

NUMERICAL SIMULATION OF MORPHOLOGY OF POLYMER CHAIN COILS IN COMPLEX FLOWS*

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Abstract A new coupled finite element formulation is proposed to calculate a conformation tensor model in two complex flows: a planar contraction flow and a planar flow around a symmetrically placed cylinder. The components of conformation tensor are first computed together with the velocity and pressure to describe the change of morphology of polymer chain coils in flow fields. Macroscopic quantities of viscoelastic flow are then calculated based on the conformation tensor. Comparisons between the numerical simulations and experiments for stress patterns and velocity profiles are carried out to prove the validity of the method.

Keywords: Viscoelastic flow; Morphology; Complex flows; Conformation tensor model; Finite element method (FEM).

INTRODUCTION

The relation between the complex viscoelastic properties of polymer melts and their multi-scale structures as well as dynamics is a key issue in modern materials science and engineering. During processing those structures experience actions of flow and change with both position and time at a flow path. It is well accepted that morphology of polymer chain coils is one essential level of the structures that relate to the macroscopic and microscopic properties. In order to simulate the coils evolution in flow fields, we studied a phenomenological model of chain coils of polymer melts and solutions as well as a new kind of finite element approach.

Conceptually, an imaginary conformation ellipsoid is supposed to describe the shape of chain coils of polymer melts and solutions, which is represented by a second rank conformation tensor C , and to be related to the volume element in mathematical sense in continuum mechanics. After adopting the Hookean free energy and the dissipation parameter for Hookean dumbbell, we have derived an evolution equation of the conformation tensor through Beris and Edwards' approach^[1]. Usually, the Hookean element has a constant volume and behaves in a linear way while chain coils possess changeable envelope volume and has nonlinear property in flow fields. Therefore, it is necessary to make the modulus of Hookean element from a constant to a nonlinear function with the conformation tensor of chain coils. It was noted many years ago that the stress can be written in a time-strain separable form from stress relaxation data for polymer melts. That is, the modulus could be expressed as a product of the modulus depending on relaxation time and the damping function relying on melt strain that relates with the change of the imaginary conformation ellipsoid. Thus, we obtained a rheological model of polymer chain coils represented by the conformation tensor in a flow^[2]. The advantage of this model lies in its simplicity therefore it is easy to solve any engineering problems in polymer processing, and feasible to couple with dynamic equations of the polymeric fluids. Furthermore, the envelope volume of the chain coil is related to chain

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entanglement that is closely related to the characteristic property of polymeric materials, namely, the viscoelasticity.

During the last decade, significant progress has been made in the development of numerical algorithms for calculating the viscoelasticity of the polymer melts and solutions in flow fields. The so-called streamline-upwind/Petrov-Galerkin (SUPG) method of Brooks and Hughes^[3] is widely used to overcome the convergent difficulty caused by the convective term. An alternative to SUPG method is the discontinuous Galerkin (DG)^[4] in which the stress tensor is approximated discontinuously from one element to the next. Using these effective numerical approaches high Weissenberg number is obtained for viscoelastic flow problems with the variables (u , p , τ). Kajiware^[5] simulated the converging flow of low density polyethylene (LDPE) using a single-mode Phan-Thien-Tanner (PTT) model and compared the calculated stress with experiments. It was found that the predicted normal and shear stresses deviate only 20%. Baaijens^[6] reviewed the application of different constitutive equations and several mixed finite element methods in the numerical simulation of complex flows. All these similar investigations used the conventional approaches based on the conservation laws for mass, momentum and energy, which cannot describe internal microstructure changes of polymer melts and solutions in flow fields. The method of using the conformation tensor model with internal parameters to compute a complex flow field directly and then calculating the macroscopic quantity such as stresses has not been reported yet.

