

A Theoretical Study on Transitional Shear Flow Behavior of the Compressible and Isothermal Thermoplastic Polymer

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Abstract By extending the virtual conformational element of the polymer chain, a dynamic end-to-end (ETE) vector was presented to describe the chain's instantaneous morphology based on the spring-bead theory. A feasible viscoelastic model was proposed to describe the rheological behavior of the isothermal thermoplastic polymer materials, based on the molecular kinetics, thermodynamics, and continuum mechanics method. The model is simplified as the generalized Newton's law. Its integral formula with similar form to the K-BKZ model was also derived. Rheological experiments were carried out with the isotactic polypropylene material. The experimental results reveal that the viscoelastic model exhibits a three-stage rheological characteristic. There is a distinct high-elastic rheological region in the middle stage, reflecting the pseudoplastic fluids properties. Compared with the Ostwald-de Waele power law model, the viscoelastic model shows a better agreement with the rheological practices.

Keywords Shear flow; Theoretical model; Thermoplastic polymer; Rheological experiments

Citation: Liu, D. L.; Zhou, F.; Fang, K. A theoretical study on transitional shear flow behavior of the compressible and isothermal thermoplastic polymer. *Chinese J. Polym. Sci.* 2019, 37, 518–526.

INTRODUCTION

The flow of polymer materials is a complicated process, as the viscosity of plastics, apart from temperature and pressure, depends on the molecular mass, molecular mass distribution, and the deformation rate. As viscoelastic materials, polymers exhibit a rich variety of nonlinear flow phenomena. Nonlinear flow behaviors of these polymers depend on how the chain entanglement responds to external deformation.^[1] These make polymer processing rather complex. Processing of the molten polymer materials, for instance, injection molding, incurs considerable changes in rheological and thermo-mechanical properties due to a complex deformation and high deformation rates under shear flow conditions.^[2–4] The macromolecules ‘remember’ some of these treatments in the final products in the form of conformation changes (*i.e.* orientation, crystallization) and residual stresses, which affects the final mechanical and optical properties of products.^[5] Undoubtedly, successful control and characterization of the internal morphology and resultant properties would lead to increasing possibilities of tailoring products for wider applications. Rheometry is therefore of great importance in quality control and process control. So is it in assessing the usefulness of any proposed constitutive model for test material.

A polymeric melt is neither a simple liquid nor an elastic solid in mechanical response, and shows various types of unusual flow behaviors.^[6–9] The rheology of the polymeric liquids has been intensively studied for several decades both experimentally and theoretically.^[10] Theoretically, advances have been made mainly in phenomenological theories, which have clarified the interrelations between various phenomena and shown the universal behaviors of the polymeric melts. For instance, the Ostwald-de Waele power law model, the Bird-Carreau model, and the Cross model are among the most preferred pure viscosity models.^[11] The Maxwell model and the Kelvin-Voigt model are two commonly used linear viscoelastic models,^[12] which are constructed by a spring and a dashpot in series and in parallel, respectively. Moreover, more complex combinations of them, *i.e.* the generalized models, are always used to better describe the real material response.^[13] Another widely used constitutive equation for linear viscoelastic materials is derived from the Boltzmann's superposition principle.^[14,15] Other nonlinear viscoelastic models, such as the upper covered Maxwell (UCM) model,^[16] White-Metzner model,^[17] Phan-Thien Tanner (PTT) model,^[18] Johnson-Segalman model,^[19] Giesekus-Leonov model,^[20] Oldroyd-B Model, and K-BKZ model,^[21,22] have also been built to provide robust predictions in the case of polymer materials. Especially, the K-BKZ model, one of the most successful models, has been widely used in research works and industrial applications. Such a functional relation is termed as a constitutive equation and coupled with hydrodynamic equations, which gives

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Received September 29, 2018; Accepted December 24, 2018; Published online January 29, 2019

a complete description of the rheological properties. These publications provide some appropriate numerical methods to discuss the morphological evolution of the polymer materials. Nevertheless, an obvious disadvantage of them is that all the calculation courses are slow and cumbersome. In addition, based on the empirical or semi-empirical viscoelastic models, the numerical approaches present merely a seeming result of the shear behavior, owing to the self-deficiency of the phenomenological method.

Compared with the phenomenological method, the molecular theory is regarded as an ideal way to characterize the transient relation between the polymer morphology evolution and stress response in dilute and concentrated solution systems. In this field, the simplest non-linear kinetic theory of a dilute polymer solution is recognized as the finitely extensible non-linear elastic (FENE) dumbbell model.^[23] The simplest tube model of the entangled linear polymer melts is the Doi-Edwards model.^[24] The calculation of non-Newtonian flows finite elements and stochastic simulation technique (CONNFESSIT) method,^[25] as the third classical kinetic molecular theory, is the first implementation of the stochastic approach. This method combines Brownian dynamic techniques that estimate the temporal polymer dynamics with finite-element techniques that estimate the spatial variations in flows and stresses. Some of these approaches have previously been used to well solve the engineering problems in practice. However, such molecule-based equations can only yield quantitative information on the distribution of polymer conformations within a macroscopic fluid element in the form of averaged quantities. Owing to some disadvantages of each method, it is impossible to obtain clear results of the shear flowing process.

