

MODELING THE CHAIN CONFORMATION OF POLYMER MELTS IN CONTRACTION FLOW*

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Abstract A constitutive model of quasi-Newtonian fluid based on the type of flow is used in abrupt planar contraction flow. The numerical results from finite element analysis are consistent with experimental data for stress patterns and velocity profiles in the flow field. The chain conformations of polymer melts are then investigated in such a planar contraction by using the phenomenological model with internal parameters proposed by the author. That is, the shape and orientation of polymer chain coils are predicted and discussed in different flow regions of the contraction flow field that possess simple shear flow, extensional flow, vortical flow, and mixed flow respectively.

Keywords Polymer melts, Chain conformation, Contraction flow, Modeling, Computer simulation

INTRODUCTION

An abrupt contraction manifests the significantly different flow behavior of Newtonian and non-Newtonian fluid. Generally, there are various approaches to simulate the fluid flow in the contraction channel depending on the description method of polymer melt. One approach focuses mainly on utilizing various viscoelastic constitutive models in simulations. Li *et al.*^[1] used a one-mode Phan-Thien and Tanner (PTT) constitutive model to calculate the 4:1 planar contraction flow with a Lagrangian-Eulerian method. The numerical predictions agree with the experimental reports fairly well. However, the viscoelastic flow simulation of polymeric fluid is rarely employed in engineering design due to its difficult problem formulation and high computational costs to solve non-linear constitutive equations. The other approach takes into consideration that the complex rheological behaviors of polymer melts, such as shear-thinning and extension-thickening viscosity, often play a more important role than viscoelasticity in contraction flow^[2]. This allows us to take advantage of simple velocity-pressure algorithms in numerical computations, where a generalized Newtonian constitutive equation with shear-thinning viscosity is often used to solve shear-dominated flow in industrial applications, such as injection molding.

However, in planar contraction flows where extensional flows exist, predictions from a generalized Newtonian formulation can be quite different from the real polymeric flow. Therefore, use of a constitutive equation, which can predict shear as well as extensional viscosity, is required for an accurate simulation of such flows. To weaken the limitations of generalized Newtonian models without changing the simplicity, Schunk and Scriven^[3] introduced a concept of a quasi-Newtonian fluid (QNF), whose viscosity function depends on both rate-of-deformation tensor and relative-rate-of-rotation tensor. Following this idea, Ryssel and Brunn^[4] introduce a quasi-Newtonian fluid model to simulate the non-Newtonian flow in abrupt planar contraction. They concluded that a quasi-Newtonian fluid yielded an overshoot of centerline velocity after entering the contraction region.

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They continued their work^[5] to conduct a comparison of the flow of an inelastic quasi-Newtonian fluid with a viscoelastic fluid. Thompson *et al.*^[6] presented a new constitutive equation for the simulation of contraction flow and proposed that the new equation perform much better than differential constitutive equation like the Oldroyd-B model in computational effort and convergence problems. Gupta^[7] developed finite-element software for simulating contraction flow of polymer. They used a truncated power-law model to represent shear viscosity as well as extensional viscosity.

All the similar investigations above use the conventional approaches based on the conservation laws for mass, momentum, and energy, which can not describe internal microstructural changes of polymer melt in the flow field. However, as we know, polymer complex fluids have various internal microstructures, which are subject to change under flow and contribute to the extra stress. The phenomenological model previously provided by the author^[8] could predict the shape and orientation of the chain coils of polymer melts in flow fields. Therefore this model is used in an abrupt planar contraction flow for the quasi-Newtonian fluids. That is, after the accurate simulations of the quasi-Newtonian fluids, the evolutions of conformation of polymer melt in such flow fields are calculated.

In this paper, the abrupt planar contraction flows of quasi-Newtonian fluids are assumed to be under steady, isothermal conditions. Finite element analysis is used to calculate the flow fields. Numerical simulation is undertaken for 3.29:1 planar contraction flow. The computed results are compared with the experimental data from Schoonen^[9] and Verbeeten^[10] to examine the validity of numerical simulation. And stable, accurate simulation results are obtained from the comparison between them.