How to calculate the components of the conformation tensor in a flow field is another problem. We once adopted a 3.29:1 contraction flow geometry as a test field and used a decoupled finite element method to compute flow variables and the chain conformation, *i.e.* the calculation of the conformation tensor based on the velocity gradient computed from the conservation laws for mass, momentum and energy, and the constitutive model of viscoelastic fluids^[7]. That is an easy but inaccurate way without considering the effects of the changes of conformation on the flow. In order to correlate both effects, a new coupled finite element method is proposed in this paper to compute velocity-pressure-conformation tensors simultaneously and then calculate the stress and other viscoelastic properties of the polymer melts and solutions in complex flow fields. Firstly, we will work out coupled weak forms including velocity, pressure, and conformation tensor from coupled dynamic equation and continuous equations. Then a finite element code will be used to compute the conformation evolution of LDPE melts and a 5% polyisobutylene solution in tetradecane (PIB/C14) in both the abrupt planar contraction flow field and the planar flow around a cylinder. The computational results will be compared with the experimental data as well as the results computed from PTT model for velocity and stress distributions.

BASIC EQUATIONS

In what follows, u , p and τ denote the velocity field, the pressure and the extra-stress tensor respectively. For incompressible, isothermal, steady state viscoelastic flows the conservation equations for mass and momentum may be expressed as follows, respectively:

$$\nabla \cdot u = 0 \quad (1)$$

$$-\nabla \cdot \tau + \nabla p = 0 \quad (2)$$

A phenomenological conformation tensor model proposed by the author has been chosen as the constitutive equation of the flow. This model yields not only a shear-thinning in simple shear but also an extensional viscosity in simple extension, which is shown in Ref. [2]. The author assumed that the free energy and the recoverable force would increase when the polymer chain was extended and oriented. Therefore, the shear modulus G should be increased with chain extension. A simple expression was proposed to describe this relation:

$$G = G_0 \cdot h(C) = G_0 / |C|^{n+1} \quad (3)$$

where G_0 the modulus at rest, $h(C)$ the damping function, n the flow index of the power law model.

Based on the above idea and follow the Hamilton-Poisson bracket formulation, the phenomenological model is obtained as:

$$\left(\frac{DC}{Dt} - \nabla u \cdot C - C \cdot \nabla^T u\right) = \lambda_c (C \cdot C - C) \quad (4)$$

$$\tau = G (C \cdot C - C) \quad (5)$$

where t is time, $\lambda_c = G/\eta_0$ denotes the inverse of relaxation time of the materials in flow, η_0 is the zero-shear viscosity, superscript T denotes a tensor transpose. $D/Dt = \partial/\partial t + u \cdot \nabla$ is the substantial or material time derivative. The conformation tensor C_{ij} is assumed to be symmetric, positive and definite. From the physical point of view, the determinant of conformation tensor C_{ij} ($\det C$) may represent the degree of entanglements of polymer chains in flow field and the trace of C_{ij} ($\text{tr} C$) may be a quantity related to the entropy. Moreover, the extension degree and orientation angle of polymer coil can be described through computing the eigenvalues and eigenvectors of tensor C_{ij} .

NUMERICAL METHOD

In this section we will construct a new numerical method, which can be applied to simulate the complex viscoelastic flow problems with lower computational cost and which calculates the components of conformation tensor in the flow fields directly. Comparison with the measurement was carried out to indicate the validity of the method.

Firstly, we rewrite the governing set of equations for the flow problem in dimensionless form:

$$\nabla \cdot u = 0 \quad (6)$$

$$-\nabla \cdot \tau + \nabla p = 0 \quad (7)$$

$$We \cdot \left(\frac{\partial C}{\partial t} + u \cdot \nabla C - \nabla u \cdot C - C \cdot \nabla^T u\right) = -(C \cdot C - C)/|C|^{n+1} \quad (8)$$

$$\tau = (C \cdot C - C)/|C|^{n+1} \quad (9)$$

where Weissenberg number $We = \lambda_0 \langle u \rangle / h$, λ_0 is the characteristic time of the polymeric melts at rest, $\langle u \rangle$ is the mean upstream velocity and h is the downstream channel height in a contraction flow. Weissenberg number is used as a characterization of material elasticity in investigated flows and flow conditions. After the stress tensor τ in the momentum equation is substituted by Eq. (9), simultaneous equations which are completely determined by the velocity field u , the pressure field p and the conformation tensor field C are obtained. Therefore, a direct mixed finite element procedure based on (u, p, C) can be constructed. The strong formulation of the problem can be expressed as:

Find $(u, p, C) \in U \times P \times C$ such that

$$\nabla \cdot u = 0, \text{ on } \Omega \quad (10)$$

$$-\nabla \cdot \left[(C \cdot C - C)/|C|^{n+1} \right] + \nabla p = 0, \text{ on } \Omega \quad (11)$$

$$We \cdot \left(\frac{\partial C}{\partial t} + u \cdot \nabla C - \nabla u \cdot C - C \cdot \nabla^T u\right) = -(C \cdot C - C)/|C|^{n+1}, \text{ on } \Omega \quad (12)$$

with boundary conditions $u = u_0$ on $\partial\Omega_u$ and $C = C_0$ on $\partial\Omega_C$. U , P and C are function spaces defined on the flow domain Ω for u , p and C , respectively.