From the previous research work,^[26] a modest pseudo-high-elastic model was proposed to describe the relationship between the transient macromolecular morphology and stress response of polymer in injection molding. The model was studied based on the thermodynamics, statistical mechanics, and continuum mechanics by using the kinetic molecular theory and the necessary simplification and hypothesis. Moreover, the compressible property of polymer melts was considered, and another transitional relation expression was derived base on the entropy-elastic deformation theory.^[27] In these studies, polymer melts were reckoned as a simple shear flow with the shear viscosity overlooked and the temperature variation ignored. The molten polymer was assumed to be continuum macromolecules with a homogeneous phase. Each molecule was simplified as a coarse-grained bead-spring chain being surrounded by and tangled with others. It was also considered to be an ideal chain with three-dimensional random walk, where each step may be of different lengths and the step lengths correspond to the statistical segments of the polymer chain.

Based on the previous research, the aim of this paper is to present a new progressive theoretical model with the essential simplification and hypothesis, which can expound the transitional shear flow behavior of the compressible and isothermal polymer materials more reasonably. For this purpose, a dynamic end-to-end (ETE) vector was used to de-

scribe the instantaneous morphology of polymer chain firstly. By coupling with the thermodynamics, statistical mechanics, and continuum mechanics theories, a viscoelastic mathematical model was deduced to describe the instantaneous macromolecules shear flow behavior. Then, rheological experiments were designed with isotactic polypropylene (PP) material. At last, the fitness and effectiveness of the model were discussed by comparing with the Ostwald-de Waele power law model.

THEORETICAL METHODS

Physical Model

As viscoelastic materials, polymers show a rich variety of nonlinear flow phenomena. For easy conduction of the conjectural research, only the factors regarding the processing control are considered. The theoretical research was conducted under the following assumptions.

(1) Polymer melts are regarded as experiencing a simple shear flow in an unstinted field, which exhibits more elasticity than viscosity under transitional filling conditions. The shear viscosity is overlooked.

(2) It is deemed to be a mass of continuum macromolecules with a homogeneous phase.

(3) The variation of temperature is neglected while the variation in volume mass of macromolecules is considered.

(4) A monomer chain is described as the molecular segment between successive points of cross-linkage, and each chain contains chain segments of the same number, length, and structure. In micro-fields, the flowing pattern is presented as the segment movement as well as the particle diffusion.

(5) Polymer melts are represented as a mass of continuum macromolecules. Each molecule is simplified as a coarse-grained bead-spring chain being surrounded by and tangled with others.

(6) It is also considered to be an ideal flexible polymer chain with three-dimensional random walk, in which each step may have a different length and the step lengths in the walk correspond to the statistical segments of the polymer chain.

(7) The microscopic dimension changes of each chain of components are proportional to the macroscopic dimension changes, conforming to the affine motion.^[28]

According to the foregoing hypothesis, the molecule is considered as a random coil being covered with a virtual conformation sphere in the initial stage. The virtual sphere would unwrap and disentangle as an ellipsoid, and then become a conformation pipeline under the shear stresses overloaded conditions. In this model, the only difference from the traditional ETE vector is that it is replaced by a dynamical one and defined as the long axis of the virtual conformation element of the chain, as showed in Fig. 1.

Mathematical Model

The statistical mechanic method is an excellent method to deal with the transient conformation of macromolecular chains. Using the random walk model and classic statistical arguments,^[29] the probability distribution of the end-to-end

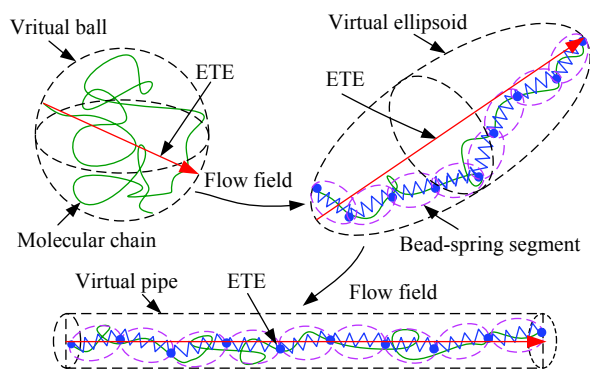


Fig. 1 Physical model of the molecular chain's ETE vector

(ETE) length, r , of an isolated polymer chain can be written as:

$$p(r) = \left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3r^2}{2nl^2}} \quad (1)$$

where n represents the number of links in the chain, l is the length of each link in the chain, r is the ETE vector of the macromolecular chain, and $p(r)$ represents the probability distribution of ETE of the isolated chain.

The entropy of the statistical chain was founded according to the general principles of statistical thermodynamics from the Boltzmann result as follows:

$$s = k \ln(p(r) V_m) \quad (2)$$

where s is the entropy of a single chain, k is the Boltzmann constant, and V_m denotes the volume element of the chain.