This paper is organized as following. In Section 2 are presented the conservation and the QNF constitutive models based on the type of flow, also the boundary conditions for the contraction geometry. The phenomenological models with internal structure parameters are presented in Section 3. The numerical methods, used to solve governing equations and evolution equation of conformation tensor, are introduced in Section 4. In Section 5, the results and discussion part, the comparisons with experiments^[9] and predictions of the chain conformation in the contraction flow are presented. Finally, the concluding remarks are given in Section 6.

GOVERNING EQUATIONS AND BOUNDARY CONDITIONS

The steady state and isothermal creep flow of an incompressible fluid are governed by a set of conservation and constitutive equations. The mass, momentum conservation equations are as follows:

$$\nabla \cdot \mathbf{v} = 0 \quad (1)$$

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

where $\mathbf{v}$ is the velocity, p the pressure, $\boldsymbol{\tau}$ the extra-stress tensor. For a quasi-Newtonian fluid model (QNF), the constitutive equation can be written as

$$\boldsymbol{\tau} = \eta_{\text{QNF}} \mathbf{D} \quad (3)$$

where $\mathbf{D}$ is the rate of deformation tensor, defined as $[\nabla \mathbf{v} + (\nabla \mathbf{v})^T]/2$ and η_{QNF} is a quasi-Newtonian viscosity function that can account for shear thinning as well as extension thickening according to the type of flow. That is to say, besides the rate of deformation tensor $\mathbf{D}$, a second kinematic quantity is needed to provide information about the type of flow. Following Astarita^[11], we use the relative-rate-of-rotation tensor $\overline{\mathbf{W}}$ to reflect the extensional properties of the flow field:

$$\overline{\mathbf{W}} = \mathbf{W} - \Omega \quad (4)$$

where $\mathbf{W}$ is the vorticity tensor, defined as $[\nabla \mathbf{v} - (\nabla \mathbf{v})^T]/2$, Ω the rate of rotation of $\mathbf{D}$ at a particle. If $\mathbf{e}_i$ are the unit vectors along the principal axes of $\mathbf{D}$, the definition of Ω is:

$$D\mathbf{e}_i/Dt = \Omega \cdot \mathbf{e}_i \quad (5)$$

where D/Dt is the substantial time derivative. Because $\overline{W}$ is a difference between two angular velocities, it is clear that it is a frame-indifferent quantity. Astarita^[11] claimed that the ratio

$$R = \frac{\text{tr} \overline{W}^2}{\text{tr} D^2} \quad (6)$$

could be used to classify type of flow. R has the interesting property of taking the values of 0 in pure extension and 1 in shear flows. Depending on the value of R , the viscosity function is given as follow^[3]:

$$\eta_{\text{QNF}} = \eta(S, R) = f(R) \eta_{\text{sh}} + (1 - f(R))(1/4 \eta_{\text{ex}}) \quad (7)$$

where S is defined as $\sqrt{(\text{tr} D^2)/2}$ and $f(R)$ is an arithmetic weighting function. The shear viscosity is approximated by the Carreau-Yasuda model (CYM)^[12] whose four parameters allow a great flexibility in fitting experimental data. The viscosity function is

$$\eta_{\text{sh}} = \eta_0 (1 + (\lambda_{\text{cy}} S)^\alpha)^{(n-1)/\alpha} \quad (8)$$

where η_0 denotes the zero-shear-rate viscosity, λ_{cy} the time constant, n the “power-law exponent” and α a dimensionless parameter describing the transition region between the zero-shear-rate region and the power-law region. It will be shown later that the model approximates the experimental data rather well (in Fig. 1). For the extensional viscosity experimental data are not available and we chose the following expression^[4]:

$$\eta_{\text{ex}} = 4\eta_0 \frac{1 + \alpha_{1E} S^2}{1 + \alpha_{2E} S^2} \quad (9)$$

whose functional form yields a finite valued infinite-extension-rate viscosity. The extension parameters α_{1E} and α_{2E} can be chosen independently from those of CYM. For the following simulations we use the extension parameters with an extension parameter ratio of $\alpha_{1E}/\alpha_{2E} = 14.5$.