The mixed variational formulation, in which the Galerkin weighted residual method is used for the momentum and continuity equations and the streamline-upwind technique (SU) for the constitutive equation, is stated as follows:

Find $(u, p, C) \in U \times P \times C$ such that

$$\int_{\Omega} q_h \nabla \cdot u d\Omega = 0, \forall q_h \in P \quad (13)$$

$$\int_{\Omega} [(C \cdot C - C)/|C|^{n+1} : \nabla v_h - p \nabla v_h] d\Omega = \int_{\partial\Omega} (C \cdot C - C)/|C|^{n+1} : n v_h d\partial\Omega, \forall v_h \in U \quad (14)$$

$$\int_{\Omega} \left[We \cdot \left(\frac{\partial C}{\partial t} + u \cdot \nabla C - \nabla u \cdot C - C \cdot \nabla^T u \right) + (C \cdot C - C)/|C|^{n+1} \right] : \gamma_h d\Omega + \int_{\Omega} (\alpha u \cdot \nabla \gamma_h) : (u \cdot \nabla C) d\Omega = 0, \forall \gamma_h \in C \quad (15)$$

The streamline-upwind factor α is chosen to be

$$\alpha = h/|u|_m \quad (16)$$

where h is the element size along the local flow direction and $|u|_m$ is a mean value of the velocity magnitude over the element and q_h, v_h, γ_h denote the corresponding elements belonging to the approximation spaces of u, p, C , respectively.

It is well known that a compatibility condition, LBB-condition^[8], needs to be satisfied between the velocity and pressure interpolation. The addition of the weak form of the constitutive equation imposes compatibility constraints on the interpolation of the triple conformation-velocity-pressure. Here, the velocity is approximated by continuous quadratic polynomials, the pressure by piecewise discontinuous linear polynomials, and the conformation tensor by piecewise discontinuous linear polynomials. Such kind of discretization is found to be sufficiently stable and convergent up to high Weissenberg numbers.

RESULTS AND DISCUSSION

The numerical results based on the above formulations together with the material parameters are now presented and discussed. In order to verify the validity of the coupled FEM, the results of numerical simulation for velocity profiles in two complex flows, *i.e.* planar contraction flow and planar flow around a cylinder, are compared with the experiment data for PTV (Particle Tracking Velocimetry) and the predicted stress with FIB (Flow Induced Birefringence).

To obtain the material data in the conformation tensor model considered here, the shear and elongational experiments which were performed on the LDPE (Stamylan LD 2008 XC43) melt and PIB/C14 solutions should be recovered^[9, 10]. The zero-shear viscosity (η_0) of LDPE melts and PIB/C14 solution can be achieved from the steady-state viscosity data. Then the simple power law model is used to fit the viscosity curve, and the flow index n for the power law model can be obtained. The material parameters are listed in Table 1, and the conformation tensor model is used to fit the viscometric shear data of LDPE melts and PIB/C14 solution based on these parameters. Figure 1 shows the comparison between the model prediction and experimental measurements. It is clear that this conformation tensor model can describe the viscoelasticity of polymer melts and solution in simple shear flow quite well.