Next, substituting the probability function from Eq. (1) to obtain the entropy for a single chain:

$$s = k \left[\frac{3}{2} \ln \left(\frac{3}{2\pi nl^2} \right) - \frac{3}{2nl^2} r^2 + \ln V_m \right] \quad (3)$$

The transient decrement in the entropy of a single chain after a unit of time δt can be calculated as follows:

$$\delta s = s - s_0 = k \left(-\frac{3}{2nl^2} \delta r^2 + \ln J \right) \quad (4)$$

where the subscript "0" denotes the initial value of the components, and the normal one denotes the transient values in the next time. δs represents the infinitesimal decrement of the entropy. δr^2 is the transient deformation increment of the polymer chain. $J = V_m/V_{m,0}$ represents the volume ratio of the molecule. Note that the first and second terms on the right-side of Eq. (3) are canceled out. They are constants due to the invariability of the bond number and bond length for a given macromolecule in current context. It is also noteworthy that the distribution density function is coincidental throughout owing to the hypothesis of random walk theory.

From the first law of thermodynamics, the change in the internal energy by a process per unit mass is

$$T \delta s - p_m \delta V_m + f_m \delta l_m = 0 \quad (5)$$

where T is the absolute temperature in thermodynamics, f_m is the entropically elastic force of the chain, δl_m is the deformation length of the chain, p_m is normal pressure on the system, and δV_m is the change of volume. $f_m \delta l_m$ represents

the mechanical work of system due to the deformation, whereas $p_m \delta V_m$ represents the pressure volume work. As a simple shear fluid, the transient morphology of polymer chain derives mainly from the disentanglement and elongation rather than the change of its volume. Generally, $p_m \delta V_m$ is much smaller than $f_m \delta l_m$. The principal increment of the internal energy comes from the entropically elastic force of the chain, similar to the rubber elasticity. So it is timely to ignore the second term on the left side in Eq. (5).

Substituting Eq. (4) into Eq. (5) gives:

$$f_m = \frac{1}{\delta l_m} kT \left(\frac{3}{2nl^2} \delta r^2 - \ln J \right) \quad (6)$$

Consequently, the deformation stress corresponding to the macromolecular conformation is obtained as follows:

$$\sigma_m = \frac{kT}{\delta V_m} \left(\frac{3}{2nl^2} \delta r^2 - \ln J \right) \quad (7)$$

where σ_m is the deformation stress of the molecular monomer, being regarded as the principal source of the entropically elastic stress here, and δV_m is the volume increment of the polymer chain.

Now consider that there is a group of macromolecular chains as an element which contains q chains. In the element, each ETE vector of the single chain is represented by $r_1, r_2, \dots, r_q$, correspondingly. The entropy of each chain is presented by $s_1, s_2, \dots, s_q$, and the volume element is represented by $V_1, V_2, \dots, V_q$, respectively. Then, the entropy of a chain-group is the sum of the entropies of each individual chain, as given in the following formula:

$$\begin{aligned} S &= k \left[\frac{3}{2} \ln \left(\frac{3}{2\pi nl^2} \right) - \frac{3}{2nl^2} r_1^2 + \ln V_1 \right] + k \left[\frac{3}{2} \ln \left(\frac{3}{2\pi nl^2} \right) - \frac{3}{2nl^2} r_2^2 + \ln V_2 \right] + \dots + k \left[\frac{3}{2} \ln \left(\frac{3}{2\pi nl^2} \right) - \frac{3}{2nl^2} r_q^2 + \ln V_q \right] \\ &= k \left[\frac{3q}{2} \ln \left(\frac{3}{2\pi nl^2} \right) - \frac{3}{2nl^2} (r_1^2 + r_2^2 + \dots + r_q^2) + \ln(V_1 V_2 \dots V_q) \right] \end{aligned} \quad (8)$$

where S represents the sum of the entropies of each polymer element.

The above equation shows that the entropy of the polymer microelement can also be founded according to the general principles of statistical thermodynamics result. Accordingly, if we assume the polymer microelement as a whole and define its ETE vector as R , there is a fictitious macromolecule whose ETE vector modulus square is the sum of all monomers' therein, i.e., $R^2 = r_1^2 + r_2^2 + \dots + r_q^2$. Of course, the ETE vector of the fictitious macromolecule has no direct relation with that of its internal chains, and there is no explicit physical relationship between them.

$$S = k \left[\frac{3q}{2} \ln \left(\frac{3}{2\pi nl^2} \right) - \frac{3}{2nl^2} R^2 + \ln(V_1 V_2 \dots V_q) \right] \quad (9)$$

Consequently, the transient decrement in the entropy of polymer microelement after a unit of time, δt , can be calculated as follows:

$$\delta S = k \left(-\frac{3}{2nl^2} \delta R^2 + \ln \frac{V_1 V_2 \cdots V_q}{V_{0,1} V_{0,2} \cdots V_{0,q}} \right) \quad (10)$$

where δR^2 is the transient deformation increment of the fictitious macromolecule.

Definition of the equivalent volume ration of element is:

$$\bar{J} = \frac{V_1 V_2 \cdots V_q}{V_{0,1} V_{0,2} \cdots V_{0,q}} \quad (11)$$

For the moment, suppose that the volume ratio of each chain is in equality so as to cut the calculating process:

$$\bar{J} = \left(\frac{V_1}{V_{0,1}} \right)^q = \left(\frac{V_2}{V_{0,2}} \right)^q = \cdots = \left(\frac{V_k}{V_{0,k}} \right)^q = \cdots = \left(\frac{V_q}{V_{0,q}} \right)^q = J^q \quad (12)$$

Substituting Eq. (12) into Eq. (10) gives:

$$\delta S = k \left(-\frac{3}{2nl^2} \delta R^2 + \ln \bar{J} \right) \quad (13)$$

In the same way, the same result can also be deduced from Eq. (7):

$$\sigma = \frac{kT}{\delta V} \left(\frac{3}{2nl^2} \delta R^2 - \ln \bar{J} \right) \quad (14)$$

where σ is the shear stress of the macromolecular coil in a unit of time δt . This formula describes the relationship between the shear stresses and configuration strain of macromolecules.

