

STRUCTURE EVOLUTION OF POLYMER CHAINS FOR NECKING FORMATION IN HIGH-SPEED FIBER SPINNING PROCESS*

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Abstract Finite element method is used to simulate the high-speed melt spinning process, based on the equation system proposed by Doufas *et al.* Calculation predicts a neck-like deformation, as well as the related profiles of velocity, diameter, temperature, chain orientation, and crystallinity in the fiber spinning process. Considering combined effects on the process such as flow-induced crystallization, viscoelasticity, filament cooling, air drag, inertia, surface tension and gravity, the simulated material flow behaviors are consistent with those observed for semi-crystalline polymers under various spinning conditions. The structure change of polymer coils in the necking region described by the evolution of conformation tensor is also investigated. Based on the relaxation mechanism of macromolecules in flow field different types of morphology change of polymer chains before and in the neck are proposed, giving a complete prospect of structure evolution and crystallization of semi-crystalline polymer in the high speed fiber spinning process.

Keywords: Semi-crystalline Polymer; Crystallization; High-speed Fiber Spinning Process; Conformation; Finite Element Method (FEM).

INTRODUCTION

During the fiber spinning process of semi-crystalline materials such as Nylon and polyethylene terephthalate (PET), the viscoelastic melt undergoes structural changes due to high tensile stress and the flow induced crystallization (FIC) mechanism. Moreover, a neck-like deformation has been observed in the high-speed non-isothermal melt spinning experiments^[1, 2]. As a result of the above effects, spun fibers can be produced with superior mechanical and transport properties, including solid modulus, elongation at break and dye acceptance^[3, 4]. Therefore, the high speed fiber spinning of polymeric materials is an industrial process of great commercial importance and many researches have been carried out to elucidate the physics of the process, especially the occurrence of necking phenomenon and the related structural change of polymer chains in the necking zone.

A critical experimental work on the neck-like deformation was carried out by Perez and Lecluse^[2], who first observed this phenomenon in the high speed spun PET. Also, necking phenomena of PET and other crystallizing polymers were observed by many other authors^[5–7]. Because necking phenomenon has not been observed for non-crystallizing polymers thus far, it is generally believed to be somehow related to the crystallization process. However, Haberkorn and co-worker^[1] studied the on-line evolution of filament structure by means of wide-angle X-ray scattering (WAXS) and found that crystallization takes place only at the end of the necking process. This means that the neck-like deformation is not primarily caused by the onset of crystallization.

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Viscoelasticity, as is well known, plays an important role in the process of polymer materials and is also believed to be essential for the necking phenomenon. However, Devereux and Denn's work^[8] indicated that viscoelasticity alone is not sufficient to reveal the essence of melt spinning process and FIC is suggested, after taking into account the explanation of the formation of necking. The description of FIC was originated by Eder *et al.*^[9], who based their theory on the shear rate as the driving force for crystallization.

Although the mechanism involved in the necking process has not been clearly understood until now, there are several attempts to describe the necking phenomenon by mathematical method. Combining the effects of non-isothermal, viscoelasticity, high tensile stress, phase transition and FIC, a series of models have been proposed by many authors^[10–12] to help us understand the physical meaning of the necking process. Recently a mathematical model (1-D) based on the formulation of Doufas *et al.*^[12] has been developed for the simulation of both low- and high-speed melt spinning process. In this model system both an amorphous phase, simulated as a modified Giesekus fluid, and a semi-crystalline phase, approximated as rigid rods that grow and orient in the flow field, are coupled through the stress and momentum balance and the feedback of crystallinity to the system relaxation times. A good agreement between the predictions and the spinline data such as velocity, temperature and birefringence shows the validity and correctness of the model^[13]. However, a leading-order radial variation in the spinline was naturally neglected due to a one-dimensional analysis by the author, which does not accord with the fact^[3, 4–6]. This provides the motivation for the present work where a 2-D FEM approach has been used to study the non-isothermal melt spinning process with ongoing crystallization.

The structure of polymer melt undergoes great changes due to the FIC during the melt spinning process. Kulkarni *et al.*^[10] used an inhomogeneous structure model which explicitly takes into account FIC for representing the necking phenomenon in high-speed fiber spinning process. In his work the amorphous phase was modeled by the extended White-Metzner model. By neglecting the non-isothermal, surface tension, air drag and other effects, structure evolution in the necking region was investigated and an explanation was provided for the molecular relaxing during the transformation from the amorphous to the semi-crystalline phase. In recent years great progress has been made in the theory of polymer dynamics which helps us to understand the flow behaviors and reptation mechanism in various flow fields^[14–18]. Considering the convective constrain release (CCR) the problem of excessive shear thinning was solved. Moreover, Mead *et al.*^[16] proposed a model incorporating both chain stretch and CCR and other refinements have been carried out on CCR. Based on the above theories the structure change of polymer coils and extension relaxation mechanism in the necking region is another problem considered in this paper.

