Simulation for Dry Spinning Process with new Hybrid Expression of Diffusion Coefficient Dependent on Solvent Concentration and Temperature

T. Yamada*, G. Li and K. Tada

Graduate School of Natural Science & Technology, Kanazawa University,
Kakuma-machi, Kanazawa, Ishikawa, 920-1192, Japan e-mail:tyamada@t.kanazawa-u.ac.jp

---

Abstract

The optimum processing conditions for dry spinning process of segmented poly(urethane-urea) (SPUU) – solvent (dimethylformamide (DMF) or dimethylacetamide (DMAc)) system have been desired to be predicted by computer simulations because of high cost and difficulties in experiment. Previous simulation model with a diffusion coefficient obtained from Moiré Method has the issue that simulated residual solvent concentration is somewhat lower than practical residual solvent concentration for SPUU-DMF system.

As DMAc has been substituted for DMF because of its lower toxicity, it is desire to newly measure diffusion coefficient of SPUU-DMAc system. Recently, the authors have newly measured the diffusion coefficients of DMAc for SPUU-DMAc system with Film (diffusion in the solid state) and Dope (diffusion in the liquid state) methods, and tried to simulate the spinline behavior during dry spinning with them. The simulation has led to the following results that residual solvent concentration simulated by Dope method is almost same as that by Moiré method. Residual solvent concentration simulated by Film method is much higher and that by Dope method is somewhat lower than practical residual solvent concentration, respectively.

Though a spinline changes from the liquid state to the solid state in a practical dry spinning process, Moiré pattern, Dope and Film methods cannot express the change of state from liquid to solid. Therefore, Hybrid method has been proposed, which can express the change of state with the fixed state transition points under the assumption that each state transition of liquid-semisolid-solid occurs at only given solvent concentrations independently of temperature. Residual solvent concentration simulated by Hybrid method is higher than practical one. The difference between the simulated result and practical one is assumed to be caused by the state transition points of fixed residual solvent concentrations only independently of temperature.

The state of spilnline continuously changes with both solvent concentration and spinline temperature from liquid to solid via semisolid in a practical process. The state transition points from liquid to semisolid and from semisolid to solid depend on both solvent concentration and temperature. In the semisolid state between the liquid and solid states, the diffusion coefficient greatly changes with solvent concentration. It is necessary to express the diffusion coefficient as a continuous function of both solvent concentration and temperature. In order to remove the restriction in fixed state transition points of Hybrid method, a new method which is called “Logistic method” is proposed. Logistic method can express the diffusion coefficient of solvent in a spinline continuously changing from liquid to solid with solvent concentration and temperature by a logistic function. Logistic method can predict the closer residual solvent concentration to a practical one than Hybrid method, but the residual solvent concentration simulated by Logistic method is slightly lower than that obtained by practical plant. This small difference is very important for the design of dry spinning chamber and the grasp of optimum dry spinning conditions. It can be estimated that the difference between simulated result and practical one is caused by the imperfect expression of diffusion coefficient as a function of solvent concentration and temperature because of the difficulties in accurately determining the parameters in a logistic equation.

In order to predict the residual solvent concentration closer to that in a practical process, new Hybrid method which can accurately express the state transition points changing with solvent concentration and temperature is proposed in this study. This method expresses the dependence of diffusion coefficient on both solvent concentration and temperature in the spinline, where the whole dry spinning process is divided into three sections depending on the state of spinline such as liquid state (near the spinneret), semi-solid state and solid state (near the take-up position).

The differences of simulated residual concentration among new Hybrid method and other ones will be discussed in this study.

Keywords: Dry spinning process; Dimethylacetamide; Segmented poly (urethane-urea); Diffusion coefficient; Simulation; Mathematical model

---

1. Introduction

Because the amount of residual solvent greatly affects the process ability of spinline and the characteristics of filament, the optimum processing conditions have been desired to be predicted by computer simulations because of the high cost for experiments. However, few papers have been reported on it.

In the previous works concerned with dry spinning model, the diffusion coefficient obtained from Moiré pattern has been used for dry spinning simulation. Ishihara et al. [1] reported the simulation results for the dry spinning which could predict the spinning behaviors of spinline in the dry spinning process under the assumption of Newtonian fluid. Recently, Yamada et al. [2],[3] proposed simulation models with power-law and viscoelastic fluids. Since the diffusion coefficient obtained from Moiré pattern gives the mutual diffusion coefficient for the liquid-liquid system, the Moiré pattern method [4] may be applied to the simulations only near the spinneret, but it cannot be always applied to those of solid state near the take-up position.