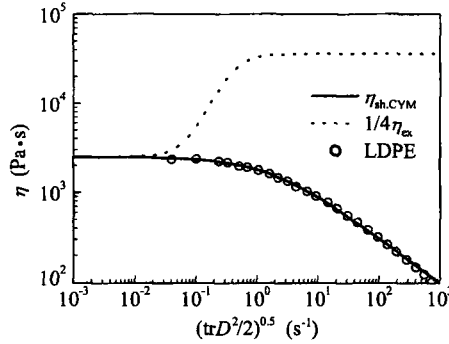


Fig. 1 Flow curve of the LDPE melt fitted with the Carreau-Yasuda model and extensional viscosity function

The planar contraction geometry with boundary conditions is shown Fig. 2. The upstream radius is $H = 3.29$ mm and $h = 1$ mm for the downstream radius. The lengths of upstream and downstream are taken as 20 h and 20 h. The inlet velocity is supposed to be a fully-developed one. The velocities at the centerline and the wall satisfy symmetry and no-slip condition, respectively.

PHENOMENOLOGICAL MODEL WITH INTERNAL STRUCTURE PARAMETER^[8]

Conceptually, the shape of the polymer chain for polymer melts can be represented by an imaged conformation sphere. The polymer chain is extended and oriented under flow field, thus the conformation sphere evolves into a conformation ellipsoid. Finally the ellipsoid becomes a conformation pipe when the shear or extension rate is

extremely high.

We use the internal structure tensor C_{ij} to describe the conformation of the polymer chain, which is defined as the second moment of the configuration space distribution function ψ , i.e., $C_{ij} = \int R_i R_j \psi dR$, in which R_i is the end-to-end vector.

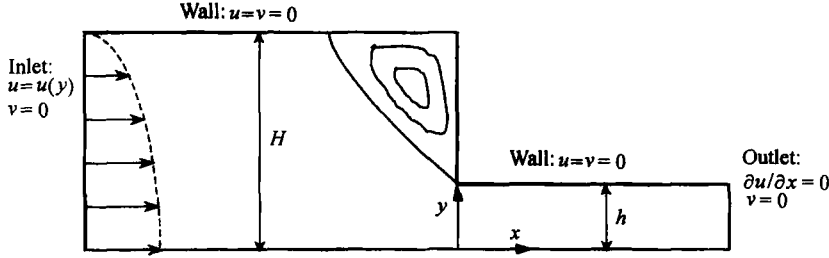


Fig. 2 Flow geometry with boundary conditions

As the polymer chain is extended and oriented, the free energy as well as the recoverable force of the chain increases. This means that more force is needed to extend the chain for overcoming the recovery force. Therefore the shear modulus G should be increased with chain extension. A simple power-law relation between G and $\det C$ is used^[8]:

$$G = G_0(\det C)^{n-1} \quad (10)$$

where G_0 is the modulus at rest, n the flow index of the power-law model.

Following Hamiltonian-Poisson bracket formulation, the evolution equation of internal structure tensor of polymer chain is obtained^[8]:

$$\frac{\partial C_{ij}}{\partial t} = C_{ik} \nabla_k U_j + C_{jk} \nabla_k U_i + B(C_{ik} C_{kj} - C_{ij}) \quad (11)$$

where t is the time, U_i the velocity, and $B = G/\eta_0$. It is obvious from the above equation that C_{ij} is determined by the velocity gradient $\nabla_i U_j$, shear modulus G and time t .