Table 1. Material characterization of LDPE melts and PIB/C14 solution

Materials	n	λ_0 (s)	G_0 (Pa)	η_0 (Pa · s)
LDPE melts	0.46	17.4	133	2306
PIB/C14 solution	0.48	0.13	10.95	1.424

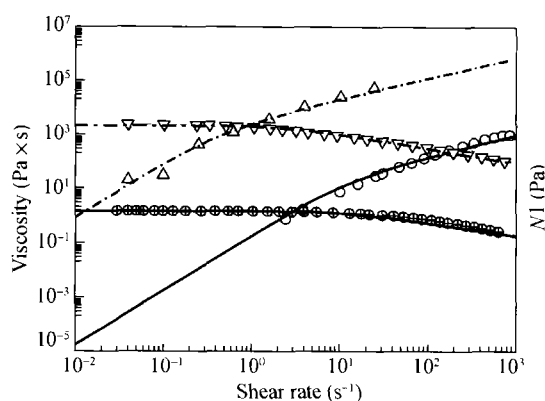


Fig. 1 Comparison between the model prediction and experiments in the simple shear flow of LDPE melts and PIB/C14 solution, respectively

△: Viscosity for LDPE; ▽: The first normal stress difference $N1$ for LDPE; ⊕: Viscosity for PIB/C14; ○: $N1$ for PIB/C14

Planar Contraction Flow

PIB/C14 solution

The numerical results for the first normal stress difference $N1$ along the centerline of 3.97:1 contraction flow of PIB/C14 solution at four We ($We = 0.38, 0.49, 0.55, 0.66$) are compared with the experiments^[11] in Fig. 2. $x = 0$ corresponds to the re-entry of planar contraction flow, and the maximum of $N1$ appears at this point. The first normal stress difference increases with the increasing We . The results of our simulations can capture the peak position of $N1$ along the centerline quite well. At the highest Weissenberg number ($We = 0.66$), only a small amount of deviation is observed.

LDPE melts

Based on the above algorithm, the problem of viscoelastic flow in contraction flow has converged at a very high Weissenberg number ($We = 5.5$). Here the results of simulation of velocity and stress distribution at $We = 5.5$ are compared with the experiments experienced on LDPE melts from Schoonen^[9]. Firstly the predicted velocity profiles for $We = 5.5$ at four cross-section lines ($x/h = -6, -4, -1, 1$) and that at centerline are presented in Fig. 3, which are compared with the PTV data. From Fig. 3(a) it can be seen that the numerical results over-predict the velocity of the flow over the centerline. In the upstream, the predicted velocity increases earlier and slower than the experimental data along the centerline. This deviation may be caused by the simple and phenomenological modification to the shear modulus in the conformation tensor model, which has been discussed above. Over the centerline of contraction flow, the polymer coil is extended greatly. The closer to the contraction point (*i.e.* $x = 0, y = 0$), the stronger extension may be experienced on the polymer coils. In this case the relation between the shear modulus in the free energy formulation and the conformation tensor may not be described with a simple power law model. That is also the important reason for the deviation of other macroscopic quantities in the extension-dominant regions. In spite of that numerical simulation gives an excellent agreement for the velocity peak at the position $x/h = 0.5$.

In Fig. 3(b) on the cross-section line $x/h = -1$ and $x/h = 1$, the similar difference of velocity distribution recurs. And from numerical results at $x/h = -4$, it seems that the conformation tensor model predicts a larger undeveloped region than the experiments, *i.e.* the change of the velocity profile occurs farther away from the contraction zone. Nevertheless for a large scale $y/h > 0.5$, the computed values work fairly well with the experimental data.

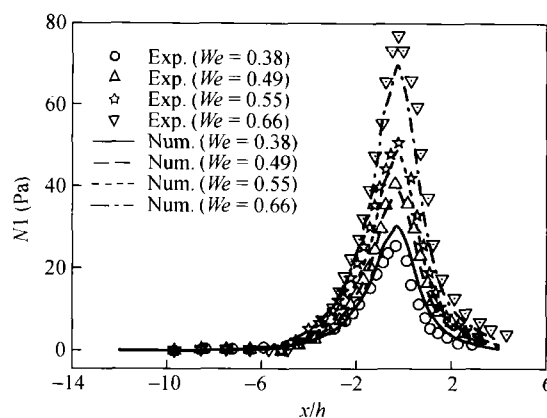


Fig. 2 Comparison between numerical simulation and FIB measurements of the first normal stress difference $N1$ along the centerline of 3.97:1 planar contraction at four flow rates