However, the authors cannot find the diffusion coefficient applicable to the whole dry spinning process. The diffusion coefficients in the liquid (dope) and solid (film) states have been reported in our previous work[5] where the diffusion coefficient by Dope method is almost equal to that by Moiré pattern method and ten times or more of that by Film method. The diffusion coefficients obtained by Dope method and Film method have been applied to the prediction of spinline behavior in the whole dry spinning process under the assumption of the linear change in diffusion coefficient in the each zone divided into three states such as liquid, semisolid and solid, whose method was called “Hybrid method” in our previous works[6],[7]. However, the state of spilnline continuously changes with both solvent concentration and spinline temperature from liquid to solid via semisolid in a practical process. It is difficult to determine the change point of state where the state of spinline changes from the liquid state to the semisolid and from the semisolid to the solid. If the diffusion coefficient which changes with temperature and solvent concentration can be expressed by a continuous function of temperature and solvent concentration, the above problem can be solved.

So, it has been tried to express the diffusion coefficient as a continuous logistic function of temperature and solvent concentration with the method called Logistic method[8]. Logistic method can be expected to give better prediction of residual solvent concentration in the dry spinning process than both Dope and Film methods judging from the information of practical plant.

The Logistic method has a difficulty that it is very difficult to accurately determine the parameters in a logistic equation. Moreover, the diffusion coefficient of dope in the dilute solution close to the pure solvent is estimated to be different from that in the viscous solution though the diffusion coefficient of dope by the Logistic method is assumed to be almost constant. Therefore, the authors have proposed a new Hybrid method in order to solve these problems in this work.

2. Mathematical Modeling for Dry Spinning Process

2.1 Dry spinning process

Figure 1 shows the schematic diagram of dry spinning process. From this figure, polyurethane-solvent dope of mass flow rate (W_N), temperature (T_N) and solvent concentration (ω_{S0}) at the spinneret is extruded out of the nozzle located on the top of dry spinning chamber. Spinline is stretched in the spinning chamber divided into several sections. Each section (ex. kth section) is independently controlled at a given temperature (T^*_k) and a given air velocity (V_y). The solvent is removed from the spinline. Several spinlines are twisted and become a filament at the position of X_{tw}. The filament is wound on the take-up device at the speed of (V_w), where a fine circular dope extruded from the spinneret to the twisting position is defined as a spinlene and several spinlines twisted is defined as a filament after the twisting position in this paper.

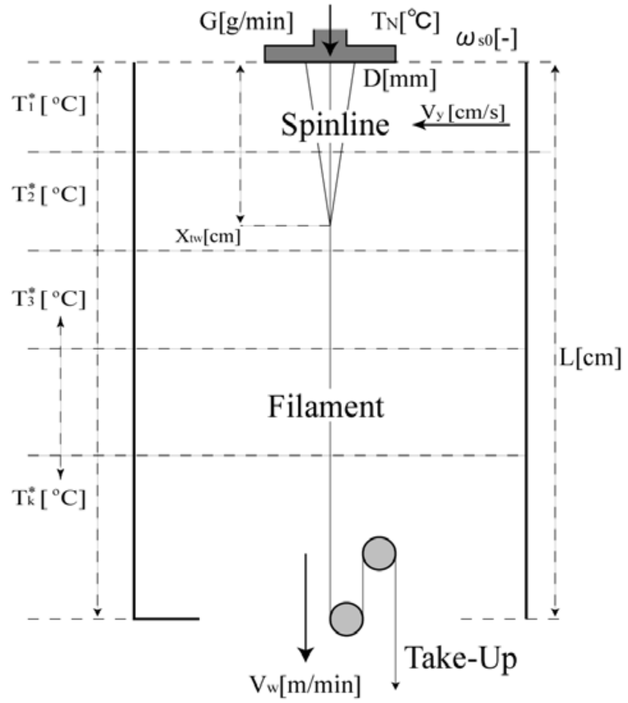

Fig.1 Schematic diagram of dry spinning process

2.2 Assumptions for mathematical modeling

The following assumptions have been made for mathematical modeling of the dry spinning process in a steady state.13):