The conformation tensor C_{ij} is assumed to be symmetric, positive and definite. From the physical point of view, the conformation tensor C_{ij} can be regarded as a measure of the internal strain associated with a chain coil of polymer melts under consideration. Whenever C_{ij} is determined, the radii of conformation ellipsoid and angles between axes and coordinates can be calculated through eigenvalues and eigenvectors of tensor C_{ij} .

The phenomenological model yields not only a shear-thinning viscosity in simple shear but also an extensional viscosity in simple extension, which is show in literature Refs. [8] and [13].

NUMERICAL METHODS

To solve the non-linear couple system of conservation Eqs. (1), (2) and (3), a finite element method (FEM) is used for the spatial discretization. In the FEM, the flow domain is subdivided into a finite number of triangular elements (see Fig. 3). For a quasi-Newtonian fluid model, the stress can be explicitly substituted out of the momentum equation to obtain a non-linear Stokes equation. Therefore, a common viscosity-pressure formulation is used in the finite element calculation. A modified Newtonian iteration^[14] is used to solve conservation equations for velocity, pressure field. The stress field is further calculated using the results of velocity field. To solve Eqs. (11), we employ a fourth/fifth order Runge-Kutta method^[15] to compute the conformation tensor C_{ij} .

RESULTS AND DISCUSSION

The numerical results based on the above formulations are now presented and discussed. Numerical simulations

are undertaken for 3.29:1 planar contraction flow of polymer melt. The numerical results of stress is compared with experimental data from FIB (Flow Induced Birefringence^[9, 10]). The predicted velocity are compared with the experimental results from PTV (Particle Tracking Velocimetry^[9, 10]). Finally, the conformations of polymer melt are predicted according to the phenomenological model with internal structure parameter.

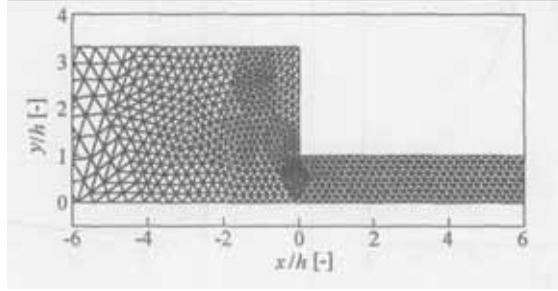


Fig. 3 Partial view of the finite element meshes used in the abrupt planar contraction

Comparison with Experimental data

In order to verify the validity of numerical simulation results, we make a comparison between calculated stress field, velocity field and the experimental ones from Schoonen^[9].

First, the comparison is carried on the isochromatic patterns. The full field isochromatic pattern is shown in Fig. 4(a), together with the computed stress pattern (Fig. 4b) for the QNF model. The computed stress patterns are calculated according to Eq. (13)^[16]:

$$N = \frac{Cd}{\lambda} \sqrt{4\tau_{xy}^2 + N_1^2} \quad (13)$$

where N is the fringe order, C the stress optical coefficient, λ the wavelength, τ_{xy} the shear stress, N_1 the first normal stress difference.

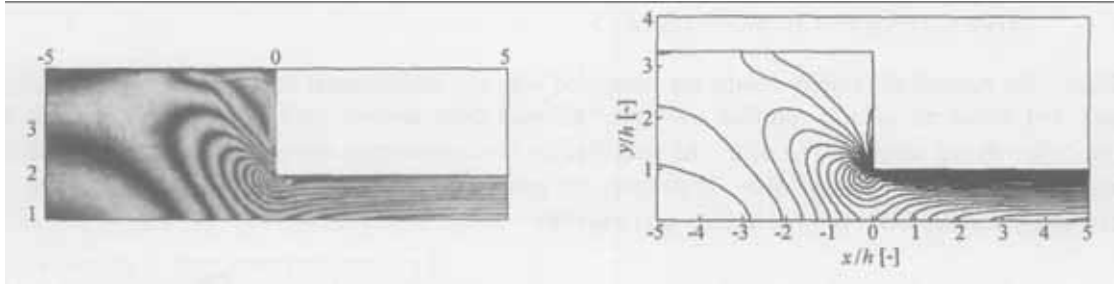


Fig. 4 Comparison of the isochromatic patterns between experimental and numerical results (a) Experiments, (b) Numerical

It can be seen from Fig. 4 that a rather good agreement with the measured isochromatic pattern is obtained for the QNF flow: in the fully developed region upstream of contraction, the same number of fringes are predicted as measured; in the region just before contraction, the fringes become “butterfly” shaped, which is also calculated by the QNF model; in the fully developed region downstream, the parallel fringes are predicted as experimental results.