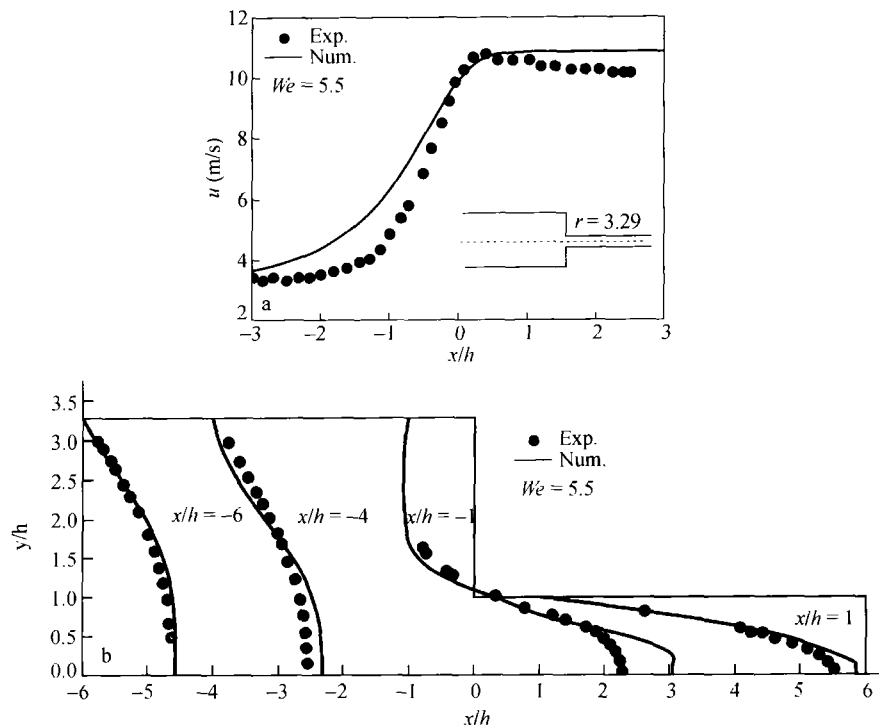


Fig. 3 Comparison of numerical results and the experiments for velocity profile at different cross-sections
a) Over centerline; b) $x/h = -6, -4, -1$ and 1 , where r represents the contraction ratio

Secondly, for more quantitative comparison, stress measurement along the centerline is compared with the numerical results. Figure 4 shows the distribution of the normal stress difference $N1$ from experiments and numerical simulations. The first normal stress difference shows a maximum at the entrance as in Fig. 2. Numerical simulations based on the conformation tensor model can also predict such phenomena, and accurately capture the position and maximum of $N1$. However, at both downstream and upstream of contraction flow the model over-predicts $N1$ value as compared with the stress measurement. The deviation at the upstream appears larger than that at the downstream. The former deviation may be caused by the unstable flow near the contraction region and the latter may be due to non-fully developed flow in those regions. Schoonen^[9] predicted the distribution of the first normal stress difference $N1$ along the centerline using the classical PTT and Giesekus model and found these model under-predicted the experiments. They ascribed this deviation to the poor description of the elongational behavior by these models. This is also the possible reason for the unsatisfactory prediction of the conformation tensor model, since only shear experiments are used in determination of the parameters.

Planar Flow around a Cylinder

The results are presented in this section for the planar flow around a symmetrically placed cylinder. It has been proposed as a benchmark problem for numerical techniques. Figure 5 schematically shows the geometry and definition of dimensions. For this kind of flow, We is made as follows:

$$We = \frac{\lambda_0 \langle u \rangle}{R} \quad (17)$$

with $\langle u \rangle$ the mean upstream velocity, and R the radius of the cylinder, and λ_0 the characteristic relaxation time of the fluid at rest.

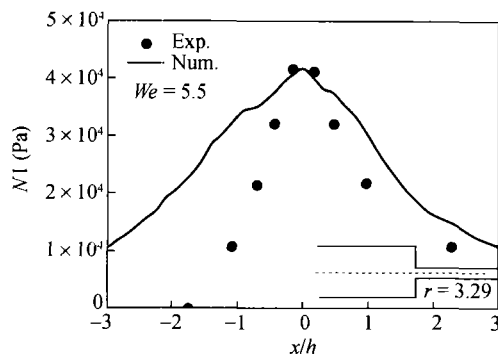


Fig. 4 Calculated and measured $N1$ in the 3.29:1 planar contraction flow over the cross-section for $We = 5.5$