According to the continuum mechanics theory, the instantaneous deformation stress of the macromolecular coil is given by:

$$F = \delta A \hat{n} \cdot \sigma \quad (15)$$

where F is the deformation force of the element, δA is the area of arbitrary surface of the macromolecules unit, $\hat{n}$ is the normal vector of the arbitrary surface, and σ is the deformation stress of the macromolecular coil.

Further, the conformation stress of any polymer element is calculated by using continuum mechanics. It is also represented as a three integral expression, conveniently expressed in the mathematical form:

$$F = \iiint_{\Omega} [\psi_1(r) \psi_2(r) \sigma_m] \partial x \partial y \partial z \quad (16)$$

where $\psi_1(r)$ denotes the probability distribution of the chain's ETE in element, which always fits for the Gaussian distribution function, $\psi_1(r) = p(r)$. $\psi_2(r)$ represents the probability of the molecular ETE belonging to the cross section (the normal vector) of δA . To simplify the calculation progress, we relax the definition: the polymer element always keeps cubic shape. The total volume of the element is V , and each chain accounts for one portion of the total. $\psi_2(r)$ is obtained by using the graphical method, and expressed as follows:

$$\psi_2(r) = V^{-\frac{1}{3}} p(r) \quad (17)$$

Inserting Eqs. (1), (7), and (17) into Eq. (16) gives

$$F = kTV^{\frac{2}{3}} [(\hat{n} \cdot \sigma \langle r \cdot r \rangle) - (\hat{n} \cdot \sigma \langle \ln J \rangle)] \quad (18)$$

Here, the function $\langle r \cdot r \rangle$ and $\langle \ln J \rangle$ are defined as:

$$\begin{aligned} \sigma \langle r \cdot r \rangle &= \iiint_{\Omega} [\psi(r) \sigma(r \cdot r)] \partial x \partial y \partial z \\ &= \iiint_{\Omega} \left\{ \left[\left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3r^2}{2nl^2}} \right] \left(\frac{3}{2nl^2} \delta r^2 \right) \right\} \partial x \partial y \partial z \\ &= \frac{3}{2nl^2} \left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} \left[(\delta r^2 - 3) e^{\delta r^2} + \alpha_1 (\delta r^2 - \alpha_2)^2 + \alpha_3 \right] \end{aligned} \quad (19)$$

$$\begin{aligned} \langle \ln J \rangle &= \iiint_{\Omega} [\psi(r) \cdot \ln J] \partial x \partial y \partial z \\ &= \iiint_{\Omega} \left\{ \left[\left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3r^2}{2nl^2}} \right] \cdot \ln J \right\} \partial x \partial y \partial z \\ &= \left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} e^{\delta r^2} \ln J \end{aligned} \quad (20)$$

where α_1 , α_2 , and α_3 are the constants of the model.

Integrating once more together with Eq. (15), and being aware of the relationship between δA and V , the results are shown as follows:

$$\begin{aligned} \sigma &= kT \left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} \left\{ \frac{3}{2nl^2} \left[(\delta r^2 - 3) e^{\delta r^2} + \right. \right. \\ &\quad \left. \left. \alpha_1 (\delta r^2 - \alpha_2)^2 + \alpha_3 \right] - e^{\delta r^2} \ln J \right\} \end{aligned} \quad (21)$$

Normally, it is obvious that there is some proportional relationship between ETE of the molecular monomer and element based on the affine motion hypothesis, so it is reasonable to regard this equation as the expression of the polymer element, that is:

$$\begin{aligned} \sigma &= kT \left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} \left\{ \frac{3}{2nl^2} \left[(\delta R^2 - 3) e^{\delta R^2} + \right. \right. \\ &\quad \left. \left. \alpha_1 (\delta R^2 - \alpha_2)^2 + \alpha_3 \right] - e^{\delta R^2} \ln \bar{J} \right\} \end{aligned} \quad (22)$$

Generally, there are always three principal stresses and principal stress directions of the polymer microelement, in which only the positive strains are presented and the shear strains are zero. If we give the components of strain tensors in an arbitrary orthonormal coordinate system, their directions are confined to the principal axes of strains. According to the strain tensor theory,^[30] we can get:

$$\begin{aligned} \sigma &= kT \left(\frac{3}{2\pi nl^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} \left\{ \frac{3}{2nl^2} \left[(\varepsilon - 3) e^{\varepsilon} + \alpha_1 (\varepsilon - \alpha_2)^2 + \alpha_3 \right] - \right. \\ &\quad \left. e^{\varepsilon} \ln \bar{J} \right\} \end{aligned} \quad (23)$$

where ε is the strain tensor of the coil.