GOVERNING EQUATIONS

A complete and detailed description on a high-speed fiber spinning process and models development is provided in Refs. [11] and [12]. For an incompressible polymeric melt, the total viscoelastic extra-stress tensor σ can be written as^[19]:

$$\sigma = \sigma_a + \sigma_{sc} \quad (1)$$

where σ_a and σ_{sc} are the extra-stress contributions from amorphous and semi-crystalline phases, respectively. The extra-stress tensor σ must obey the momentum equation, which for a steady-state flow in the absence of volume forces, is reduced to:

$$-\nabla p + \nabla \cdot \sigma + 2\eta \nabla \cdot \mathbf{D} = 0 \quad (2)$$

where p stands for the pressure, η denotes the shear viscosity and $\mathbf{D}$ is the rate of deformation tensor.

Stress Contribution σ_a in the Amorphous Phase

The polymer chains in the amorphous phase can be described by a second rank conformation tensor $\mathbf{C}$, which represents the second moment of the end-to-end vector $\mathbf{R}$ of the polymer chains^[20]. The stress in the amorphous phase is obtained from $\mathbf{C}$ based on the single mode Giesekus model as follows^[21]:

$$\sigma_a = G \cdot E \cdot \left[\frac{3}{1-x} \mathbf{C} - \mathbf{I} \right] \quad (3)$$

where G is the zero shear modulus of polymer melts, E is the nonlinear spring force factor, x is the degree of transformation and $\mathbf{I}$ is the unit tensor. E depends on the fractional extension of the chains and is defined as:

$$E = \frac{1}{1 - \frac{\text{tr} \mathbf{C}}{N_0}} \quad (4)$$

where N_0 is the number of statistical links and $\text{tr} \mathbf{C}$ represents the trace of conformation tensor $\mathbf{C}$. The constitutive equation required for conformation tensor $\mathbf{C}$ is given by:

$$\lambda_a(T) \overset{\nabla}{\mathbf{C}} + \frac{1}{3(1-x)} \left[(1-\alpha) \mathbf{I} + \alpha \frac{3}{(1-x)} E \mathbf{C} \right] E \left[\frac{3}{(1-x)} \mathbf{C} - \mathbf{I} \right] = 0 \quad (5)$$

where ∇ denotes the upper-convected derivative used for objectivity reasons. Two parameters are invoked in the Eq. (5): the mobility factor α and a relaxation time λ_a . In this model the temperature dependence obeys the Arrhenius law, and is given by:

$$\lambda_a(T) = \lambda_{a,0} \exp \left[\alpha_\lambda \left(\frac{1}{T - T_0} - \frac{1}{T_a - T_0} \right) \right] \quad (6)$$

where α_λ is the coefficient that depends on the activation energy, T_a is the reference temperature, and T_0 is the scaling factor required for a non-absolute temperature scale.

Stress Contribution σ_{sc} in the Semi-Crystalline Phase

Crystallization is assumed to begin when the axial temperature of the filament reaches the equilibrium melting point (T_m^e) and crystallization corresponds to the transfer of N statistical links from the amorphous (melt) phase to the semi-crystalline phase at any arbitrary position along the spinline under the conditions of both under-cooling and stress. The formed semi-crystalline phase is modeled as a collection of rigid rods. Let $\mathbf{Z}$ denotes a dimensionless orientation tensor for the semi-crystalline phase, that is defined as $\mathbf{Z} = \langle uu \rangle - \mathbf{I}/3$, where u is the unit vector along the rod axis and the bracket $\langle \cdot \rangle$ denotes an average with respect to the distribution function of the semi-crystalline phase. The stress in the semi-crystalline phase is taken from $\mathbf{Z}$ as follows:

$$\sigma_{sc} = 3G \left(\mathbf{Z} - \frac{\mathbf{I}}{3} + 2\lambda_{sc} (\nabla v)^T : \langle uuuu \rangle \right) \quad (7)$$

where the shear modulus G is assumed to keep the same value as that of the amorphous phase. The time constant λ_{sc} depends on the degree of transformation x and temperature T :

$$\lambda_{sc}(x, T) = \lambda_{sc,0}(T) \exp(Fx) \equiv c' \lambda_a(T) \exp(Fx) \quad (8)$$

in which c' and F are additional model parameters that have to be determined from experimental data. As observed, λ_{sc} exhibits the same temperature dependence as λ_a .