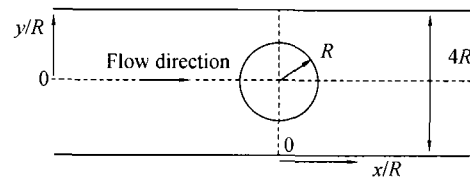


Fig. 5 Schematic of the flow around a cylinder of an LDPE melt
The radius is R , the height of the channel is $4R$ and the center of cylinder is at $x = 0, y = 0$

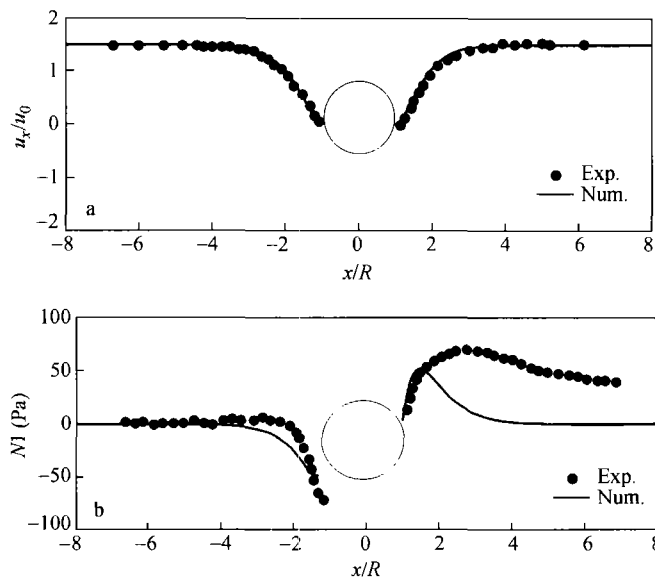


Fig. 6 Comparison of velocity u_x and the first normal stress difference $N1$ and along the symmetry line of a planar flow around a cylinder of PIB/C14 solution

PIB/C14 solution

Figure 6 shows the velocity profile and the first normal stress difference distribution along the centerline for PIB/C14 solution from experiments^[12] and simulations for $We = 0.216$. Along the centerline, good agreement between the predicted and measured velocity profile is observed. In Fig. 6(a), both the predicted and the measured data show that the flow speeds drop down at $x/h = -3$ toward the cylinder and speeds up at the symmetrical position $x/h = 3$. Little difference about $N1$ is observed at the upstream of the flow geometry (Fig. 6b). At the downstream $N1$ distribution is under-predicted by the model. Experimentally, after undergoing the unstable flow, the stress reaches a maximum and then relaxes gradually, while the numerical simulation shows a fast jump followed by a much faster decrease along the centerline. The above phenomenon may be caused by the physical essence of the model of conformation ellipsoid. Physically, in the flow field the conformation sphere changes into a conformation ellipsoid, even conformation pipe under a high shear rate. When the flow vanishes the conformation sphere recovers, which means the relaxation of the deformation and orientation of the macromolecule will vanish simultaneously. This may not be consistent with the actual motion of the polymer coil. The process of slacking molecular orientation is longer than that of the deformation, *i.e.* the macromolecular orientation lasts longer than the deformation without any flow. Therefore, the predicted stress relaxes much faster than the experimental data.

LDPE melts

The measured velocity profile by PTV^[9] and the predicted velocity distribution ($We = 1.2$) at five different cross-section lines are shown in Fig. 7. It is clear that the numerical simulation results are similar and in good agreement with the experiments. At higher We the convergent solution also gives an exact prediction of the velocity profile compared with the measurements. This indicates the better performance of the numerical simulation of the conformation tensor model in a planar flow around a symmetrically placed cylinder than in a contraction flow.

