}$, $t_0 = 100$ s

Predicted-1 is obtained with the parameters fitting the loop test with $t_0 = 1$ s;
Predicted-2 is obtained with the parameters fitting the loop test with $t_0 = 10$ s

If the parameters of the theoretical models reflect the basic viscoelastic characteristic of the fluid, the predicted flow behaviors at the other similar flow condition, for example all the similar triangular shear loop flows here, should be acceptable, although there would be some differences between the predictions and the experiments. From this point, the deviations between the theoretical predictions and the experiments shown in Figs. 5–7 indicate that the capability of MK model is superior to that of VHuang model on the prediction of the thixotropy loop test, although MK model cannot describe the long-time shearing thixotropy loop quantitatively and there also exist some predicted deviations for the MK model.

The constitution of the theoretical model should take the responsibility for its capability of characterizing the rheological properties of viscoelastic fluid. For the VHuang model, its right second term represents the effect of elasticity of viscoelastic fluid, and such an elastic effect will increase unboundedly with the increasing deformation of fluid because there is no damping function in the elastic term and no critical strain. In addition, whether the idea of Huang[9] adopted in the VHuang model, *i.e.* regarding the thixotropy as the independent property of fluid parallel to viscosity, is reasonable still needs more researches to testify. In fact, the effect of thixotropy property is usually represented by the change of viscous and/or elastic properties with time evolution for more cases[3, 4] in the characterization on thixotropy, and this idea is adopted by the MK model. Furthermore, the MK model uses the widely accepted upper convected Maxwell model to reflect the viscoelastic properties, which guarantees the qualitative reasonability of MK model in characterizing the time-dependent rheological property of viscoelastic fluid. Last, the complex of kinetic equation of MK model maybe also enhances some capability of the model. Further work by adopting the combination of the multimode Maxwell model (or the traditional non-linear viscoelastic model) and the kinetic equation to characterize the time-dependent viscoelasticity of the thixotropy loop test is needed in order to develop a much better theoretical model.

CONCLUSIONS

A new thixotropic Maxwell model (MK model) was proposed in the present paper, which was constituted by making the combination of the upper convected Maxwell model and a rate-type kinetic equation. MK model contains five parameters. Three reported triangular-form thixotropy loop tests of the LDPE melt (PE-FSB-23D022/Q200) were described here by using the MK model, and the results show that the calculations of MK model show good agreement with the thixotropy-loop experiments with the short- and the medium-time shearing process, but show some deviation with the long-time shear test.

The fitted results of MK model were compared with those of VHuang model, another simple thixotropy-type model containing five parameters. The comparisons show that MK model can well describe the stress overshoot behavior of the viscoelastic LDPE melt, while VHuang model cannot. There exist some reasonable aspects in the constitution of MK model. But for the long-time thixotropy loop test, the fitted result of VHuang model approaches the experimental stress loop, while the calculated stresses of MK model in both the rate-up and the rate-down region are almost the same at the higher shear rate, different with the experiments.

Three thixotropy loop tests of the LDPE melt were predicted here by using the MK model and the VHuang model simultaneously with the known values of parameters. It is noted that the stress deviations between the experiments and the VHuang's predictions are much larger than those between the experiments and the predictions of MK model at the same condition, which indicate that the constitution of MK model is more reasonable than that of VHuang model, although both models include five parameters. The characteristics of the constitutions of the two models were discussed. It will still be an important and interesting work to look for a powerful thixotropy-type constitutive equation or to develop a new thixotropy-viscoelasticity model in order to improve the theoretical characterization on the time-dependent viscoelastic behavior, especially for the thixotropy loop test with long time shearing.

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