

Crystallization behavior during the gel spinning of ultra-high molecular weight polyethylene

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SUMMARY

A computer simulation model was established to analyze the crystallization behavior during the gel spinning of semi-dilute solution of ultra-high molecular weight polyethylene in paraffin oil. A numerical calculation was carried out to predict the temperature and crystallinity profile within a filament. The effects of the fiber radius, cooling temperature, and spinning temperature on the cooling time were discussed for searching the optimum cooling condition during the spinning.

INTRODUCTION

High-performance polyethylene (PE) fibers are being considered for replacement of conventional materials in a number of military and civilian applications due to advantages offered by their superior specific strength and modulus, coupled with excellent chemical resistance and low moisture absorption [1]. The theoretical possibility of preparing high-strength fibers from PE has been known to exist since the sixties [2-4]. The basic principle is quite simple: as the length of molecules in the PE fibers and their degree of longitudinal orientation increase, the mechanical properties will improve. Over the years, various attempts have been made to prepare PE fibers having a high degree of orientation and a high molecular weight. The gel-spinning process, invented in the late seventies at DSM-Research [5] and currently in development by Dyneema-Vof [6] proved to be most versatile and successful in producing high-strength PE fibers. The gel-spinning process is suitable for PE having a very high molecular weight ($>1,000,000$). The PE is first dissolved so that a dilute solution is obtained, in which the macromolecules can disentangle. The solution is spun through a spinnerette with one or more holes. Quenching produces a gel fiber in which the polymer chains remain disentangled. The fibers obtained are drawn at elevated temperature in one or more steps, yielding the high-performance PE fibers.

The influence of the process variables on the mechanical and thermal properties of the fibers has been investigated by many other researchers using a variety of experimental techniques [7-12]. However, there are apparently no literature data concerning the crystallization kinetics of PE solution. In addition, modeling and simulation to seek optimal cooling condition during the spinning are not yet attempted.

The purpose of this work was to study the nonisothermal crystallization behavior of PE solution during the spinning. For this, the crystallization kinetics was analyzed by using differential scanning calorimetry (DSC), and a numerical calculation of the temperature and crystallinity change in the running filament was carried out. And some information was provided to predict the optimum cooling condition.

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EXPERIMENTAL

The PE used in this study was Hizex Million 240M ($M_v = 1.9 \times 10^6$). The PE was dissolved in paraffin oil ($\rho = 0.85 \text{ g/cm}^3$, viscosity at 20°C of about $1.4 \times 10^{-1} \text{ Pa sec}$) after addition of antioxidant (2,6-di-tert-butyl-p-cresol) at a concentration of 5% by weight. The experimental procedure for the preparation of PE solution has been described in detail elsewhere [7,11]. The gel was cut into small pieces prior to calorimetric measurements. Analyses of the crystallization kinetics of PE solution were accomplished with 10 mg samples in a Perkin Elmer DSC4. The samples were first heated to 20°C above the melting point and kept for 10 min. The samples were crystallized at constant cooling rates.

CRYSTALLIZATION KINETICS

Most of the approaches for describing the kinetics of crystallization are based on Avrami equation or its modified forms. The use of the Avrami equation, however, becomes very complicated in the description of nonisothermal crystallization of polymers. Recently, Lee and Kim [13] derived a new kinetic equation for the nonisothermal crystallization and investigated the possibility of its application. This equation, in contrast to the Avrami equation, is written in the differential form:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_D}{RT}\right) \exp\left(-\frac{\psi T_m^0}{T(T_m^0 - T)}\right) \alpha^{2/3} (\alpha_{eq} - \alpha) \quad (1)$$

where α is the degree of crystallinity varying from zero to the equilibrium value; E_D is the activation energy for diffusion; T_m^0 is the equilibrium melting temperature; A and ψ are constants.

From the dynamic DSC data, a best set of kinetic parameters for the crystallization of the PE solution were determined through a Marquardt's nonlinear regression algorithm [14] and a fourth order Runge-Kutta integration technique [15]. The parameters in Eq.1 were obtained as:

$$\begin{aligned} A &= 9.09 \times 10^4 \text{ (/sec)} \\ E_D &= 7.17 \times 10^3 \text{ (cal/mole)} \\ \psi &= 8.67 \times 10^1 \text{ (K)} \\ T_m^0 &= 3.97 \times 10^2 \text{ (K)} \end{aligned}$$

The correlation coefficient, R^2 , for the regression was 0.993. The comparisons between the measured and calculated crystallinity changes are shown in Fig.1. The experimental and calculated results show fairly good agreement, which indicates that the model equation is appropriate to describe the nonisothermal crystallization kinetics of the PE solution.