1) A spinline is a continuum without phase change and its cross section is circular.
2) Distributions of concentration and elongational viscosity in a spinline are axially symmetrical.
3) Effective surface area (A_{eff}) of spinline for diffusion decreases with the number (n) of spinlines twisted as follows: $A_{Eff}=\left(\frac{n+2}{2n}\right)A_{Surf}$, ($n\geq 3$)
4) Density, specific heat and thermal conductivity of spinline are constant in the dry spinning process.
5) Temperature and velocity of spinline are changeable in the axial (spinning) direction of spinline but are constant in the radical direction of spinline at a given position of the dry spinning process.
6) Diffusion of solvent in the axial direction of spinline is negligible in comparison to that in the radial direction of spinline.
7) The contribution of kinetic energy and work done by forces such as gravitational, viscous and external ones are negligible.
8) Energy transport by radiation is negligible.
9) Energy conduction in the axial direction is negligible.
10) The energy movement due to the flow in the radial direction is negligible in comparison with that in the axial direction.
11) Rheological behavior of spinline obeys a Newton fluid.
12) The difference on the surface of spinline between the enthalpy of the solvent in the liquid state and that in the vapor state is approximated by the heat of vaporization (L_s) of the pure solvent at its boiling temperature as follows:
$L_S=H_S-M_SC_P\left(T-T_d\right)$
13) Hot gas for drying of solvent is blown from a direction perpendicular to the spinline.
14) Vapor-liquid equilibrium relation holds for the inner and outer solvent of spinline surface as follows: $x_S=f\left(\omega_S\right)$

15) Mole fraction of solvent in the blowing gas is assumed to be 0.02 from the information of practical production plant.

2.3 Governing equation for dry spinning process

Fundamental[5] equations for governing the dry spinning process are given as follows, which composed of the equations of continuity, motion, energy, rheology and deflection derived from the macroscopic balances of traveling spinline:

(1) Equation of Continuity

$$\frac{dW}{dz} + 2\pi RM_S N_S = 0 \tag{1}$$

(2) Equation of Motion

$$\frac{dF}{dz} = W\left[\frac{dv}{dz} - \frac{g}{V}\right] + 0.23\times10^{-3}\left[\frac{W}{\rho}\right]^{0.195} V^{1.195} \tag{2}$$

(3)Equation of Energy

$$\frac{dT}{dz} = \frac{2}{\rho C_P V}\sqrt{\frac{\pi}{A}}\left[h(T^* - T) - L_S N_S\right] \tag{3}$$

(4) Equation of Rheology

$$F = A\beta\frac{dV}{dz} \tag{4}$$

(5) Equation of deflection

$$\frac{d^2 y}{dz^2} = \frac{\rho Ag\frac{dy}{dz} - \rho^* V_y^2 RC_D}{F - \rho AV^2} \tag{5}$$

2.4 Distribution of solvent concentration in the radial direction of spinline at a given position

The distribution of solvent concentration in the radial direction can be obtained from the following equation derived from microscopic balance at a given position of spinline:

$$V\frac{d\omega_S}{dx} = \frac{1}{r}\frac{d}{dr}\left(rD\,\frac{d\omega_S}{dr}\right) \tag{6}$$

2.5 Material properties and their related equations

Various properties for prediction of the spinline behavior in the dry spinning process can be estimated from the following.

2.5.1 Diffusion coefficient

Logistic method

As the state of spinline continuously changes by the solvent evaporation in the dry spinning process from the spinneret to the take-up position simultaneously, diffusion coefficient continuously changes with both solvent concentration and temperature. So, it is desired to reasonably express the diffusion coefficient as a continuous function of both solvent concentration and temperature. Therefore, the following logistic function has been tried to be adopted as a candidate of the continuous function to express the diffusion coefficient as a function ($D_{DMAc}^{Logistic}$) of both solvent concentration and temperature in this work, which is called "Logistic method" in previous work[8].

$$D_{DMAc}^{Logistic} = \exp\left[\frac{a}{1 + b\times\exp(-c\omega_s)}\right] \tag{7}$$

Where, the parameters of a, b and c in the logistic function are determined with the experimental data of sorption-desorption curves.

New Hybrid method

In order to express the diffusion coefficient of dope where polymer concentration is low near the pure solvent, the dope is divided into three regions which consists of viscous liquid, semi-viscous liquid and pseudo-pure solvent. That is, the spinline is divided into five regions which consists of solid, semi-solid, viscous liquid, semi-viscous liquid and pseudo-pure solvent as shown in Figure 2.