The constitutive equation required for the orientation tensor $\mathbf{Z}$ is proposed here:

$$\overset{\nabla}{\mathbf{Z}} = \frac{\delta}{\lambda_{sc}(x, T)} \left(\mathbf{Z} - \frac{\mathbf{I}}{3} \right) - 2(\nabla v)^T : \langle uuuu \rangle \quad (9)$$

where δ is an anisotropic drag parameter that lies in the range $0 \leq \delta \leq 1$.

A closure approximation is needed to close the equation. A hybrid closure approximation is adopted^[12]:

$$(\nabla v)^T : <uuuu> \cong (1-w) \left(\frac{1}{15} (\nabla v + (\nabla v)^T) + \frac{1}{7} ([(\nabla v)^T : Z] I + Z \cdot (\nabla v + (\nabla v)^T) + (\nabla v + (\nabla v)^T) \cdot Z \right) + w \left([(\nabla v)^T : Z] \cdot \left(Z + \frac{I}{3} \right) \right) \quad (10)$$

$$w = 1 - 27 \det \left(Z + \frac{I}{3} \right) \quad (11)$$

The scalar quantity w in Eq. (10) guarantees coordinate invariance.

Degree of Transformation

A constitutive equation coupling with flow induced crystallization is derived for the degree of transformation x , and the following equation is suggested by Doufas *et al.*^[12]:

$$\lambda_{av} \frac{Dx}{Dt} = m [-\ln(1-x)]^{\frac{m-1}{m}} (R_{max} - x) \exp \left(\xi \frac{\text{tr} \sigma}{G} \right) \quad (12)$$

where λ_{av} is a time constant, $\frac{D}{Dt} = \frac{\partial}{\partial t} + u \cdot \nabla$ is the substantial or material time derivative, m is the Avrami exponent, R_{max} is the maximum degree of transformation and ξ is the dimensionless model parameter considered here to be independent of temperature.

The time constant λ_{av} is the reverse of the Avrami constant under quiescent conditions and can be generally determined from differential scanning calorimetry or dilatometric measurement. In this work for Nylon-66 the following expression is adopted for the Avrami constant^[12]:

$$K_{av}(T) = 1.47 \times 10^{-3} \left[\frac{4\pi N_u}{3\phi_{\infty, is}} \right] \exp \left[- \left(\frac{(T-141)}{47.33} \right)^2 \right] \quad (13)$$

with N_u , the number density of nuclei initially present at the spinneret and typically 10^{10} cm^{-3} for high quality homopolymer. $\phi_{\infty, is}$ denotes the ultimate isotropic crystallinity and takes a value of 0.5 in the present work.

Energy Equation

For the simulation of flow-induced crystallization under non-isothermal conditions, the energy equation should be added to the solving equation system. In the present context, it is given by the following equation:

$$\rho C_p \frac{DT}{Dt} = \nabla \cdot [\nabla T] + \sigma : D + \rho \Delta H_f \phi_{\infty} \frac{Dx}{Dt} \quad (14)$$

where ρ is the melt density, C_p is the heat capacity, k is the thermal conductivity, ΔH_f is the latent heat of crystallization per unit mass and ϕ_{∞} is the the average absolute degree of crystallinity of the system.

It is assumed that the thermal conductivity k depends on the temperature and is independent of the degree of transformation x . A third order polynomial expression is enabled for this temperature dependence:

$$k(T) = k_0 + k_1(T-T_0) + k_2(T-T_0)^2 + k_3(T-T_0)^3 \quad (15)$$

where T_0 is a scaling temperature factor. For the heat capacity C_p , a significant dependence with respect to x is reported next to temperature dependence. Hence, the following expression is used for the mixed dependence of C_p :

$$C_p = (1-x\phi_{\infty}) (C_{a0} + C_{a1}(T-T_0) + C_{a2}(T-T_0)^2 + C_{a3}(T-T_0)^3) + x\phi_{\infty} (C_{sc0} + C_{sc1}(T-T_0) + C_{sc2}(T-T_0)^2 + C_{sc3}(T-T_0)^3) \quad (16)$$

where C_{ai} and C_{sci} ($i = 0, 1, 2$) denote the contributions of amorphous and semi-crystalline phases, respectively.

The heat of crystallization per unit mass ΔH_f is obtained as:

$$\Delta H_f(T) = \Delta H_{f0} + \sum_{i=0}^3 (C_{ai} - C_{sci}) \frac{(T - T_0)^{i+1}}{i+1} \quad (17)$$

where ΔH_{f0} is the reference heat of fusion and T_0 is a scaling factor for the temperature.