Secondly, for a more quantitative comparison, results are taken along the four cross-section line (e.g. $y/h = 0$, $y/h = 1$, $x/h = 0$, $x/h = 5$). For the stress along the center line (Fig. 5a), excellent agreement is found up to $x/h = 0$, after which the models underpredicts the experimental stress. The line $y/h = 1$ intersects the butterfly patterns and the experimental results are predicted excellently by the QNF model although the predicted values near the re-entrant corner are somewhat lower than the experimental data. At the contraction plane ($x/h = 0$), shown in Fig. 5(c), the measurements are only a little higher than the predictions. At the downstream cross-section

(Fig. 5d), some deviations appear: near the wall, the prediction line is higher than the experimental data; closer to the centerline, the experimental are under-predicted. This maybe due to non-fully developed flow in those region.

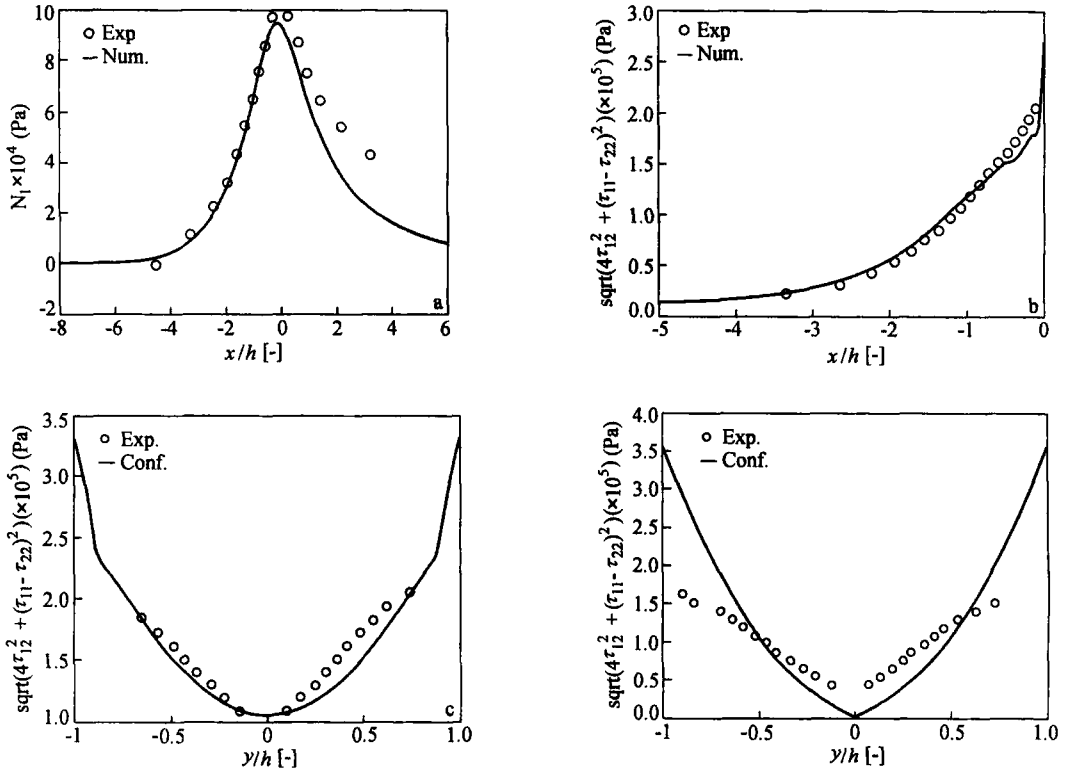


Fig. 5 Calculated and measured stress in the planar contraction flow over the cross-sections (a) $y/h = 0$, (b) $y/h = 1$, (c) $x/h = 0$, (d) $x/h = 5$