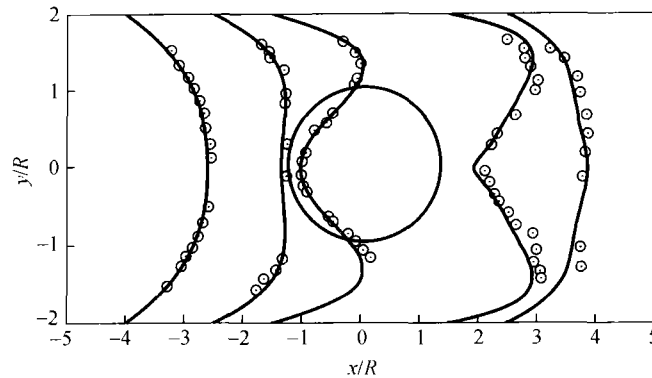


Fig. 7 Measured ($\circ$) and calculated velocities (---) along several cross-sections ($x/R = -4, -2.5, -1.5, 1.5, 2.5$)

Moreover, a comparison is carried out on the isochromatic patterns^[9]. The FBI method is based on high birefringence level and therefore applicable for polymer melts flows. For comparison the computed stress patterns are calculated according to the following equation^[9]:

$$N = \frac{C_{op}d}{\lambda} \sqrt{4\tau_{xy}^2 + N1^2} \quad (18)$$

where N is the fringe order, C_{op} the stress-optical coefficient, d the thickness of medium, λ the wavelength, τ_{xy} the shear stress and $N1$ the first normal stress difference.

The comparison of the measured and calculated isochromatic pattern is shown in Fig. 8. The agreement between the measured isochromatic patterns and those calculated by the conformation tensor model is fairly good. In those fully developed region such as $x/R = -4$ both position and number of the predicted fringes are very close to the measured pattern. At the center region where the flow rate is rather high the observed number of fringes becomes lesser and some elliptical fringes disappear. The deviation may be due to the end-effects^[9]. The similar results can be found in PTT model simulation and in that case the fringes observed in this region were more oval shaped than the predicted ones^[9].

The Conformation of Polymer Melts in Two Complex Flows

There are different types of flow regions, such as shear-dominated, extension-dominated regions in the two present complex flow domains. The components of conformation tensor are calculated to describe the deformation, extension and orientation of polymer coils in those flow regions. The distribution of the conformation ellipsoid is shown in Fig. 9 to display the evolution of polymer coils in different flow regions. At the centerline of contraction flow, pure extension is observed which indicates no shear here. Not only are polymer coils deformed but also oriented, indicating the coexistence of shear and extension at the re-entry of planar contraction flow. Due to the small velocity gradient in the vortex region, the coils deform slightly.

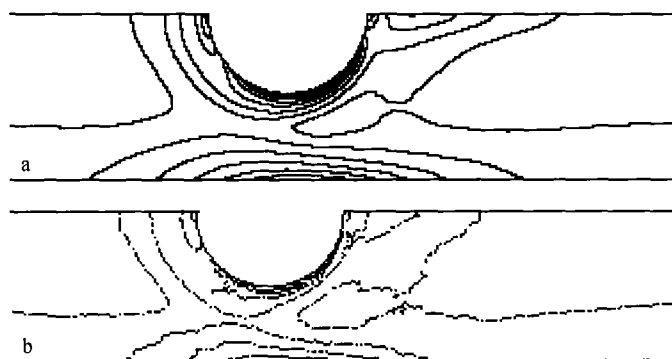


Fig. 8 Measured (a) and calculated (b) isochromatic patterns for the flow around a cylinder

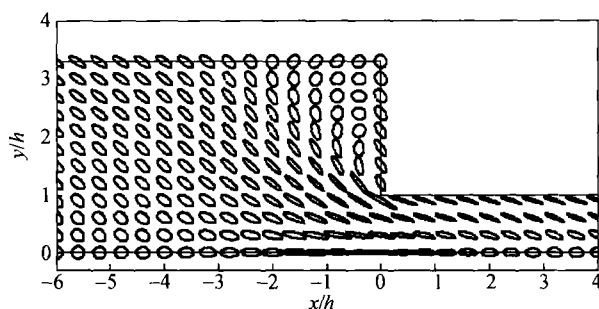


Fig. 9 The distribution of the conformation ellipsoid of LDPE melts in 3.29:1 contraction flow for $We = 5.5$