Boundary Condition

Let Γ_i , Γ_w , Γ_a and Γ_o denote the inflow boundary, no-slip wall, free surface and the outflow boundary, respectively. In the equation system for the high-speed fiber spinning process the governing equations for C , Z and x are hyperbolic of the first order, therefore the boundary conditions only at the inlet of the computational domain are required. These inlet boundary conditions are automatically imposed when the velocity distribution at the inlet of the computational domain is selected based on a flow rate. In particular, vanishing inlet conditions are imposed for x .

For the simulation of a complex flow involving FIC under non-isothermal conditions, it is necessary to evaluate the temperature field T . It obeys the energy equation, which is of the second order, so that conditions are required on all boundaries. Within the present context of FIC, the boundary conditions for the problem are summarized as follows:

$$\begin{aligned} v &= v(r) \quad x=0 \quad \text{and} \quad T=T_i \quad \text{on} \quad \Gamma_i \\ v &= 0 \quad \text{and} \quad T=T_w \quad \text{on} \quad \Gamma_w \\ v_z &= v_d \quad F_r = 0 \quad \text{and} \quad \nabla T \cdot n = 0 \quad \text{on} \quad \Gamma_d \\ \sigma \cdot n &= 0 \quad v \cdot n = 0 \quad \text{and} \quad \nabla T \cdot n = -k_a(T - T_{am}) \quad \text{on} \quad \Gamma_a \end{aligned} \quad (18)$$

where $v(r)$ denotes the velocity distribution imposed at the inlet, T_i is the temperature on inflow boundary, T_w is the temperature on wall, v_d is the draw-down velocity, F_r is the tangential force imposed at the outlet, n is the unit outward normal to a certain boundary, k_a is the transfer coefficient and T_{am} is the temperature of the surroundings. Equations (1)–(17), along with the boundary conditions (18), complete the mathematical description of the non-isothermal viscoelastic flow with FIC encountered in high-speed melt spinning process.

Mesh Information and Numerical Method

The structure and characteristics of the finite elements in the computational domain is carefully arranged to capture the variation of the flow field. Small elements are selected in the vicinity of the die exit, *i.e.* at the inlet of the computational domain.

Finite element codes embedded in Polyflow software are used to solve the governing equations for the non-isothermal fiber spinning process. A multi-frontal solver which is fast and robust is designed to solve the complex flow problems more efficiently^[19]. We apply Galerkin weighted residual method^[22] to the momentum and mass conservation equations and the DEVSS /SU method^[23] for the constitutive equation and SUPG method^[24] to the crystallization kinetics equation. Then the discrete solving systems are solved with a Newton's iteration method. Due to the high nonlinearity of the problems evolution method is adopted to improve the convergence^[19].

RESULTS AND DISCUSSION

The high-speed fiber spinning process considered in this work now is shown in Fig. 1. The nylon-66 melt was extruded through the spinneret at an extrusion temperature T_0 , then it is elongated by a take-up device with a draw-down velocity v_d being much larger than the extrusion velocity v_0 . Cooling effect is imposed on a large range of the free surface with quench air velocity v_c , and the temperature of the filament decreases, and while $T < T_m$, crystallization occurs. The radius of the spinneret is R_0 and the length of the spinline is L_0 . The material properties, processing conditions and model parameter as input parameters for calculation are summarized in Tables 1–3^[13].

