In this paper, the adaptive kinetic network model for describing the rheological properties of structured fluids has been made, which can be used to predict the change of the viscosity and entanglement density for molten low-density polyethylene (LDPE) in parallel superposition vibration force field upon steady shear flow. Recently, our new capillary dynamic rheometer has been developed, which is based on the capillary rheometer with invariable speed, and its equipment's physical model has good agreement with the pulsating extrusion process of round-section die in the condition of electromagnetic dynamic extrusion, and one of the key technologies is that the mechanical vibration force field caused by an electromagnetic field is introduced into the whole plasticating and extrusion process. Through comparing theoretical result with transient experimental data, the theoretical viscosity values and experimental values are reasonably in good agreement, and the changing amplitude of the viscosity increases with the vibration frequency or amplitude increasing, and the effects of vibration frequency or amplitude on the experimental viscosity and the theoretical viscosity are also accordant. Therefore, the precision of our extended kinetic network model for polymer melt in parallel superposition vibration force field upon steady shear flow is reasonable. Lastly, the change of entanglement density for polymer melt in vibration shear field is studied. As a result, when the vibration frequency or amplitude increases, the entanglement density decreases obviously, while the decreasing amplitude of the 1 entanglement density and the change amplitude of the viscosity increase.

ABSTRACT

INTRODUCTION

Polymer melts are often assumed to have an entangled network structure. The flow behaviour of polymer melts seems to be dominated by the entanglement phenomenon. Although the detailed nature of the entanglement is not entirely understood, it is a common assumption to consider the polymer molecules in a melt to be organized in a network of the entanglements that are temporary junctions. These entanglements can slide along the chains, disappear and reform continuously and they can...
translate, rotate and deform with the changing liquid. A kinetic network model has been developed to describe the non-linear rheological behaviour of entangled polymer solutions and melts in either steady state or transient flows. This model is based on the concept of flow-induced structure variation, controlled by the simultaneous existence of entanglement loss and regeneration. Different kinetic rate equations have been proposed by Marrucci model[1], Acieno model[2], Mewis-Cleyn model[3], Liu model[4], Mewis-Denn model[5], etc. In 1956, Lodge[6] proposed rubber-like model, which modelled entanglement network as junctions of constant population. In 1973, Marucci and coworkers[1] modelled as temporary junctions whose kinetics is governed by invariants of the extra stress tensor and thermal motion of the molecules. At the same time, the introduction of structure dependent relaxation spectra and a kinetic rate equation by Marrucci into the upper convected Maxwell model yields a versatile class of structural network models. Recently, Giacomin and Jayaseelan [7] use transient structural network theory with the upper convected Maxwell model to describe the rheological behaviour of several kinds of polyolefin melts in large amplitude oscillatory shear, which is a simple force field. From Giacomin’s research[8], we know that only Mewis-Denn model and Liu model can give the better fit for the experimental data. In order to consider the practical force field, in this paper, we extend the Liu model to study the change of the entanglement density and the viscosity for molten LDPE, and the effects of the vibration parameters on them in parallel superposition vibration force field upon steady shear flow.

**Extended Model**

The basic molecular mechanism of this model attributes the rate dependence of viscosity and normal stress difference to the decrease entanglement density with increasing shear rate. In a flow field, entanglements are being formed and disengaged constantly. For convenience, any relaxation time in spectrum is considered here. Assume that the material at equilibrium has on the average $n_0$ entanglements per molecule. After imposing steady shear, it has on the average $n_0^*$ entanglements per molecule at $t_0$. When imposing vibration, it has $n$ entanglements at $t$. $n_1$ Denotes the creating entanglements during the time of $t-t_0$, $n_2$ denotes the losing entanglements during the time of $t-t_0$. In analogy to chemical reaction kinetics, the quantity $n_0^*-n$ could be viewed as the number of vacant sites available for reentanglement, which can be called the "distance" from the equilibrium, although only in an average sense.

Adopting the same thoughtfulness of Liu’s model [4], the entanglement creation process is assumed to be effective largely through random thermal diffusion, which is assumed to be independent of shear rate $\gamma$. Its rate is:

$$\dot{n}_1 = \frac{k_1}{\lambda}(n_0^* - n)$$  \hspace{1cm} (1)

Where $\dot{n}_1$ is the entanglement creation rate, parameter $k_1$ is the kinetic rate constant for thermal regeneration of entanglements, and $\lambda$ is a relaxation time.