The diffusion coefficient in each region is dependent with temperature and solvent concentration.

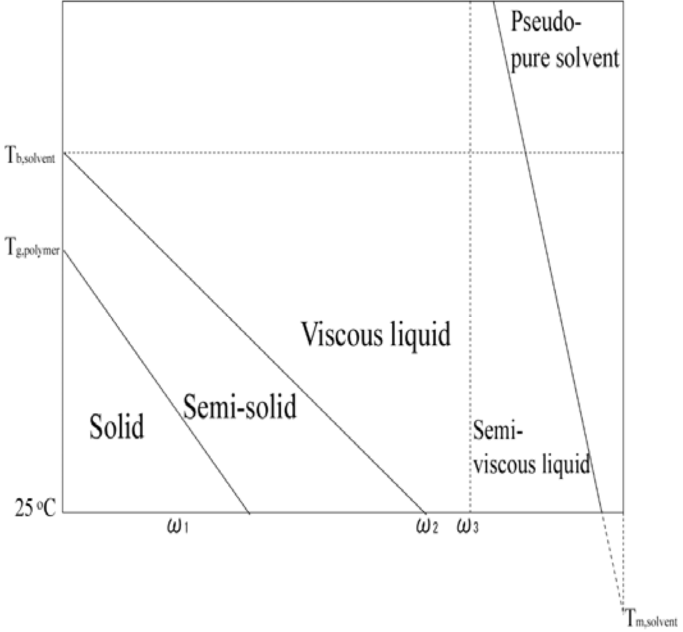

Fig.2 Change of SPUU dope (spinline) state with temperature and solvent concentration

2.5.2 Material properties and related equation

(1) Elongational Viscosity.

$$\eta_0 = 4249[1 - \omega_S]^5 \exp\left[\frac{2477}{T + 273.15}\right] \text{ (poise)} \tag{8}$$

(2) Mole Fraction of Solvent (x_S)[1].

$$x_S = P_S\omega_S \exp\left[(1 - \omega_S) + \chi(1 - \omega_S)^2\right] \tag{9}$$

(3) Vapor Pressure for Solvent (P_S)

$$P_S = 2888\exp\left[\frac{-2572}{T + 165.5}\right] \text{ (atm)} \tag{10}$$

(4) Mass-Transfer Coefficient

$$k_x = h/k' \tag{11}$$

*(5) Heat-Transfer Coefficient*6)*(h)*

$$h = 0.473\times10^{-4} A^{-0.334} V^{0.334}\left[1 + (8V_y/V)^2\right]^{0.167}$$

(6) Coefficient of Friction Drag (C_D)

$$C_D = 16\,\mathrm{Re}^{-0.6} \tag{12}$$

(7) Molar flux of solvent in spinline surface

$$N_S = k_x(x_S - x_S^*)/(1 - x_S) \tag{13}$$

3. Simulated Results and Discussion

3.1 Simulation condition for dry spinning process

To investigate the effect of diffusion coefficients on the dry spinning process, such as the temperature of spinline the concentration of solvent, the simulation was conducted under the conditions shown in Table 1, where α_z is dimensionless length from the spinneret defined as the ratio of length from the spinneret to the take-up position of spinning chamber.

Table 1 Calculation condition of dry spinning simulation

Dry spinning condition	Value	
Troughput, W_N (g/min)	1.20	
Raw material temperature, T_N (℃)	40	
Solvent concentration, ω_{s0} (%)	90	
Orifice diameter, D (mm)	0.26	
Dimensionless length of spinning chamber, α_L (-)	1	
Dimensionless twisting position, α_{tw} (-)	0.353	
Gas temperature, T^* (℃) & drying gas velocity, V_y (m/s)	T^* (℃)	V_y (m/s)
$0 \leq \alpha_z \leq 0.1647$	$T^*_1 = 200$	$V_y = 0.1$
$0.1647 < \alpha_z \leq 0.1659$	$T^*_2 = 200$	$V_y = 0$
$0.1659 < \alpha_z \leq 0.7882$	$T^*_3 = 200\text{-}80.3\ (\alpha_z\text{-}0.166)$	$V_y = 0$
$0.7882 < \alpha_z \leq 0.882$	$T^*_4 = 150\text{-}1169.0(\alpha_z\text{-}0.788)$	$V_y = 0$
$0.8823 < \alpha_z \leq 0.8847$	$T^*_5 = 40\text{-}6250.0\ (\alpha_z\text{-}0.882)$	$V_y = 0$
$0.8847 < \alpha_z \leq 1$	$T^*_6 = 25$	$V_y = 0$
Take up speed, V_w (m/min)	200	