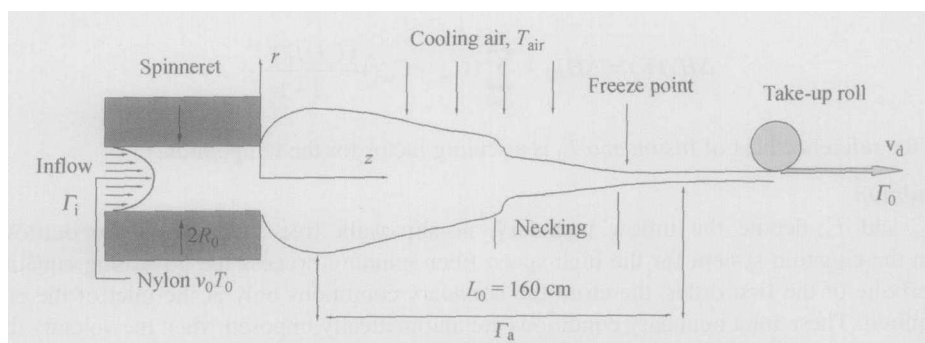


Fig. 1 Schematic diagram of a single melt spinning process

Table 1. Physical and rheological properties of Nylon-66 in the experiments

Nylon 66	Value
Density, ρ ($\text{kg} \cdot \text{m}^{-3}$)	1106
Zero-shear viscosity (280°C), η_0 ($\text{Pa} \cdot \text{s}$)	163
Melt shear modulus, G_0 (Pa)	1.1×10^5
Mobility parameter, σ	1.0
Number of statistical links per chain, N_0	200
Melting temperature, T_m^0 (°C)	265
Glass transition temperature, T_g (°C)	45
C_{sc1} [$\text{J}/(\text{kg} \cdot \text{K})$]	1.26×10^{-3}
C_{sc2} [$\text{J}/(\text{kg} \cdot \text{K}^2)$]	8.40×10^{-6}
C_{sc3} [$\text{J}/(\text{kg} \cdot \text{K}^3)$]	0
C_{a1} [$\text{J}/(\text{kg} \cdot \text{K})$]	2.10×10^{-3}
C_{a2} [$\text{J}/(\text{kg} \cdot \text{K}^2)$]	1.95×10^{-6}
C_{a3} [$\text{J}/(\text{kg} \cdot \text{K}^3)$]	0
Heat of fusion, $\Delta H_f(0)$ (J/kg)	2.1×10^5
Thermal conductivity, k [$\text{J}/(\text{m} \cdot \text{s} \cdot ^\circ\text{C})$]	0.21

Table 2. Processing conditions for melt spinning Nylon-66 in the experiments

Processing parameters	Value
Take-up velocity, v_0 (m/s)	2000–6000
Capillary tube diameter, D_0 (m)	8.5×10^{-3}
Flow rate, Q (kg/s)	3.67×10^{-5}
Temperature at exit of spinneret, T_0 (°C)	287
Spinline length, L_0 (m)	1.6
Normal velocity of quench air, v_n (m/s)	18.29
Tangential velocity of quench air, v_t (m/s)	0
Quench air temperature, T_a (°C)	21

Table 3. Model parameters

Model parameters	Value	Model Parameters	Value
F	20	σ	0.5
ξ	0.06	ϕ_∞	0.3
c	0.001	m	1

Comparison with Experimental Data

The numerical results of the velocity distribution and temperature profile along the spinline are compared with the on-line measurements performed by Doufas *et al.*^[13]. The temperature profiles are to be accurate within 5°C measured by Dupont proprietary IR gage and the velocity to within 5% by a laser velocimeter. Under the processing conditions in Table 2, we simulate the fiber spinning process with a take-up velocity 5700 m/min and

1000 m/min, representing the high and low speed fiber spinning cases, respectively. Comparison with the spinline data is shown in Fig 2. As can be seen, under both high and low take-up velocity the predicted axial velocity of the filament along the spinline works well with the experimental data. A clear distinction can be found on the evolution of the axial velocity profile along the spinline for two take-up speeds. For small distances (< 20 cm) from the spinneret the velocity distributions for two different take-up speeds are almost identical. However, as the distance beneath the spinneret increases they begin to diverge. And in the case of high speed (5700 m/min) the axial velocity along of the filament increases abruptly within a relatively narrow range, ultimately reaching a plateau value, *i.e.* the take-up velocity. This phenomenon is well known to be associated with necking and solidification and the axial location at which the velocity reaches a plateau value is always referred as the 'freezing point'. For the low speed (< 1500 m/min) melt spinning the axial velocity gradually rises along the spinline without a necking deformation, which is consistent with the experimental observations^[1, 13].

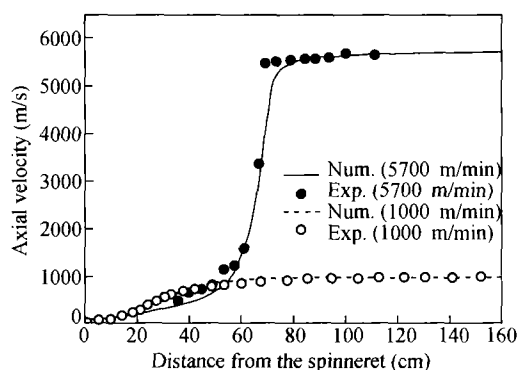


Fig. 2 Comparison of the spinline velocity profile between the numerical simulation with the experiment in both high and low speed fiber spinning process of Nylon 66