The above equation is actually an instantaneous model. It provides the molecular deformation strain and stress response in a unit time. In other words, it expounds the rela-

tionship between the deformation rate and shear stress.

$$\sigma = kT \left(\frac{3}{2\pi n l^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} \left\{ \frac{3}{2nl^2} [(\dot{\epsilon} - 3)e^{\dot{\epsilon}} + a_1(\dot{\epsilon} - a_2)^2 + a_3] - e^{\dot{\epsilon}} \ln \dot{\epsilon} \right\} \quad (24)$$

where $\dot{\epsilon}$ is the strain rate tensor of the coil.

To facilitate the derivation procedure, we prefer to believe the initial values of polymer chains which are all in absolute equilibrium. By defining the molecular volume ration at different times and adhering to the isothermal conditions, we notice that there is certain relationship between the molecular volume ration and the free volume fraction according to the free volume theory.^[27] If we relax the assumptions that the volume ratio of polymer macromolecules gives a ratio with its deformation tensor, there comes $\bar{J} = \beta \dot{\epsilon}$, β is a constant of materials, then

$$\sigma = kT \left(\frac{3}{2\pi n l^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} \left\{ \frac{3}{2nl^2} [(\dot{\epsilon} - 3)e^{\dot{\epsilon}} + a_1(\dot{\epsilon} - a_2)^2 + a_3] - (a_4 e^{\dot{\epsilon}} + a_5 e^{\dot{\epsilon}} \ln \dot{\epsilon}) \right\} \quad (25)$$

where a_4 and a_5 are constants.

Then we relax the assumptions that the coefficient term on the right side of Eq. (25) is the generalized relaxation coefficient of polymer, *i.e.* $G = kT \left(\frac{3}{2\pi n l^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}}$. This model can also be simplified as the generalized Newton's law.

This model provides a viscoelastic relationship between the shear stress and strain ratio tensor of polymer materials under simple shear flow conditions. It is deduced from the molecular kinetic, thermodynamics, and continuous medium mechanics method.

The integral form of the model is shown as follows:

$$\sigma = \int_{-\infty}^t kT \left(\frac{3}{2\pi n l^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} \left\{ \frac{3}{2nl^2} [(\dot{\epsilon}(t-\zeta) - 3)e^{\dot{\epsilon}(t-\zeta)} + a_1(\dot{\epsilon}(t-\zeta) - a_2)^2 + a_3] - a_4 e^{\dot{\epsilon}(t-\zeta)} + a_5 e^{\dot{\epsilon}(t-\zeta)} \ln \dot{\epsilon}(t-\zeta) \right\} dt \quad (26)$$

if

$$m(t-\zeta) = kT \left(\frac{3}{2\pi n l^2} \right)^{\frac{3}{2}} e^{-\frac{3}{2nl^2}} = \frac{\partial G(t-\zeta)}{\partial t} \quad (27)$$

$$\begin{aligned} S(t) &= \frac{3}{2nl^2} [(\dot{\epsilon}(t-\zeta) - 3)e^{\dot{\epsilon}(t-\zeta)} + a_1(\dot{\epsilon}(t-\zeta) - a_2)^2 + a_3] - \\ &\quad [a_4 e^{\dot{\epsilon}(t-\zeta)} + a_5 e^{\dot{\epsilon}(t-\zeta)} \ln \dot{\epsilon}(t-\zeta)] \\ &= \phi_1 \dot{\epsilon}(t-\zeta) + \phi_2 \dot{\epsilon}(t-\zeta) \end{aligned} \quad (28)$$

where t is the current time, ζ is some time in the past, $m(t-\zeta)$ is the time memory function related to the properties of

polymer materials. ϕ_1 and ϕ_2 are two invariants of the conformation strain tensor, then

$$\sigma = \int_{-\infty}^t m(t-\zeta) S(t) dt \quad (29)$$

The integral formula of the theoretical model is in accordance with the classical K-BKZ model.^[31]

This theoretical model gives a relatively sophisticated expression, which is adverse to the feasibility of calculation, so it is necessary to further simplify the expression. It is worth noting that the constants n and l are related to the polymer materials. If $\zeta_0 = 3/2nl^2$, then the upper formula can be simplified as follows:

$$\sigma = kT (\zeta_1 \dot{\epsilon} e^{\dot{\epsilon}} + \zeta_2 e^{\dot{\epsilon}} + \zeta_3 \dot{\epsilon}^2 + \zeta_4 \dot{\epsilon} + \zeta_5 - \zeta_6 e^{\dot{\epsilon}} \ln \dot{\epsilon}) \quad (30)$$

where ζ_1 – ζ_6 are constants.

At this point, this equation gives a relationship model between the conformation deformation ratio tensor and the corresponding shear stress of polymer melts with the compressible and isothermal conditions. Moreover, this theoretical model is actually an instantaneous equation according to the aforementioned research.

