ID 1056

Primary Study on the Spinning Process of Screw Extrusion for Domestic High Performance Plastics PEEK

Xu Zhongbin
South China University of Technology, Guangzhou, China (510641)
Yi Xiaosu
Institute of Aeronautical Materials, Beijing, China (100095)
Wu Shunying
South China University of Technology, Guangzhou, China (510641)
Tang Bangming
Institute of Aeronautical Materials, Beijing, China (100095)

keywords: PEEK, melt spinning, screw extrusion

Introduction

With the development of the forming technique of thermoplastic composites and with the extension of the application range of this kind of composites, PEEK resin should be made into high performance special fibers with heat and corrosion resistivity.[1] With regard to the same material, fiber products of obviously different physical mechanics performance can sometimes be obtained by different spinning techniques.[2] General spinning processing methods include: melt spinning, wet spinning and dry spinning process. High performance plastics PEEK has high viscosity, high flow temperature and lacks of suitable solvent, so it is not suitable for wet spinning or dry spinning process. Melt spinning can furthermore be classified as firegrate spinning and screw spinning. The main shortage of firegrate spinning is that the melting capacity of firegrate is confined by and changes with the melt's viscosity. Besides, the interface renewal between the melts and the ambience air is extremely slow, which causes the polymer to decompose easily. The reports concerning the PEEK melt spinning which used this kind of spinning equipment appeared in document [3][4][5].

Screw spinning has been used more and more in filaments and staple fiber spinning processes since the middle of 1970's. Its main advantage is that the retention time is short and the screw transportation interface can be renewed continuously. So, the melt capacity of screw spinning is bigger and the productive ratio is high. The deformation and flow of spinning melts during the processing course include not only the deformation and flow in the extruder, spinneret capillary and spinline, but also the visco-elastic deformation and flow in the drawing and heat setting device after the solidification of PEEK filament. The purpose of this paper is to provide a primary research result of the screw spinning process of domestic PEEK with regard to the above-mentioned aspects.

Brief rheological analysis of high performance plastics melts in screw extruder

The schematic of the experimental setup for domestic PEEK melt spinning is shown in Fig1. In the spinning process of screw extrusion, the function of screw extruder is pumping, melting and mixing the spinning material. The physical process of spinning polymer, which transforms the polymer from solid into melts in screw extruder, has been proved by experiments. According to the melt mechanism, the melting of solid material occurs on the boundary between the melting film and the solid bed through the heat conduction of the melting film. Part of the heat in the melting film comes from the barrel surface through heat conduction and the other part comes from viscous resistance of mechanical movement, which consumes mechanical work. For the screw spinning of this high performance plastics, considering the low screw speed and high barrel temperature condition, the main factor deciding the temperature distribution in melts is the linear temperature distribution caused by heat conduction, while the nonlinear distribution of temperature caused by viscous resistance is relatively less important.

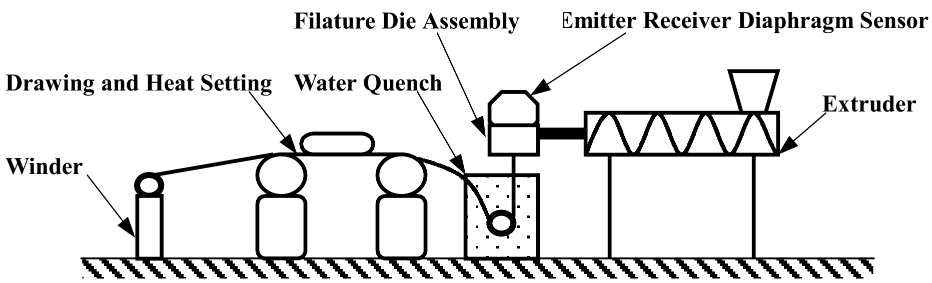

Fig. 1 The schematic of the experimental setup for domestic PEEK melt spinning

Based on the above analysis, we can deduce the following expressions of melting rate w and melt film's thickness δ from the heat equilibrium equation and the mass conservation equation:

$$w = \Phi X^{1/2} = \left\{ \frac{v_{b1}\rho_m U_2 \left[K_m (T_b - T_m) + 0.5U_1\right]}{2\left[q + C_S (T_m - T_S)\right]} \right\}^{1/2} X^{1/2} \quad (1)$$