The entanglement loss process is assumed to be caused primarily by the imposed shear and its rate is therefore dependent on the shear rate $\gamma$:

$$\dot{n}_2 = k_2\Delta\gamma n$$  \hspace{1cm} (2)

Where $\dot{n}_2$ is the entanglement loss rate, $k_2$ is the kinetic rate constant for the destruction of entanglements, $\Delta\gamma = \gamma_0 \omega \cos \omega t$ is the net shear rate after imposing parallel superposition vibration force field upon steady shear flow, and $\gamma_0$ is strain amplitude, $\omega$ is vibration frequency.

A dimensionless entanglement density is defined as $x = n/n_0$, each ranging from 0 to 1. So there are $x_m = n_m/n_0$, $x_1 = n_1/n_0$, $x_2 = n_2/n_0$, where $x_m$ is entanglement density in steady state, $x_1$ is creation entanglement density, $x_2$ is loss entanglement density.

It is clear that there is:

$$n = n_0^* + n_1 - n_2$$  \hspace{1cm} (3)

From eqn (3), it can be concluded that:

$$x = x_m + x_1 - x_2$$  \hspace{1cm} (4)

And there is:

$$\frac{dx_1}{dt} = \frac{k_1}{\lambda}(x_m - x)$$  \hspace{1cm} (5)

$$\frac{dx_2}{dt} = k_2\Delta\gamma x$$  \hspace{1cm} (6)
So the kinetic rate equation in parallel superposition vibration upon steady shear flow is:

\[
\frac{dx}{dt} = \frac{dx_1}{dt} - \frac{dx_2}{dt} = \frac{k_1(x_m - x)}{\lambda} - k_2\Delta \gamma x \quad (7a)
\]

Evidently, for the structure dependent relaxation spectra \((G_i, \lambda_i)\), the kinetic rate equation becomes:

\[
\frac{dx_i}{dt} = \frac{k_1(x_{mi} - x_i)}{\lambda_i} - k_2\Delta \gamma x_i \quad (7b)
\]

where \(G_i\) is the relaxation module for the relaxation time \(\lambda_i\).

So the entanglement density is:

\[
x = \sum_i x_i 
\]

(8)

The definition in Liu model is \(G_i = G_{0i}, \lambda_i = \lambda_{0i} x_i^{1.4}\). But Giacomin used the definition \(G_i = G_{0i}x_i, \lambda_i = \lambda_{0i} x_i^{1.4}\), where \(G_{0i}\) and \(\lambda_{0i}\) respectively are the equilibrium values of \(G_i\) and \(\lambda_i\). From \(\eta_i = G_i \Delta \gamma\), when \(x_i \rightarrow 0\), then \(\eta_i \rightarrow 0\), it does not agree with the fact. So it should be revised.

Applying the definition of Marrucci [1]:

\[
G_i = G_{0i}(\frac{x_i + \alpha}{1 + \alpha}), \lambda_i = \lambda_{0i}(\frac{x_i + \alpha}{1 + \alpha})^{1.4} \quad (9)
\]

and the viscosity is to be:

\[
\eta_i = \eta_{0i}(\frac{x_i + \alpha}{1 + \alpha})^{2.4} \quad (10)
\]

So the viscosity is:

\[
\eta = \sum_i \eta_i 
\]

(11)

Where \(\alpha\) is a constant parameter, which is determined by \(\eta_{0i} = \eta_{0}(\alpha/1+\alpha)^{2.4}\). \(\eta_{0i}\) is obtained when the entanglements are all destroyed and can be evaluated from the high \(\dot{\gamma}\) viscosity limit, \(\eta_0\) is zero shear viscosity and can be evaluated from the low \(\dot{\gamma}\) viscosity limit. The spectrum \((G_i, \lambda_i)\) can be evaluated from a small amplitude oscillatory shear test, Table 1 is the linear relaxation spectrum for LDPE (150°C)[8].