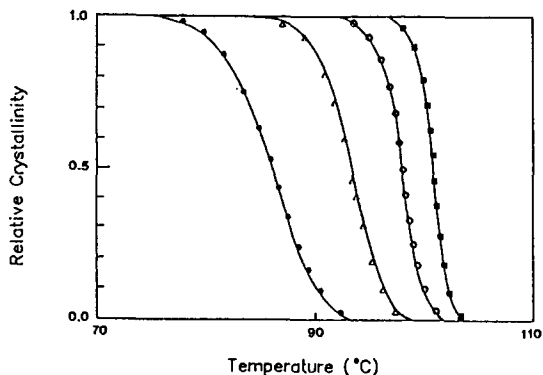


Fig.1 Comparison of the experimental data (points) with the calculated values (lines) from Eq.1 at the cooling rates (■) 5°C/min , (○) 10°C/min , (△) 20°C/min , and (●) 40°C/min

MATHEMATICAL MODEL

The one-dimensional analysis for a running filament during the spinning can be formulated in general terms by using the following assumptions.

- 1) All properties of the PE solution are constant.
- 2) The velocity gradient in the fiber quickly decreases to zero before any energy exchange between the filament and the cooling medium occurs.
- 3) The winding speed is equal to the spinning rate so that the filament diameter is independent of the distance from spinnerette. In that case the maximum tensile properties of fibers can be obtained [11].
- 4) The surface temperature of filament is constant at a value of cooling medium during the energy transfer.

The applicable form of the energy balance equation written in cylindrical coordinates, assuming radial symmetry and neglecting $\partial^2 T / \partial z^2$ (axial conduction) in comparison to the radial variation in temperature is:

$$\frac{\partial T^*}{\partial t^*} = \delta_r^* \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial T^*}{\partial r^*} \right) + \delta_c^* \exp\left(-\frac{E_D^*}{T^*}\right) \exp\left(-\frac{\psi^*}{T^*(T_m^* - T^*)}\right) \alpha^{2/3} (\alpha_{eq} - \alpha) \quad (2)$$

where the dimensionless variables are explained in Nomenclature. The appropriate initial and boundary conditions are:

$$T^* = 1 \quad \text{at } t^* = 0 \quad \text{for } 0 \leq r^* \leq 1 \quad (3)$$

$$\partial T^* / \partial r^* = 0 \quad \text{at } r^* = 0 \quad (4)$$

$$T^* = T_c^* \quad \text{at } r^* = 1 \quad (5)$$

RESULTS AND DISCUSSION

The energy balance equation was solved with the aid of a computer using explicit finite difference method with a grid size of 21 (radial direction). The base conditions for the computer simulation are summarized in Table 1.

Fig.2 shows the temperature change with time at five different locations in the radial direction. The fiber cools rapidly due to the heat transfer between the fiber and the cooling medium. The temperature at the center position steadily decreases and reaches a constant value after 15 s. The effect of the crystallization exotherm is not observed because the thermal conduction is dominant.

Fig.3 shows the crystallinity change with time. At high temperature the crystallization is thermally delayed, so the crystallization rate at the central region is slower than that at fiber surface. At the center position, the crystallization is completed in about 30 s.

Table 1. Base conditions for computer simulation

Parameter	Value (Unit)	Source
Properties of PE solution		
Density	0.85 (g/cm ³)	Ref.16
Thermal conductivity	0.00038 (cal/cm s K)	Ref.16
Heat capacity	0.54 (cal/g K)	Ref.16
Heat of crystallization	69.7 (cal/g)	Ref.17
Equilibrium crystallinity	0.72 (dimensionless)	Ref.17
Fiber dimension		
Radius	0.1 (cm)	
Spinning conditions		
Spinning temperature	170 (°C)	
Cooling temperature	50 (°C)	

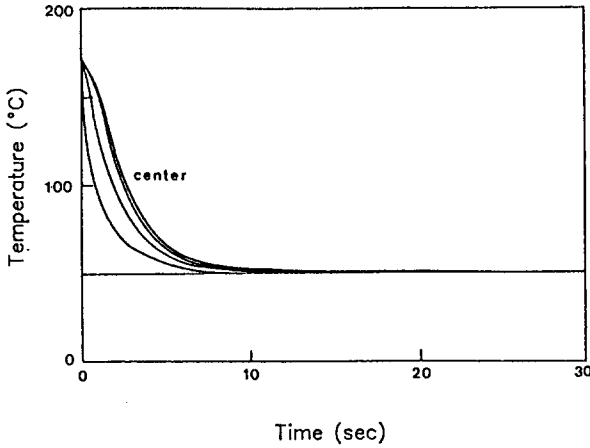


Fig.2 Temperature change at five positions in the radial direction of fiber

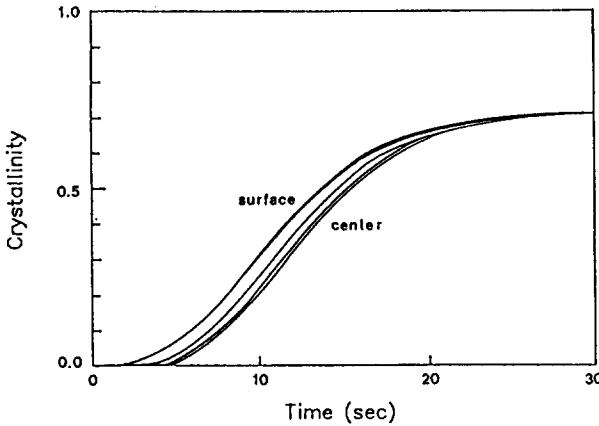


Fig.3 Crystallinity change at five positions in the radial direction of fiber

An important processing criterion is the cooling time, which is defined as the time when a set minimum crystallinity is attained in the fiber. More information is therefore needed on the crystallization behavior in the fiber to predict the optimum cooling condition. The analysis described below is carried out by simulating our model with variations in the fiber radius, cooling temperature, and spinning temperature. Unless otherwise specified, the base conditions are used in the simulation.