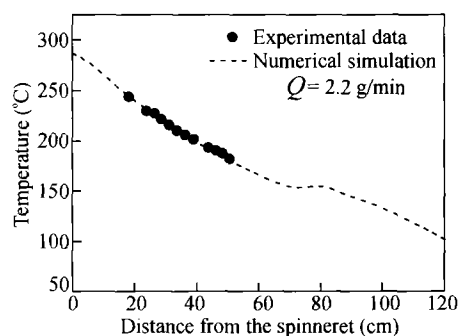


Fig. 3 Temperature profile of numerical simulation with a constant throughput compared with experimental observations

Figure 3 shows a comparison of the temperature profile on the surface of the filament along the spinline between the numerical simulation and experimental data obtained at a constant throughput (2.2 g/min) and a take-up velocity ($v_d = 5700$ m/min). As can be seen, a good agreement is observed between them in low and intermediate ranges beneath the spinneret and further details of the temperature change are detected in the numerical results, *i.e.* an obvious increase of temperature occurs above the position $L = 68$ cm due to the release of heat of crystallization, which is typical of high-speed spinning conditions. The natural capture of the variation of temperature profile due to FIC by using Doufas' model is important for explaining some observed experiences such as necking phenomenon and non-uniform fiber microstructure. Therefore, the 2-D finite element simulation results have been shown to be in very good quantitative agreement with the experimental data for velocity at both low- and high-speed conditions and temperature at high speeds. The comparison verified the validity and applicability of the model and the method.

Structure Evolution for Necking Region

Occurrence of necking

By increasing the take-up velocity, we can observe the position of the freezing point closer to the spinneret (Fig. 4). At small and intermediate distances from the spinneret the velocity distribution for two different high take-up velocities are nearly identical. With an increase in the distance beneath the spinneret the velocity profiles begin to diverge. A narrow region in the spinline where the axis velocity of the filament rises rapidly and finally reaches a stable value is referred as the necking region. Moreover, at a constant throughput 2.2 g/min and with the take-up velocity 6500 m/min the temperature profiles at the centerline and on the surface of the filament are shown in Fig. 5, together with the radius distribution of the filament along the spinline. As is shown, the

temperature along the centerline is non-uniform radially and the temperature on the surface is lower than that at the centerline due to the undercooling of the quench air, which cannot be predicted by 1-D radially uniform approach. In industrial melt processing condition, there must be a leading order radial temperature variation $\partial T/\partial r$, as demonstrated by many experiments^[25, 26]. Moreover, it is indicated recently that 1-D radially uniform models overestimate the heat convection on the surface using the average temperature, instead of the surface temperature and therefore the analysis may lead to an inaccurate temperature field^[25]. The inaccuracy of the temperature field could influence the velocity profiles, tensile stress, crystallinity, and free surface. Considering the viscoelasticity of the material, the stress is a function of both the deformation history and thermal history, therefore the non-uniform radial temperature profile along the spinline gives rise to a radially non-uniform tensile stress, which results in non-uniform molecular orientation and stretch degree, and also a leading order radial variation of crystallinity. Therefore, 2-D FEM analysis of melt spinning process overcomes the shortcoming of 1-D cross-section-averaged approach and gives more accurate and reasonable information on the flow field of the melt.

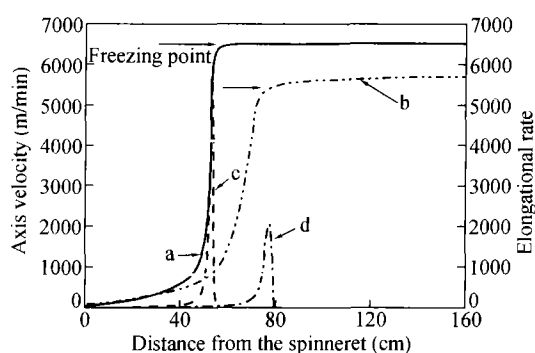


Fig. 4 Axis velocity profiles and elongational rate along the spinline for two take-up velocity and determination of the necking regions and freezing points

a) Axial velocity (6500 m/min); b) Axial velocity (5700 m/min); c) Elongational rate (6500 m/min); d) Elongational rate (5700 m/min)

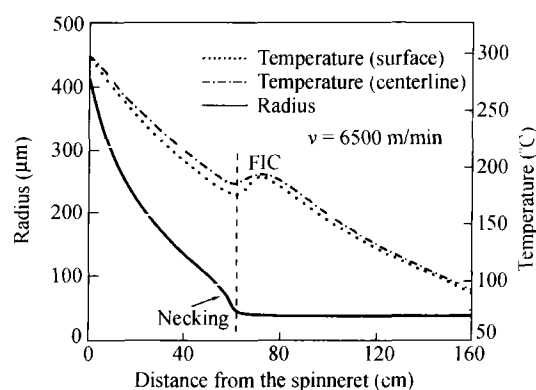


Fig. 5 Simulation results of temperature profiles (both at the centerline and surface of the filament) and radius profile of the filament with a constant flow rate ($Q = 2.2$ g/min)