Determining the kinetic rate constants \(k_1\) and \(k_2\) has heretofore been tedious. Jeyaseelan and Giacomin[9] offered a less tedious method to determine them. And in the same year, they also offered several polymer melts values of \(k_1\) and \(k_2\). In fact, most of parameters in the model can be determined by fitting the model to steady shear viscosity data. At steady state the two rate processes occur at equal pace, and the entanglement density of the system is no longer a function of time. So there are:

\[
\dot{x}_i = \dot{x}_2 \quad (12)
\]

\[
x_{mi} = \frac{k_1}{k_1 + k_2 \dot{\gamma}_m \lambda_{0}^{1.4}(1 + \alpha)\lambda_{mi} \left(1 + x_{mi}\right)} \quad (13)
\]

Where \(\dot{\gamma}_m\) is the shear rate that is no longer a function of time in steady state. The eqn (7b) is non-linear and has no analytical solution. But the numerical solution of this model can be obtained by using Runge-Kutta fifth-order ordinary differential equation solver.

**EXPERIMENTAL**

The capillary dynamic rheometer has been developed successfully in National Engineering Research Center of Novel Equipment for Polymer Processing in South China University of Technology. A sine vibration can be added in parallel direction of polymer melt flowing through capillary, so the periodic vibration force with high frequency and small amplitude is introduced into all the process of polymer melt extrusion through capillary. Here, the experimental material is LDPE, the temperature of the melt is 150°C, and \(k_1 = 0.32, k_2 = 0.1\), \(a = 0.1\).

Figure 1 denotes the velocity of polymer melts in capillary dynamic rheometer. Where \(L\) is the length of

<table>
<thead>
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<th>(i)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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</thead>
<tbody>
<tr>
<td>(\lambda_{0i}) (s)</td>
<td>0.001</td>
<td>0.005</td>
<td>0.028</td>
<td>0.14</td>
<td>0.7</td>
<td>3.8</td>
<td>20</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>(G_{0i}) (Pa)</td>
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<td>40000</td>
<td>33300</td>
<td>16600</td>
<td>8690</td>
<td>3150</td>
<td>860</td>
<td>118</td>
<td>1.85</td>
</tr>
</tbody>
</table>

**Table 1.** Linear relaxation spectrum for LDPE (150°C) [8].
the capillary, R is the radius of the capillary, ΔP is the pressure difference between the two ports. Suppose the melt flow is laminar in axial direction, and isothermal, and the ratio of L/2R is sufficiently great to ensure that a well-developed velocity profile; the melt is uncompressible and viscoelastic, the density $\rho$ is unchanged; wall slip and gravitational effects may be neglected.

In capillary the velocity and the shear stress of the melt respectively are:

$$V = \begin{bmatrix} V_z & 0 & 0 \end{bmatrix}$$  \hspace{1cm} (14)

$$\tau = \begin{bmatrix} \tau_{zz} & \tau_{rz} & 0 \\ \tau_{rz} & \tau_{rr} & 0 \\ 0 & 0 & \tau_{\theta\theta} \end{bmatrix}$$  \hspace{1cm} (15)

where boundary conditions are:

$$V_z(r, t)|_{r=R} = 0$$  \hspace{1cm} (16)

$$\tau_{rz}|_{r=0} = const$$  \hspace{1cm} (17)

Through analyzing the movement equation and using conservation of mass, the shear rate of the capillary wall can be described as:

$$\dot{\gamma} = \frac{R_0^2}{R^3} (\bar{V}_0 + A \omega \cos \omega t)$$  \hspace{1cm} (18)

where $R_0$ is the radius of the cylinder, $\bar{V}_0$ is the steady average velocity of the piston rod, and $A$ is the vibration amplitude.

Supposed:

$$\dot{\gamma} = -\frac{R_0^2}{R^3} \bar{P}_0$$  \hspace{1cm} (19)

$$\gamma_0 = -\frac{R_0^2}{R^3} A$$  \hspace{1cm} (20)

So the shear rate of the melt in the capillary wall can be described as:

$$\dot{\gamma} = \dot{\gamma}_m + \gamma_0 \omega \cos \omega t$$  \hspace{1cm} (21)

Obviously, there is $\Delta \dot{\gamma} = \gamma_0 \omega \cos \omega t$.