The crystallinity profile at the center position (Fig.4) shows the effect of the fiber radius on the crystallization rate. When increasing the fiber radius the heat transfer becomes difficult and consequently the crystallization is delayed by the higher crystallization temperature.

The effect of the cooling temperature is shown in Fig.5. The crystallization behavior is found to be highly dependent on the cooling temperature. As is well known, the temperature dependence of the crystallization rate is bell-shaped. If temperature of the maximum crystallization rate is denoted as T_k , it is expressed in terms of E_D , ψ , and T_m^0 as follows [13]:

$$T_k = \frac{T_m^0 (E_D + R\psi - \sqrt{R\psi (E_D + R\psi)})}{E_D} \quad (6)$$

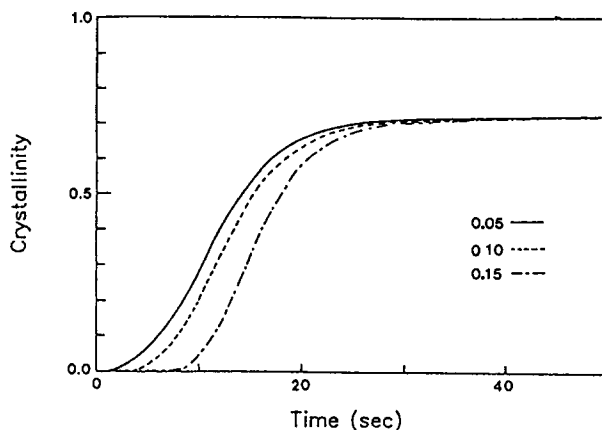


Fig.4 Effect of the fiber radius on the crystallization behavior at the center position of fiber: (—) 0.05 cm; (----) 0.1 cm; (-·-) 0.15 cm

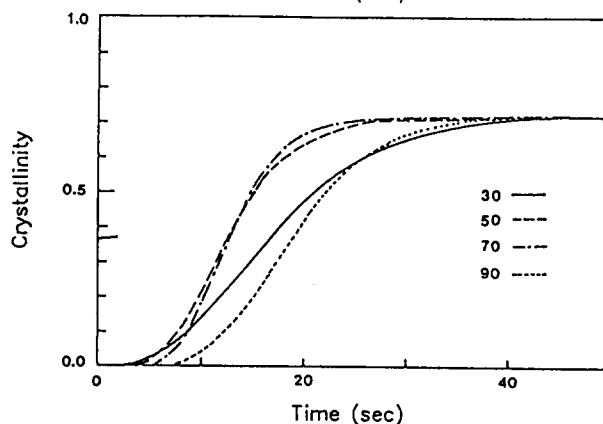


Fig.5 Effect of the cooling temperature on the crystallization behavior at the center position of fiber: (—) 30 °C; (-·-) 50 °C; (-·-) 70 °C; (.....) 90 °C

T_k of the PE solution in this system is around 70 °C. When the cooling temperature is 70 °C the fastest crystallization is realized.

Unlike the fiber radius and cooling temperature, the spinning temperature does not affect the crystallization rate since the fiber is quenched below the melting point at the early stage of the spinning.

CONCLUSION

The crystallization kinetic equation of the PE solution was obtained through dynamic DSC experiment. A computer simulation model was developed to analyze the gel spinning process. With increasing the fiber radius the crystallization is thermally delayed. At the optimum cooling temperature of 70 °C the cooling time is less than 30 s.

NOMENCLATURE

Dimensional Quantities

C_p = heat capacity
 k = thermal conductivity
 r = radial distance
 t_0 = reference time
 T_c = cooling temperature
 ρ = density

C_0 = concentration of solution
 Q_c = heat of crystallization
 R = radius of fiber
 T_0 = spinning temperature
 z = axial distance

Dimensionless Quantities

$$\begin{array}{ll}
 E_D^* & = E_D/RT_0 & r^* & = r/R \\
 t^* & = t/t_0 & T^* & = T/T_0 \\
 T_C^* & = T_C/T_0 & T_m^* & = T_m^0/T_0 \\
 \delta_C^* & = Q_C C_0 A t_0^2 / C_p T_0 & \delta_r^* & = \tilde{k} t_0 / \rho C_p R^2 \\
 \psi^* & = \psi T_m^0 / T_0 & &
 \end{array}$$

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