$$\delta = \left\{ \frac{\left[2K_m (T_b - T_m) + U_1\right] X}{v_{b1}\rho_m U_2 \left[q + C_S (T_m - T_b)\right]} \right\}^{1/2} \quad (2)$$

$$U_1 = \frac{2m_0}{\beta^2} \delta^{1-n} \left(\frac{\beta v_{b1}}{1 - e^{-\beta}} \right)^{n+1} \left(e^{-\beta} + \beta - 1 \right) \quad (3)$$

$$U_2 = 2\left(\frac{1}{1 - e^{-\beta}} - \frac{1}{\beta} \right) \quad (4)$$

$$\beta = \frac{b(T_b - T_m)}{n} \quad (5)$$

Where, K_m is the heat transfer coefficient of the melts. ρ_S ,C_S ,T_S is separately the density, specific heat and temperature of the solid bed material; T_m is the melt's temperature; ρ_m is the melt's density; q is the heat of fusion of the spinning material; T_b is the barrel's temperature; X is the width of solid bed along the coordinate axis X_1; v_{b1} is the X_1 direction part of the circular velocity of barrel surface; n is flow behavior index; m_0 and b are material parameters of the law model.

Through discussion on formula (1), we can learn how the different technological conditions have influence on the melting rate when the flow velocity remains constant. If the screw speed is raised, the velocity v_{b1} and v_{b3} increased, and the movement of melts from melt film to melt pool is improved which leads to the increase of viscous heat, thus the melt rate is raised. However, the increase of screw speed is confined by the orifice radius and the number of orifices on the spinneret. Besides, if the barrel temperature T_b is raised, the conductive term K_m $(T_b- T_m)$ increases, and the melt rate increases too, but the increase of temperature leads to the decrease of the melt viscosity of high performance plastics. So, there is a best barrel temperature T_b corresponding to the biggest melt rate.

Design of melt spinning equipment of high performance plastics

Spinneret is the important precision part in the plastic melt spinning process and is also the basic element of spinning forming. Its function is making the plastics melts which has been measured precisely extrude through the capillaries of the spinneret and become some fibers of uniform diameter. The technique parameters of the spinneret include aperture, orifice shape, orifice number and orifice array etc. The design of each part's dimension of the spinneret has great influence on the spinning forming and the quality of the fibers. The orifice shape of the spinneret is mostly round, conical and hyperbolical etc. We use the round orifice for the high performance plastics melt spinning process.

Under normal circumstances of plastics melts being extruded from orifices, when velocity or stress surpasses the critical value, irregular cross sections of outflow tow may occur, and the diameter of the outflow filaments is often bigger than that of the orifices. This is the relaxation phenomenon of visco-elastic fluid, and is called "die swell". If this kind of relaxation is too serious, the outflow melts from the orifices will wave and thus lead to spinning difficulty, and furthermore cause non-uniform diameter of the fibers after solidification.

Influence of orifice aperture

By rheological analysis of the melt flow state in the spinneret capillary, we can obtain the shearing rate at the wall of the round orifice as:

$$\dot{\gamma}_w = \left(\frac{\Delta \mathrm{Pr}_2}{2KL} \right)^{\frac{1}{n}} = \frac{(3n+1)Q}{\pi n r_2^3} \tag{6}$$

Where, r_2 is the radius of the spinning orifice; Q is the single orifice flux of the melts.

As seen, the maximum shearing rate of the melts flowing through the orifice is directly proportional to the single orifice flux and is inversely proportional to cubic of the orifice radius. The orifice aperture has great influence on the shearing rate. Therefore, the orifice radius should be determined strictly according to the fiber number, and the maximum shearing rate should be controlled under the critical value in the design of the spinneret of high performance plastics PEEK, or else serious melt fracture phenomenon might occur which can hardly be eliminated by adjusting the processing parameters.