From the depriving process, suppose that we did not consider the compressibility of the polymer material, and we would then be able to get a relatively simple formula which does not contain the latter part about the volume ratio of this formula. That means the constant of last term ζ_6 is relevant to the pressure factor of the polymer material, such as the pressure correlation coefficient in Cross model. The constant term ζ_5 in this formula indicates that there is an extrapolation length in velocity fields of the polymer melt in shear flow, which needs additional kinetic energy to overcome the potential resistance for polymer motion in startup stage. That is to say, there is an initial energy barrier of the polymer macromolecules in shear flow. Actually, it is not difficult to understand this phenomenon on the molecular level or in a micro-field. The long-chain characteristics of a polymer molecule determine the entangled interaction between molecules in shear flow; the static polymer chain needs to first overcome the intermolecular force, the kink force, and the internal friction limit of the surrounding macromolecules before flowing. Only the shear stress increases to a certain value will the migration phenomena be initiated and become apparent. So the constant ζ_5 is related to the activation energy of polymer material. The constants ζ_1 – ζ_4 are relevant to the viscoelastic relaxation response of polymer material.

Furthermore, according to the above research, Eq. (30) is actually an instantaneous model. In micro-field, this model provides the molecular deformation strain and shear stress response instantaneously, while in macro-field, it expounds the relationship between the deformation rate and shear stress. For easy conduction of the theoretical research, the rheological behavior of polymers is idealized as a simple shear flow in this study. Only one component of velocity vectors has a non-zero value, and the gradient of velocity is constant and perpendicular to the velocity itself. If we define an orthonormal coordinate system with the three axes

defined as the principal stresses and principal stress directions of the polymer microelement, the shear stress as well as the strain tensor can be decomposed into three axes, with x , y , and z directions set as the shear stress (shear strain) direction, the neutral direction, and the velocity gradient direction, respectively. The deformation gradient in simple shear can also be deduced and expressed as follows:

$$\tau = kT (\zeta_1 \dot{\gamma} e^{\dot{\gamma}} + \zeta_1 e^{\dot{\gamma}} + \zeta_3 \dot{\gamma}^2 + \zeta_4 \dot{\gamma} + \zeta_5 - \zeta_6 e^{\dot{\gamma}} \ln \dot{\gamma}) \quad (31)$$

where τ is the shear stress of the polymer coil, $\dot{\gamma}$ is the shear rate.

EXPERIMENTAL SET-UP

In this study, sample data of the shear stress against shear rate were extracted using rheological tests. The commonly used thermoplastic polymer of isotactic polypropylene (PP) material, GP-1007FC from LG Chem, was selected as a sample material. The basic physical and mechanical properties of PP are shown in Table 1. The HAAKE

MARS60 rotational rheometer, made by Thermo Electron (Karlsruhe) GmbH, Germany, was employed. The P25/Ti-02150398 type rotor was selected as a plate rotor, and the specimens were prepared by the steady shear rheological tests. When the panel temperature was heated up to the set point, the plate rotor dropped down, and then the testing procedure launched.

In experiments, the first test was executed to verify the performances of the proposed model under a higher shear condition. The temperature of 195 °C, the shear rate at a range of 0 s⁻¹ to 1500 s⁻¹, shear time of 150 s, and gap of 1 mm were applied. Each test was fed with a same mass of PP material about 0.85 g, and the same experiment was repeated several times to reach a steady phase. In the second experiment, the shear rate at a range of 0 s⁻¹ to 90 s⁻¹ and shear time of 30 s were performed under a lower shear condition. Material temperatures were set at 215, 220, and 225 °C, successively. PP material in each test was fixed at about 0.29 g, fluctuating from 0.2873 g to 0.2936 g. The same test was also repeated several times to reach a steady phase. By extracting specimens from the experimental results, the sufficient sample data were recorded.

RESULTS AND DISCUSSION

To save space in visualizing the obtained values along with their testing parameters, the calculated data of the first experiment are given in a definite figure. Fig. 2(a) depicts the fitted result of the theoretical model Eq. (31) by randomly sampling two times; the scatter points represent the experimental results and the curves denote the fitted results of the viscoelastic model.

It can be seen from Fig. 2(a) that the two experiments show a similar curve tendency within the trail window. The