Thirdly, the numerical velocity results are compared with the experimental data from PTV^[9]. Results of calculated and measured velocity profiles over four different cross-sections ($x/h = -6, -4, -1, 1$) and the centerline ($y/h = 0$) are shown in Fig. 6(a). The velocities for the cross-section are made dimensionless with the two-dimensional mean upstream velocity. In general, the predicted velocities are in good agreement with the measured data points for QNF, showed in Figs. 6(a) and 6(b).

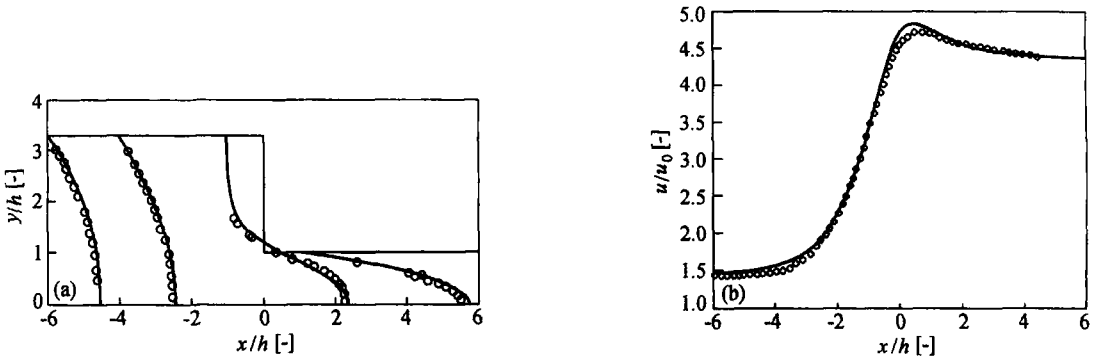


Fig. 6 Calculated and measured velocity profiles in the planar contraction flow over four cross-sections (a) $x/h = -6, -4, -1, 1$, and over the centerline (b) $y/h = 0$

It can be concluded that for the investigated contraction flow, the quasi-Newtonian Fluid model with the

shear-thinning and extension-thickening viscosity is well able to describe the rheological behaviors of polymer melts.

Predictions of the Conformation of Polymer Melts in the Contraction Flow

The flow of polymeric fluid through an abrupt contraction involves the deformation, extension, and orientation of polymer chains caused by extension and shear flow. There are some different types of flow region, such as shear-dominated, extension-dominated region, in contraction flow domain. The conformation tensor is calculated to describe the deformation, extension and orientation of the polymer chains in those flow fields.

Figure 7 shows the distribution of dimensionless trace ($\text{tr}C$) for the conformation tensor, which represents the change of a kind of volume related to the chain extension. It can be seen from Fig.7 that the chains of polymer melt are extended the most in the region just before contraction as well as near the slit wall downstream, medium near the reservoir wall upstream, and smallest near the corner region of reservoir (vortex region) as well as close to the centerline far upstream and downstream. The results indicate that the macromolecule chains of the polymer melt suffered different extension at different type of flow fields.