3.2 Solvent concentration and spinline deflection

Figure 3 shows the changes in solvent concentration and spinline deflection during dry spinning from the spinneret to the take-up position for Logistic and new Hybrid methods, respectively. It can be seen from Figure 3 that the solvent concentration of spinline is almost constant just after the spinneret **(**Part(A)), the solvent concentration rapidly decrease **(**Part(B)**)** and finally the solvent concentration becomes constant **(**Part(C)**)**.

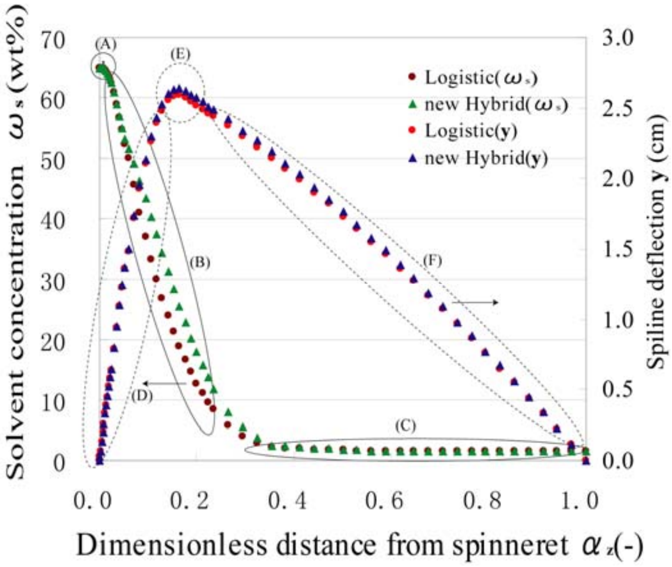

Fig.3 Changes in solvent concentration and spinline deflection during dry spinning from the spinneret to the take-up position

Such solvent concentration profile is caused by the following reasons:

In Part(A), it is the reason why the vaporization of solvent from spinline cannot occur because the concentration of solvent on the spinline surface is lower than the mole fraction of solvent included in the blowing gas just after the spinneret, where Part(A) is dependent on diffusion coefficient.

For the rapid decrease of solvent concentration in Part(B), it is the reason why the solvent rapidly begins to vaporize from the spinline surface when the concentration of solvent on the spinline surface becomes higher than the mole fraction of solvent in the blowing gas and the vaporization accelerates the diffusion of solvent in the spinline. The degree of decrease in solvent concentration is dependent on diffusion coefficient. The difference between the solvent concentration by Logistic method and that by new Hybrid method is due to the the change of SPUU spinline state with temperature and solvent.

For the almost constant solvent concentration of Part(C), it is the reason why the diffusion coefficient becomes very low when the spinline becomes solid-state and as a result the solvent concentration on spinline surface becomes lower than that in the solvent-containing blowing gas.

Next, it can be seen from Figure 3 that the spinline deflection increases with distance from the spinneret and takes a maximum near the endpoint of gas-blowing. Therefore, the spinline fixed at both the spinneret and take-up points is deflected with its elongation by blowing gas near the spinneret and the deflection is integrated from the spinneret to the endpoint of blowing (Part(D), (E)).

After the endpoint of blowing (Part(F)), the deflection decreases with distance from the spinneret to the take-up. Therefore, no gas blows on the spinline and the stiffness increases with the decreases in solvent concentration and temperature.

The behavior of spinline deflection by new Hybrid method is almost similar to that by Logistic method over the whole dry spinning process.

3.3 Distribution of solvent concentration in the spinline

Figures 4 and 5 show the change in the solvent concentration distribution in the radial direction durion the dry spinning process estimated by Logistic and new Hybrid methods, respectively. In Figures 4 and 5, the solvent concentration at the center of spinline denotes i=1 and that at the surface of spinline denotes i=5.