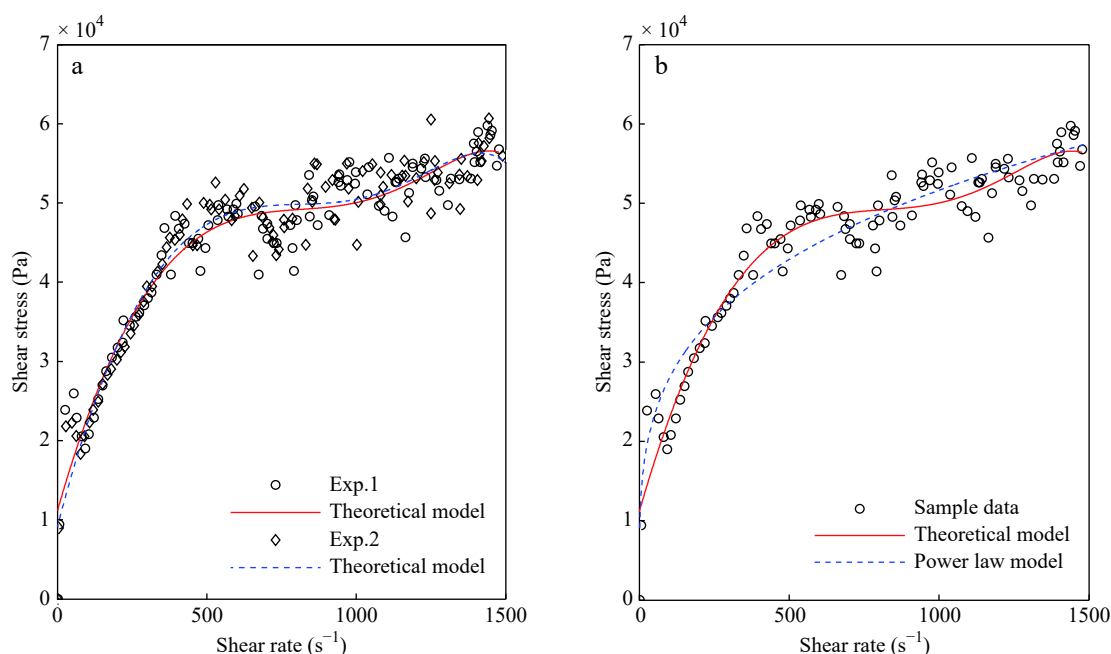


Fig. 2 Fitted results of the rheological experiments under higher shear rate condition: (a) The overall graphs of the shear stress against shear rate; (b) Theoretical model versus Ostwald-de Waele power law model

shear stress increases monotonically with the rise of shear rate in the initial stage, whereas it shows a peak value around 47846 Pa before the shear rate reaching about 536 s^{-1} and the shear time about 53 s. In the middle stage, the stress exhibits a slow increasing trend until reaching another peak point, corresponding to the shear stress roughly 51275 Pa, shear rate about 1175 s^{-1} , and shear time about 118 s. Then the curves show that the deformation becomes difficult, and give a general uptrend again in the final stage.

It is known that the polymer macromolecules give an elongation deformation owing to the shear stress loaded in shear flow, which leads to partial disentanglement and deformation of the polymer chain. Moreover, the disentanglement and elongation are still constrained with the counterforce coming from the others. In the initial stage, the disentanglement and entanglement rate of the polymer macromolecules keep in dynamic equilibrium due to the lower shear rate condition. The apparent viscosity of material remains as a constant. These results in the quasi-linear climbing trend of the curve. In the middle of the graph, the polymer coil will overcome the tangle force progressively as well as the constraints of tangled macromolecular chains (groups), and become easier to disentangle and deform under the steady shear flow conditions. PP material is a pseudoplastic polymer whose apparent viscosity decreases with the increase of shear rate, *i.e.* shear thinning; its flow displays a high-elastic behavior. A lower shear stress would induce a larger deformation in this stage. When the shear rate increases more, the disentanglement and elongation of the polymer chains become difficult. There is almost no entanglement of the macromolecules as the entanglement point is destroyed under the higher shear rate condition. The curves exhibit Newtonian fluid property again. The entire fitted curves predicted by the theoretical model agree well with the actual shear flow behavior of polymer melts.

Progressively, these specimen data extracted from the first experiment were substituted into the theoretical model and the classical Ostwald-de Waele power law model; the corresponding graphs of shear stress against shear rate are given in Fig. 2(b). The black scatter circle points in the figure represent the experimental results and the red solid and blue dashed curves denote the fitted result of the theoretical model and Ostwald-de Waele power law model, respectively. Table 2 presents the fitted results of constants in models, where m is a constant of materials and n is the non-Newtonian index in the Ostwald-de Waele power law model. The analysis of variance (ANOVA) was performed to determine the fitness of the model, as illustrated in Table 3, where SSE, RMSE, R -square (R^2), and adjusted R -square (R_{adj}^2) represent the sum of square due to error, root mean squared error, coefficient of determination, and degree-of-freedom adju-

Table 2 Constants of different models of PP material at 195°C

Model	Constants					
Theoretical model	$k\zeta_1$	$k\zeta_2$	$k\zeta_3$	$k\zeta_4$	$k\zeta_5$	$k\zeta_6$
	77.03	-289.96	81.18	211.72	24.48	1.42
Power law model	m	n				
	8177	0.2668				

Table 3 ANOVA results of different models of PP material at 195°C

Model	SSE	RMSE	R^2	R_{adj}^2
Theoretical model	9.043×10^8	3102	0.929	0.9252
Power law model	1.177×10^9	3466	0.9076	0.9066

ted coefficient of determination, respectively.

As shown in Fig. 2(b), the theoretical model exhibits a more reasonable tendency to describe the objective facts in comparison with the classical power law model. Especially, the theoretical model reflects the three-stage rheological property of polymer materials. There is a distinct shear thinning rheological region in the middle stage, reflecting the pseudoplastic fluids properties. This consequence is also exhibited by ANOVA result in Table 3, in which the theoretical model illustrates a smaller value of SSE and RMSE, and a bigger value of the R -square and the adjusted R -square. This indicates the speculative model matches well with the practical engineering applications.

Under the lower shear rate condition, the sample data and the fitted curves of the viscoelastic models at various temperatures were given in Fig. 3. Table 4 collects the fitted results of each constant in the two models. Table 5 summarizes the corresponding ANOVA results.