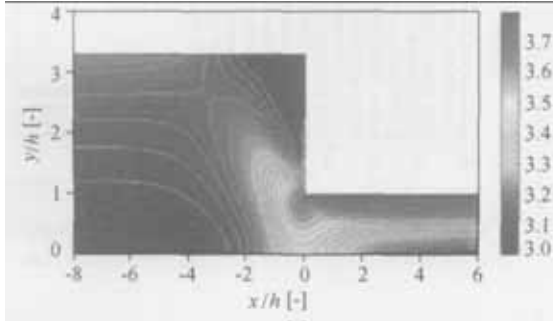


Fig. 7 Contours of trace of conformation tensor ($\text{tr}C$)

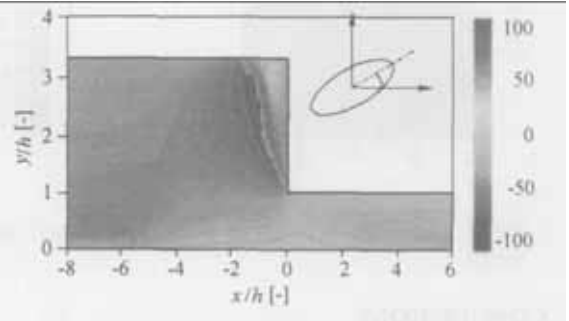


Fig. 8 Contours of orientation angle of conformation ellipsoid

The contours of the orientation angle of polymer chains in the contraction flow are shown in Fig. 8. In the corner region of reservoir, the large changes of θ from -100° to 100° together with small changes of $\text{tr}C$ in the responding location of Fig. 7, can be ascribed to rotation (but little deformation) of molecules at such a vortex region. At the centerline, the preferred polymer-chain orientation is in the flow direction, so the orientation angles vanish. In the region far upstream and downstream, *i.e.*, the fully-developed region, the polymer molecules are subjected to the simple shear field, where the conformation will not only undergo deformation but also rotate. Therefore, the values of θ vary from 0 near the centerline to a maximum, and finally to a smaller one close to the wall.

In order to investigate the changes of envelope volume of the polymer chains in the contraction flow, the distribution of $\det C$ is shown in Fig. 9. It can be seen from the figure that the envelope volume of polymer coils decreases in the region where the chains are extended. The reason for the decrease of conformation volume may be due to the disentanglement of polymer chains under flow.

The distribution of the conformation ellipsoid, as shown in Fig. 10, is obtained according to the calculated values of conformation tensor components. It can be seen that the conformation ellipsoid evolves into different shapes in different flow regions:

In extension-dominated region (centerline region just before abrupt contraction), the preferred polymer-chain orientation is in the direction of the flow field. Hence it will induce the maximum extension of chains producing a recoverable force that may result in a large resistance to deformation and cause a thickening viscosity. C_{12} nearly vanishes and $C_{11} > C_{22}$ indicate the extension of the chains. The conformation ellipsoid is changed into pipe at the highest extensional point, whereas the orientation angel is kept zero during the extensional flow. And the value of the ratio R in this region is nearly zero, which indicates the extension of local flow field acting on the polymer chains.

In the shear-dominated region (near the wall of downstream), the value of the ratio R is close to 1; therefore, the polymer chains are sheared into the conformation ellipsoids even into the pipes. The preferred orientation of the conformational ellipsoid corresponds to the direction of the flow. The presence of vorticity across the flow field encourages molecules to rotate thereby reducing the degree of stretching of the macromolecule chains. The tendency of molecules to rotate, versus elongate, depends on the type and magnitude of the flow field. If there exists a shear component in the local flow field, the molecule rotates as it is stretched, which depends on the magnitude of shear rate.

In the vortical region (entry corner region), little change of the shape of the ellipsoid can be found. The changing of orientation angles indicates the rotation of polymer chains. And the corresponding value of $R \gg 1$ reflects nearly solid-body motion, which was demonstrated by Thompson *et al.*^[6].