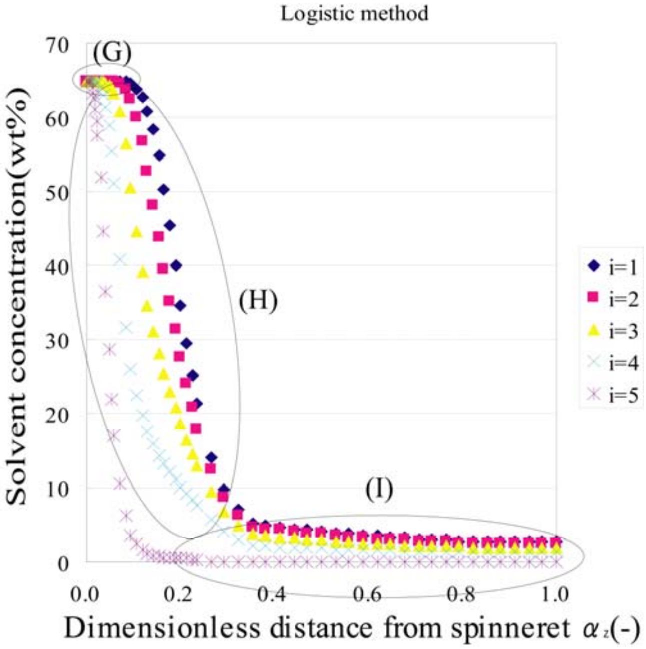

Fig.4 Changes in solvent concentration distribution during dry spinning from the spinneret to the take-up position estimated by Logistic method

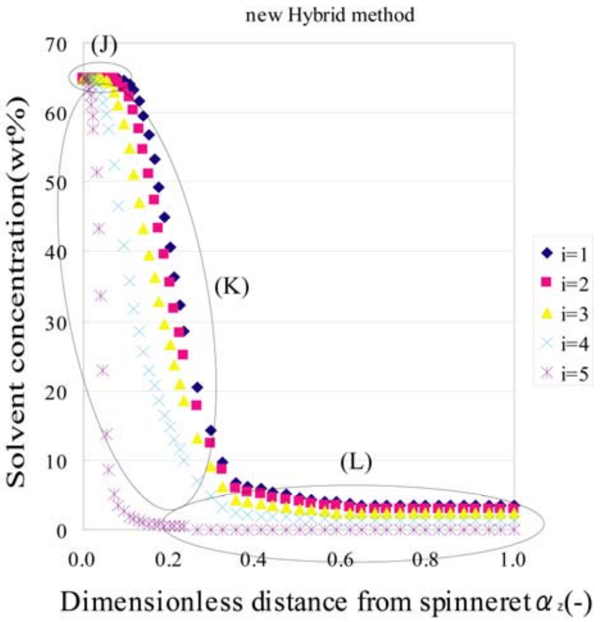

Fig.5 Changes in solvent concentration distribution during dry spinning from the spinneret to the take-up position estimated by new Hybrid method

It can be seen from Figures 4 and 5 that the solvent concentration at the spinline surface (i=5) by new Hybrid method rapidly decreases similarly to that by Logistic method and then becomes constant at very low solvent concentration. However, the solvent concentration distribution in the inside of spinline by new Hybrid method is wider than that by Logistic method as shown in Parts(H) and (K).

Both the distribution of solvent concentration by Logistic method and that by new Hybrid method are narrow and becomes almost constant with approaching to the take-up position in Parts(I) and (L).

3.4 Spinline temperature

Well, Figure 6 shows the gas (ambient) temperature pattern is assumed as indicated in Table 1.