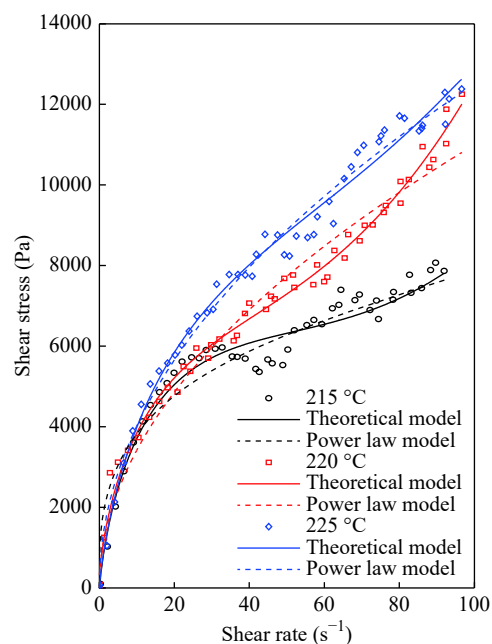


Fig. 3 Fitted results of the rheological experiments under lower shear rate condition

It can be seen from Fig. 3 that the distribution of data points shows a similar trends at 215, 220, and 225 °C. All the curves in the theoretical model of different temperatures reflect three stages, similar to those in Fig. 2. Meanwhile, the lower the temperature is, the more obvious the high-elastic effect is. Initially, the shear stress shows a quasi-linear rapid increasing tendency with the rise of the shear rate. This is the so-called first Newtonian area. The shear stress reaches to a peak value around 5930 Pa of 215 °C, 5950 Pa of 220 °C, and 6750 Pa of 225 °C, corresponding to the shear rate about

Table 4 Constants of different models of PP material at different temperatures

Temperature (°C)	Model	Constants					
215	Theoretical model	$k\zeta_1$	$k\zeta_2$	$k\zeta_3$	$k\zeta_4$	$k\zeta_5$	$k\zeta_6$
		21.72	-79.10	18.47	57.38	65.16	-0.17
220	Power law model	m	n				
		1816	0.3176				
225	Theoretical model	$k\zeta_1$	$k\zeta_2$	$k\zeta_3$	$k\zeta_4$	$k\zeta_5$	$k\zeta_6$
		22.11	-80.12	16.94	55.17	65.72	-0.11
225	Power law model	m	n				
		1010	0.5209				
225	Theoretical model	$k\zeta_1$	$k\zeta_2$	$k\zeta_3$	$k\zeta_4$	$k\zeta_5$	$k\zeta_6$
		20.29	-72.49	16.33	48.19	54.42	-0.15
225	Power law model	m	n				
		1282	0.495				

Table 5 ANOVA results of different models of PP material at different temperatures

Temperature (°C)	Model	SSE	RMSE	R^2	R_{adj}^2
215	Theoretical model	7.006×10^6	399	0.9559	0.9553
	Power law model	9.942×10^6	475.3	0.9397	0.9383
220	Theoretical model	3.918×10^6	298.4	0.9909	0.9898
	Power law model	1.139×10^7	497.7	0.9704	0.9697
225	Theoretical model	5.752×10^6	361.5	0.9893	0.9881
	Power law model	7.148×10^6	396.9	0.9847	0.9841

30, 25, and 26 s⁻¹, shear time about 9, 8.5, and 8.5 s, respectively. Then the curves turn into the high-elastic deformation stage, until the shear stress reaches to another peak value around 6990 Pa of 215 °C, 9000 Pa of 220 °C, and 10150 Pa of 225 °C, respectively. The shear time is about 18.4, 18.9, and 19.6 s while the shear rate rises to about 72, 72, and 65 s⁻¹ successively. Finally, the deformation becomes difficult when it reaches an equilibrium value after an adequate preparation and enters the so-called second Newtonian area.

Generally speaking, the corresponding curve of the theoretical model exhibits a three-stage rheological characteristic. Except for the first and second Newtonian area, there is a distinct high-elastic rheological region in the middle stage, reflecting the feature of pseudoplastic fluids. The theoretical model agrees well with the actual shear flow behavior of polymer melts.

Moreover, Fig. 3 indicates clearly that the theoretical model shows a better agreement with the rheological practices than the power law model does. This result is also exhibited by ANOVA result in Table 5, in which the theoretical model reaches a smaller value of SSE and RMSE and a bigger value of the R -square and the adjusted R -square.

CONCLUSIONS

By coupling with the thermodynamics, statistical mechanics, and continuum mechanics theory, a viscoelastic mathematical model was deduced to describe the instantaneous shear flow behavior of the compressible and isothermal thermoplastic polymer with the essential simplification and hypothesis. The integral formula with a same form of the K-BKZ model was derived. The common thermoplastic polymer, polypropylene,

was used to conduct the rheological tests. The sample data were collected and fitted. The analysis of the variance (ANOVA) method was performed to determine the fitness of the model. Compared with the Ostwald-de Waele power law model, the experimental results indicate that the theoretical model is effective and robust, and exhibits a three-stage rheological characteristic. Especially, there is a distinct high-elastic rheological region in the middle stage, reflecting the pseudoplastic fluid property. The scientific result is helpful for studying the transient shear stress and conformation response of polymer materials under shear flow conditions.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51565034), the National Key Technology Research and Development Project of Jiangxi Province, China (No. 20151BBE50033), and the Key project of Scientific research of the Education Department of Jiangxi Province, China (No. 150009).

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