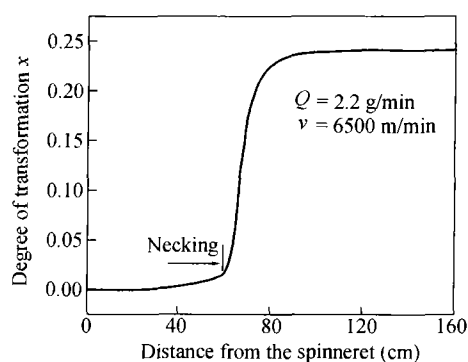


Fig. 6 Numerical results of degree of transformation profile along the spinline at a constant throughput and take-up velocity

From Figs. 4 and 5 we can say that necking phenomenon begins to take place at a position close to 60 cm, and a stable neck is locked finally. When the necking begins the transformation of amorphous phase to semi-crystalline phase occurs simultaneously. However only a small fraction of crystallization occurs actually in the

necking region (Fig. 6), and most of the crystallization takes place beyond the neck, where the filament reaches a stable velocity plateau.

Structure change in necking region

The profile of axial velocity along the spinline is very different at the position along the spinline. From Fig. 4 we can conclude that the axial velocity of the fiber increases a little before necking and sharply during necking. Therefore, the polymer residence time also varies along the spinline. The higher the take-up velocity is, the less residence time is required for the polymer melt to stay during fiber stretch process. The polymer residence time Δt between the axial position z_a and z_b can be calculated as follows:

$$\Delta t = \int_{z_a}^{z_b} \frac{dz}{v_z(z)} \quad (19)$$

where $v_z(z)$ denotes the axial velocity along the spinline. For a take-up speed of 6500 m/min the calculated residence time distribution is displayed in Fig. 7. Notice that the necking is estimated to occur in about 5.4 ms, which is of the same order of magnitude as the experimental measurement by Haberkorn *et al.*^[1].

It is accepted that necking phenomenon in the high-speed fiber spinning should be related to FIC and the structure change of the polymer chains in this region. In the melt state, conceptually, polymer chains can be imagined as an intercrossed viscoelastic matrix^[27]. The allowed possible conformation of the representative polymer chain is almost confined to an imagined sphere-like region as shown in Fig 8. The constraint imposed by other chains can be regarded as a large amount of random obstacles. In the flow field, as the shear rate or extension rate increases, the polymer chain will be oriented and stretched to a conformation of ellipsoid. When the deformation rate is very high, the chain segments may be excluded from the ellipsoid and polymer chains are disentangled at the same time, and then the long chains will array themselves in a parallel way, which is an optimal configuration for crystallization^[27].

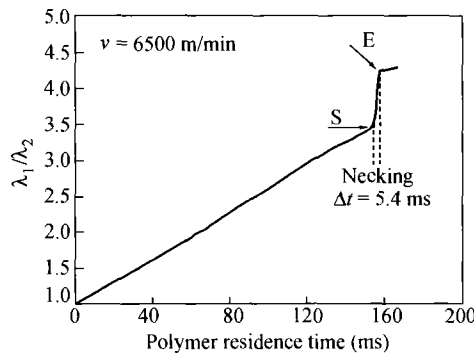


Fig. 7 Evolution of the degree of stretch of the filament versus the residence time along the spinline

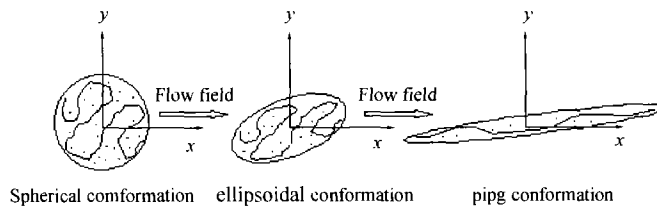


Fig. 8 Schematic illustration of conformation sphere in flow field

The conformation tensor C_{ij} in the single-mode Giesekus model is used to represent the conformation change of polymer chains in flow field. As is known, the eigenvalues of the conformation tensor C_{ij} which are denoted as $\lambda_1, \lambda_2, \lambda_3$, can be used to describe the change of principal axis and two secondary axes of the

conformation ellipsoid. Through evaluating the evolution of the three eigenvalues it can reflect the structure change of the polymer coils in a flow field in a mesoscopic scale. To describe the extension degree of the polymer coils, here we define a parameter to describe the extension degree of a polymer coil:

$$ED = \lambda_1/\lambda_2 \quad (20)$$

In a quiescent state, *i.e.* no flow imposed $ED = 1$, which means the long flexible polymer chain orients randomly and is wholly sphere-like. While the flow field is imposed the polymer chain is extended and oriented, leading to $ED > 1$. The stronger the flow field is imposed, the more highly the polymer chain is extended, *i.e.* the greater ED is. However, the chain cannot be stretched infinitely and there exists a maximum value of ED , which is consistent with the research of Ianniruberto and Marrucci^[28]. According to the conclusion drawn by Fetters^[29] and Fang^[30], the maximum stretch ratio of the polymer coils falls in the range of 3–6, depending on the polymer.

Numerical simulation also predicts a spike-like profile of the elongational rate $\dot{\epsilon}$ within the necking region along the spinline (Fig. 4). In the necking region it is calculated that the value of $\lambda_R \dot{\epsilon}$ is greater than the unit along the spinline with λ_R the Rouse relaxation time of the melt^[14]. Therefore, there exists a much stronger elongational flow field within the neck than before the neck, which leads to a distinct influence on the structure change of polymer chains. In Fig. 7 we can detect easily the structure evolution of polymer coils along the spinline. As is shown, at a large range before the necking region the extension degree of the polymer coil increases linearly versus the residence time. For this relatively weak flow we can imagine the stretch relaxation of the polymer coils is dominated by the reptation in this region, *i.e.* to be stretched a polymer chain must overcome the friction induced by the topological interactions and an irreducible part^[28].

$$\xi = \xi_{\text{topol}} + \xi_{\text{irr}} \quad (21)$$

where ξ is the total friction, ξ_{topol} is the friction of the topological interaction with other chains, ξ_{irr} is the reducible friction. Therefore, a linear and gradual increase of the chain elongational degree can be observed in Fig. 7. Also, this reptation process can be accelerated by convective constraint release (CCR) proposed by Marrucci in a moderate flow^[28, 31]. However, within the necking region where there is a very fast flow ($\lambda_R \dot{\epsilon} \gg 1$), the stretch relaxation is controlled by the irreducible Rouse-like friction, which is the basic and intrinsic friction of the polymer melt. Under this reptation mechanism the relaxing chain will not feel the entanglement as obstacles to conformation changes any longer and can orient and be stretched easily. Therefore, in the necking region we can find an abrupt increase of the elongational degree of the polymer coils (in Fig. 7) between the two points ‘S’ and ‘E’ due to the change of reptation mechanism in this region. Moreover, the sudden stretch and release of topological constraints occur within a very short time, for example about 5.4 ms (in Fig. 7). The time interval is not enough for the well-oriented polymer chains to crystallize, which contains three stages: nucleation, growth and perfection, therefore only a very small fraction of crystallization can be found in the necking region (Fig. 6) and the size of the crystals is supposed to be very small. However, after necking the highly extended and oriented polymer chains are closer to a crystal state than random ones and the rate of crystallization increases, which can be observed clearly in Fig. 6. Most crystallization which takes place just beyond the neck and amorphous phase has been changed to semi-crystalline phase. Finally, it is interesting to note that the fully extended chain formed in such a elongational flow field will lead to chain crystals and then results in shish-kebab structures, which has been observed by Petermann *et al.*^[32].

CONCLUSION

In this paper based on the mathematical model developed by Doufas *et al.*, 2-D finite element method was adopted to simulate the fiber spinning process instead of 1-D radially uniform approach. Numerical results of velocity and temperature profile along the spinline were compared with the experimental data and a good agreement was reached. This verified the validity and applicability of our method provided that it is a new approach for optimizing the melt spinning processes of semi-crystalline polymer materials, such as Nylon and PET.

From the numerical analysis of the process, necking phenomenon arises naturally from the high-speed stretch and undercooling by the quench air. In the necking region, an abrupt increase in the velocity and a sudden decrease in the radius of the filament could be observed, which was helpful to determine the necking region. Also, a small fraction of crystallinity occurred in the necking region. This small fraction of small crystals may be the primary nuclei for further crystallization.

The elongational rates in the necking region and at other positions along the spinline are quite different, so polymer chains should undergo structural changes differently along that line. In the necking region corresponding to a very fast flow, entanglement is no longer potential topological obstacles and the polymer chain behaves like a Rouse chain, which can be stretched easily. Before the neck corresponding to the moderately fast flow, however, the elongational relaxation is controlled by reptation and topological interaction should be considered. Therefore, the elongational degree of the polymer coils was observed to increase gradually before the neck during the spinning process.

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