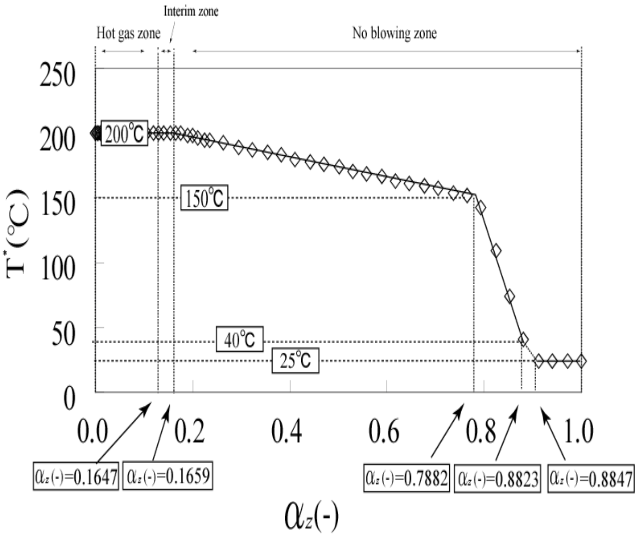

Fig.6 Example of gas (ambient) temperature pattern set in the spinning chamber

The whole region is divided into three zones: 1) Hot gas zone($0 \leq \alpha_z \leq 0.1647$) with temperature as 200 °C, 2) Interium zone ($0.1647 < \alpha_z \leq 0.1659$) with no gas and temperature as 200 °C, and 3) No blowing zone. According to the linear alteration of temperature in spinning chamber, the No blowing zone is divided into four regions as $0.1659 < \alpha_z \leq 0.7882$, $0.7882 < \alpha_z \leq 0.8823$, $0.8823 < \alpha_z \leq 0.8847$ and $0.8847 < \alpha_z \leq 1$, respectively. The final temperature for the first three regions is set as 150°C, 40°C, and 25°C, respectively. And the temperature in final region is supposed as constant as 25°C.

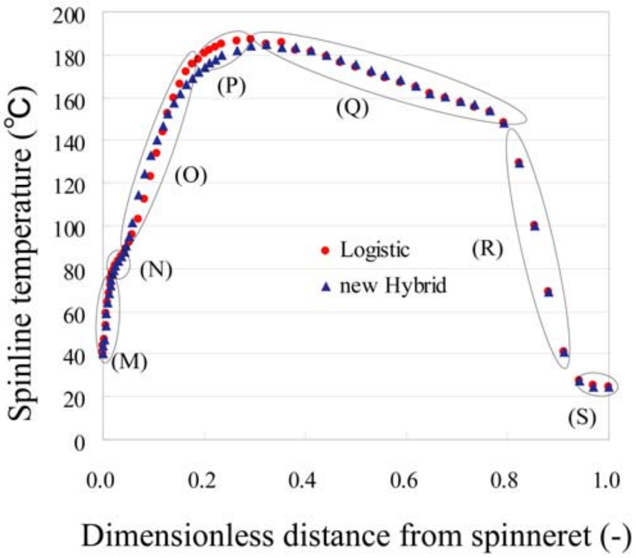

Fig.7 Change in spinline temperature during dry spinning from the spinneret to the take-up position

Figure 7 shows the change in spinline temperature during dry spinning from the spinneret to the take-up position for Logistic and new Hybrid methods.

In Part(M) the spinline temperature rapidly increases just after the spinneret, in Part(N) the degree of temperature rise becomes low and the spinline temperature rapidly increases again and reaches at a maximum point where the spinline temperature by Logistic method is lower than that by new Hybrid method. Therefore, in Part(M) the solvent cannot vaporize from the surface of spinline because of lower solvent concentration on the spinline than that in the blowing gas so that the spinline temperature increases by the hot blowing gas, in Part(N) the solvent begins to vaporize after the solvent concentration on the spinline surface is higher than that in the blowing gas so that the degree of temperature rise reduces because of the evaporative latent heat. In Part(O) the solvent concentration on the spinline surface becomes low so that the solvent in the spinline continuously diffuses to the spinline surface and then the spinline temperature again increases, where higher the diffusion coefficient is the spinline temperature becomes lower. As the diffusion coefficient by Logistic method is higher than that by new Hybrid method, the spinline temperature by Logistic method becomes lower than that by new Hybrid method in Part(O).

In Part(P) where the heat given by the hot blowing gas becomes equal to the heat removed by evaporation of solvent, the spinline temperature reaches at a maximum point. As the solvent concentration by Logistic method with higher diffusion coefficient becomes lower than that by new Hybrid method in

Part(P), the spinline temperature by Logistic method becomes dissipation due to solvent evaporation.

In Parts(Q) to (S) the spinline temperature follows a similar pattern of gas (ambient) temperature pattern set in the spinning chamber because of very low solvent vaporization.