With the on-line collection system, the capillary entry pressure can be measured instantaneously. Therefore the shear stress of the capillary wall in Z-direction can be approximately described by Juan Zhang [10]:

$$\tau_R = \frac{R \Delta P(t)}{2L} - \frac{\rho R_0^2 A \omega^2}{6R} \sin \omega t =$$

$$\frac{RP(1)}{2L} - \frac{2\rho \pi^2 R_0^2 A t^2}{3R} \sin \omega t$$  \hspace{1cm} (22)

and the viscosity can be described as:

$$\eta_R = \frac{\tau_R}{\dot{\gamma}}$$  \hspace{1cm} (23)

RESULTS AND DISCUSSION

Figure 2 is a plot of the experimental values and the theoretical values of viscosity vs. T in one period. From Figure 2, it is clear that the two values are reasonably in good agreement, although there is a little error. In fact, the experimental viscosity is still approximation, which is valued by eqn (23) with the measuring pressure, so it has some reasonable error in terms of measuring.

Figure 3 is a plot of comparison of the experimental values and the theoretical values of the viscosity with different vibration frequency in one period. From these three figures, it is clear that the changing amplitude of the viscosity increases with the increasing vibration frequency and the effects of vibration frequency on the experimental viscosity and the theoreti-
The theoretical and experimental values of viscosity are in accordance.

Figure 4 is a plot of comparison of the experimental values and the theoretical values of viscosity with different amplitude in one period. From these three figures, it is also clear that the change amplitude of the viscosity increases with the amplitude increasing. The viscosity change trend of the amplitude effect is the same as that of the vibration frequency effect. At the same time, the effects of amplitude on the experimental viscosity and the theoretical viscosity are also accordant.

From Figure 2 to Figure 4, it is clear that the precision of the extended kinetic network model for polymer melt parallel superposition vibration force field upon steady shear flow is reasonable. But how to explain the effect of vibration parameters (amplitude and frequen-
cy) on the melt viscosity? So study should be focused on the change of entanglement density for polymer melt in vibration shear field.

Because the strain rate is in cosine expression, which is periodic, the solution of eqn (7b) is also periodic. Figure 5 is a plot of the entanglement density vs. $T$ in one period with the different vibration frequency and the same amplitude. It is seen that the entanglement density decreases with the vibration frequency increasing, while the decreasing amplitude of the entanglement density increases with the vibration frequency increasing. Figure 6 is a plot of the entanglement density vs. $T$ in one period with the same vibration frequency and the different amplitude. It is seen that the entanglement density decreases with the amplitude increasing, while the decreasing amplitude of the entanglement density increases with the amplitude increasing. It is because that increasing vibration frequency or amplitude can make the amplitude of the shear rate increasing, which makes the rate of disentanglement increasing. It can be induced that the entanglement density decreases and the number of vacant sites increases, and it is in favour of the reptation of molecular quickly. Therefore the viscosity decreases.

As a result, when vibration frequency or amplitude is larger, the shear rate is larger, it makes the destruction rate of entanglement density to decrease, free volume to increase, the force between molecules to decrease, and the effect of the molecular orientation becomes stronger which results in the material tensile strength and stiffness increase. At last, the reptation of molecular becomes quicker, and so the viscosity decreases. At the same time, frequency or amplitude increases means the intensity of the vibration force field is being increased and the ability of overcoming viscoelastic resistance is strengthened. Therefore, the changing amplitude of the viscosity increases with frequency or amplitude increasing.

CONCLUSION

A series of novel monoazo disperse dyestuffs based on using the extended kinetic rate equation, the change of the viscosity and the entanglement density for molten LDPE in parallel superposition vibration force field which upon steady shear flow are being predicted. Through many experiments, the theoretical viscosity values and experimental values are reasonably in good agreement, their change trend is accordance with time, and the effect of vibration frequency or amplitude on them is also predictable. In conclusion, the entanglement density decreases with vibration frequency or amplitude increasing, while the decreasing amplitude of the entanglement density and the changing amplitude of the viscosity both increase with vibration frequency or amplitude increasing.

REFERENCES

4. Liu T.Y., Soong D.S., Williams M.C., Time-dependent rheological properties and transient structural states of entangled polymeric liquids: A kinetic network model,