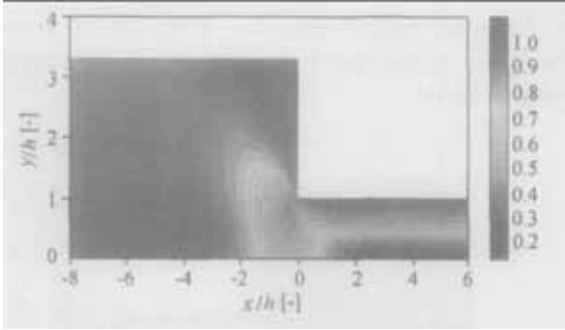


Fig. 9 Contours of determinant of conformation tensor (detC)

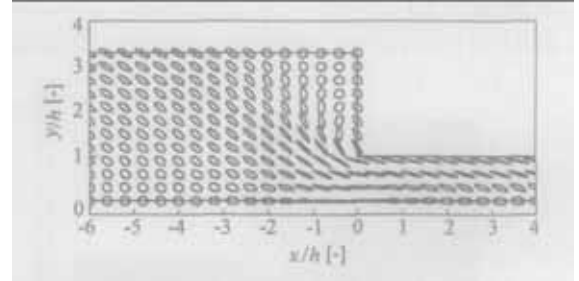


Fig. 10 The distribution of the conformation ellipsoid of polymer melts in the contraction flow

CONCLUSIONS

In this paper, we conducted finite element analysis for the abrupt planar contraction flow of a polymer melt described by a quasi-Newtonian fluid model. A phenomenological model with internal structure parameters was used to predict orientation and deformation of polymer chains in contraction flow. The melt velocity together with the velocity gradients were obtained by numerical simulation first, and the stress field is later computed using the results of velocity gradients according to the quasi-Newtonian model. The computed stresses and velocity are compared with experimental data from FIB and PTV, respectively. The results show good quantitative agreements between them, from which we may conclude that the quasi-Newtonian model can describe the complex rheological behaviors of polymer melts in contraction flow. The conformation tensor was calculated to demonstrate the deformation and rotation of polymer chains in different locations of the contraction flow field due to different types of flow. According to the magnitude of the ratio R , the flow region can be divided into three sub-domains as extension-dominated flow region, shear-dominated flow region and nearly pure rotation flow region. The polymer chains behave in different ways at those different regions, which can be demonstrated by the distributive pattern of the conformation ellipsoids.

REFERENCES

- 1 Li, X.F. and Zhao, D.L., *Acta Polym. Sini.* (in Chinese), 2000, (4): 432
- 2 White, S.A., Gotsis, A.D. and Baird, D.G., *J. Non-Newt. Fluid Mech.*, 1987, 24: 121
- 3 Schunk, P.R. and Scriven, L.E., *J. Rheol.*, 1990, 34(7): 1085
- 4 Ryssel, E. and Brunn, P.O., *J. Non-Newt. Fluid Mech.*, 1999, 85: 11
- 5 Ryssel, E. and Brunn, P.O., *J. Non-Newt. Fluid Mech.*, 1999, 86: 309
- 6 Thompson, R.L., Souza Mendes P.R. and Naccache, M.F., *J. Non-Newt. Fluid Mech.*, 1999, 86: 375
- 7 Gupta, M., *Polym. Eng. Sci.*, 2000, 40(1): 23

- 8 Zhou, C.X., Chinese J. Polym. Sci., 1999, 17(2): 151
- 9 Schoonen, J.F.M., "Determination of Rheological Constitutive Equations using Complex Flows", PhD thesis, Eindhoven Technology University, Netherlands, 1998
- 10 Verbeeten, W.M.H., "Computational Polymer Melt Rheology", PhD thesis, Eindhoven Technology University, Netherlands, 2001
- 11 Astarita, G., J. Non-Newt. Fluid Mech., 1979, 6: 69
- 12 Carreau, P.J., De Kee, D.C.R. and Chhabra, R.P., "Rheology of Polymeric Systems: Principles and Applications", Henser Publishers, New York, 1997
- 13 Huang, X.H. and Zhou, C.X., Polym. Eng. Sci., 1999, 39(11): 2313
- 14 Deuflhard, P., Numer. Math., 1974, 22: 289
- 15 Dormand, J.R. and Prince, P.J., J. Comp. Appl. Math., 1980, 6: 19
- 16 Martyn M.T., Nakason C. and Coates P.D., J. Non-Newt. Fluid Mech., 2000, 91: 123