3.5 Elongational viscosity

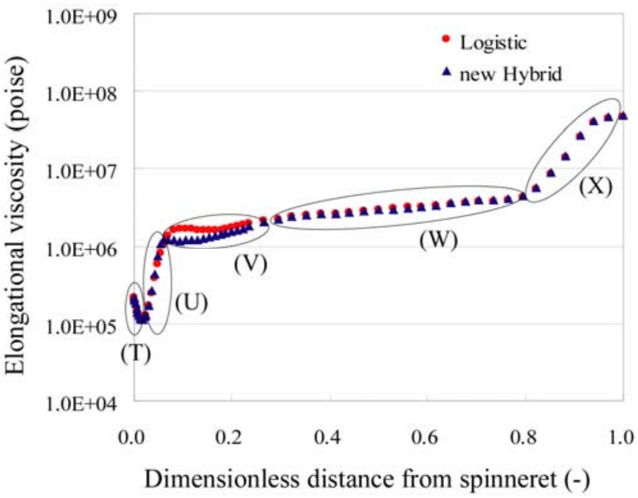

Fig.8 Change in elongational viscosity during dry spinning from the spinneret to the take-up position

Figure 8 shows the change in elongational viscosity during dry spinning from the spinneret to the take-up position for Logistic and new Hybrid methods.

In Part(T) the elongational viscosity rapidly decreases just after the spinneret, because the spinline temperature rapidly increases without the solvent evaporation. In Part(U) the elongational viscosity increases with the decrease in solvent concentration due to evaporation.

In Part(V) the changes by new Hybrid method are difference from those by the Logistic method. It is the reason why the solvent concentration by the Logistic method is lower than that by new Hybrid method.

The elongational viscosity increases with the decrease in temperature in Parts(W) and (X) with little change in solvent concentration, almost dependently on spinline temperature only.

4. Conclusion

A new expression (new Hybrid method) for diffusion coefficient has been proposed which can be expected to estimate a wide range of polymer concentration than Logistic method previously proposed. The new Hybrid method can be predicted the spinline behavior from the spinneret to the take-up position, such as the changes in velocity, tension, cross section area, spinning stress, temperature, solvent concentration, deformation speed, deflection, elongational viscosity and radial distribution of solvent concentration under given dry spinning conditions.

Two kinds of expressions (Logistic and new Hybrid methods) for diffusion coefficient have been newly discussed to simulate the dry spinning process where the state of spinline changes from the liquid state to the solid state. It has been confirmed the new Hybrid method can give the similar and wider predictions to Logistic method.

higher than that by new Hybrid method because of heat

Reference

[1] Ishihara, H., Tani, K., Hayashi, S. and Ikeuchi, H., "Studies on Dry Spinning of Polyurethane-urea Elastomers: Theory and Experiment", J. Polym. Eng., **6**, pp.237-261 (1986).

[2] Yamada, T., Yanagi, N. and Nishida, T., "Spinning Simulation of Spandex Fiber", Proceeding of 11th Annual Meeting of The Japan Society of Polymer Processing, Tokyo, E106, PP.239-240 (2000).

[3] Yamada, T., Yanagi, N. and Nishida, T., "Simulation for Dry Spinning of Spandex Fiber", Proceedings of Sixteen Annual Meeting of The Polymer Processing Society (PPS-16), Shanghai, China, PP.629-630 (2000).

[4] Ono, H. and Ohaza,Y., "Sen-I no Keisei to Kouzouno Hatsugen: 3.Kodansei Sen-I no Boushi to Kozo (Fiber processing and Structural Development : Chapter 3 Spinning and Structure of High modulus Fibers", Kagaku Zokan, **50**, Kagaku Dojin Publishing Co., pp.157-179 (1971)

[5] Li, G., Yamada, T., Tada, K., Katsuo, K., and Ishihara, H., "Simulation for Dry Spinning Process of Segmented Poly(urethane-urea) Fibers", Seikei kakou, in press.

[6] Yamada, T., Li, G., Tada, K., Katsuo, K. and Ishihara, H., "Simulation for Dry Spinning Process of Degmented Poly(Urethane-Urea) Fibers", Proceedings of the polymer processing Society (PPS-2005), Quebec City, Paper Filed in CD-ROM, pp.1-2 (2005).

[7] Li, G., Yamada, T., Tada, K., Katsuo, K. and Ishihara, H., "Simulation of Dry Spinning Process of Segmented Poly(urethane-urea) Fibers", Polymer Processing Society 22nd Annual meeting (PPS-22), Yamagata, Japan, Paper Filed in CD-ROM, pp.1-2(2006).

[8] Yamada, T., Li, G., Tada, K., Katsuo, K. and Ishihara, H., "Simulation for Dry Spinning Process under Dependence of Diffusion Coefficient on Solvent Concentration expressed as a Logistic Function", Proceedings of the Europe/Africa Meeting of the Polymer Processing Society (PPS-2006), South Africa, Paper Filed in CD-ROM, pp.1-14(2006).