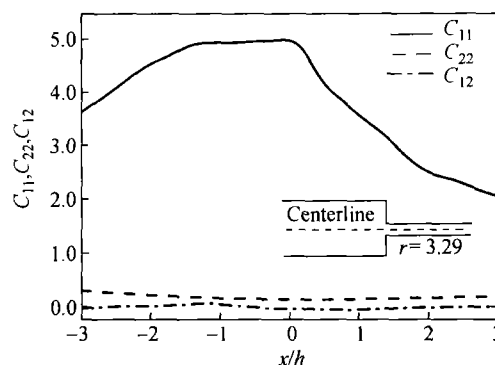


Fig. 10 A plot of the distribution of C_{11} , C_{22} , C_{12} over the centerline in contraction flow for LDPE melts

The distributions of C_{11} , C_{22} and C_{12} , along the centerline region of 3.29:1 contraction flow of LDPE are shown in Fig. 10. In this region C_{12} nearly vanishes which represents that the orientation angle is zero. $C_{11} \gg C_{22}$ indicates the high extension degree of the chain. This may result in a large extension of polymer chains and a strong resistance to deformation, therefore causing a thickening viscosity.

To investigate the influence of the shear and extension flow on the changes of envelope volume of the polymer chain, the distribution of $\det C$ in the 3.29:1 contraction flow and the planar flow of LDPE around a cylinder is shown in Fig. 11. It can be seen from the figure that the envelope volume of polymer coils decreases in the region where the polymer chain is extended. The conformation ellipsoid may evolve into a conformation pipe in the high extensional region. This results is similar with Liang's^[7]. The reason for the decrease of conformation volume may be due to the disentanglement of polymer chains under flow.

CONCLUSION

In this paper, a new finite element formulation was conducted to calculate a conformation tensor model proposed by the author in a planar contraction flow and a planar flow around a symmetrically placed cylinder. The numerical results were compared with the experiment data from FIB and PTV to investigate the validity of our method: for PIB/C14 solutions the predicted $N1$ fits the measurements along the 3.97:1 contraction flow at four flow rates. At high Weissenberg number the numerical simulation cannot capture the flow behavior of LDPE melts in contraction flow perfectly. A small deviation was observed in the comparison between the velocity profiles along the centerline and at four cross-section lines. Relatively better performance of the conformation tensor model was found in the flow around a cylinder than in the contraction flow. The comparison of the velocity distribution for both the LDPE melts and PIB/C14 solution showed good agreement with the

experiments. Also the isochromatic patterns of the fluid were taken into account and a good agreement was shown. Due to the limitation of the model itself the expected deviation of $N1$ in some unstable regions appeared. The above comparisons indicated the good applicability of our new finite element formulation for computing the conformation tensor model in complex type of flows in a sense. Finally we investigated the contour distribution of the conformation tensor in both shear-dominant and extension-dominant regions. According to the change of $\det C$, we imaged that the conformation ellipsoid changed into a conformation pipes under elongation-dominant flow.

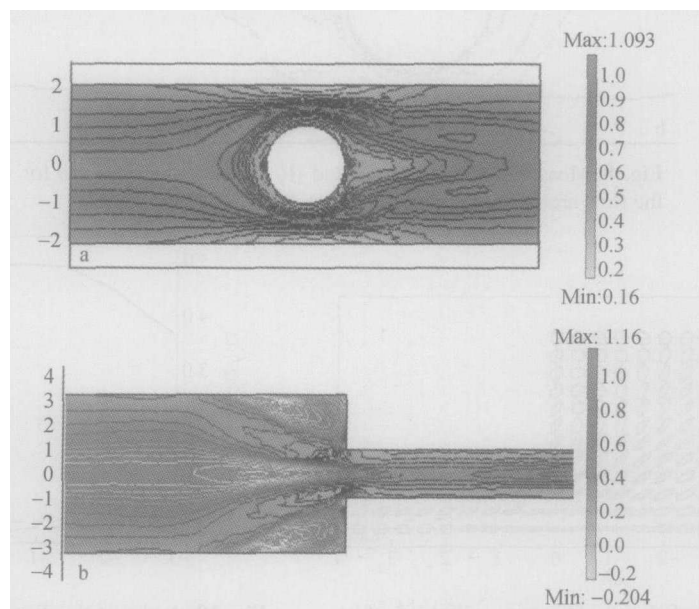


Fig. 11 Contour of determinant of conformation tensor ($\det C$) in two complex flow fields for LDPE melts
a) planar flow around a symmetrically placed cylinder; b) 3.29:1 contraction flow

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