The L/D ratio of the spinneret orifice

Raising the L/D ratio of the orifice can make the retention time of spinning melts passing through the spinneret capillary increase, and thus the swell region produced by residual stress of relaxation reduces. This leads to complete energy transformation of spinning melts when flowing in the capillary. Furthermore, with the increase of the spinneret orifice height, the inner pressure of spinning component increases and the bubble numbers of the melts in the orifice decrease, and the end breakage rate of melt spinning is reduced. However, a too large L/D may lead to the difficulty in orifice manufacture and the decrease of it's dimension precision. So the L/D ratio of the orifice should be determined according to fiber's variety, spinning melt's viscosity, spinning speed and manufacture condition etc.

Considering the influence of spinning melts viscosity, suitable L/D ratio should be chosen to ensure the quality of fiber forming. Under normal condition, L/D ratio can be 1~1.5. The higher the melt's viscosity is, the bigger the L/D of the orifice should be. It's suitable to choose a L/D value more than 2.0 for high performance plastics of high viscosity, on condition that the manufacture is convenient and the precision requirement is met.

Value of conical angle α

Reasonably choosing the conical angle α of the orifice will help reduce the flow resistance of spinning melts. For power-law fluid, the entrance pressure drop of the melts is:

$$\Delta p = p_1 - p_2 = \frac{2K}{3nSin\alpha}\left[\frac{3Q(3n+1)Sin\alpha}{4\pi n(1-Cos\alpha)^2(1+2Cos\alpha)}\right]^n\left(\frac{1}{r_2^{3n}} - \frac{1}{r_1^{3n}}\right) \qquad (7)$$

Where, r_1 is the radius of the leading-in hole of spinning orifice; K is the viscosity coefficient of non-Newtonian fluid.

In general, the conical angle α of the spinneret for melt spinning is chosen 60~120^0. When the conical angle α is less than 90^0, the resistance of the melts passing through the conical angle part is low, and thus is good for spinning. With the experimental value n and k from the relevant document[6], the Δp-α curve of PEEK has been obtained, which is shown as fig2. The entrance pressure drop arrives at the minimum value when the conical angle is 90^0. This result is calculated from the document datum of import PEEK resins, and we should modify the best conical angle value for domestic PEEK screw spinning.

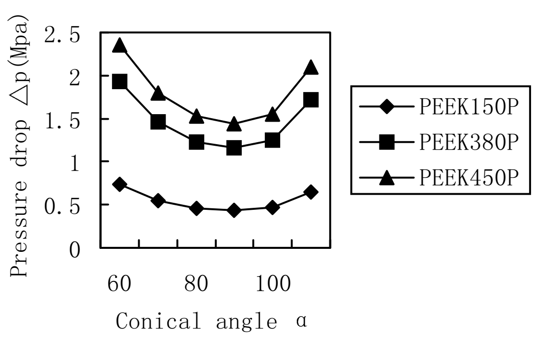

Fig. 2 The Δp—α curve of high performance plastics PEEK melts

The cooling course of high performance plastics and its influence

In melt spinning industry, filament quench is tremendously important. Precise control of the cooling rate is related closely to the predicted quality of fiber product. The rates of cooling and stretching have an effect on molecular orientation and crystallization rate. In the spinning process, the plastics melts is extruded from the orifice of the spinneret at a definite flow rate. When the filament passes through from the spinneret to the winder, it is drawn to the needed fine size and fully quenched to solidification.

The cooling of melt filament is finished in the heat exchange course of the relative movement between the filament and the coolant. The cooling condition is determined by the temperature distribution of the coolant while the temperature distribution is closely relative to the fluid dynamics of the coolant. In order to ensure the inner quality of as-spun fibers, we should consider both the influence of fluid dynamic field on the heat conduct course and the disturbance of the coolant flowing condition on the spinline when designing the filament quench forming equipment. So, a good filament quench forming equipment should satisfies:
The first, the cooling condition supplied by the equipment along the filament quench way can form the best temperature distribution on the spinline. Secondly, the disturbance of the coolant flowing condition determined by this cooling condition to the filament should be as little as possible.

Supposed that λ is a constant; the temperature distribution is axially symmetric and there is no heat conduction axially along the spinline, we can get the following equations from Fourier heat conduct law.

$$\begin{cases} \rho C_P \dfrac{\partial T}{\partial t} = \nabla \bullet (\lambda \nabla T) \\ T(r,0) = T_0 \\ \left(\dfrac{\partial T}{\partial r}\right)_{0,x} = 0 \\ \left(\dfrac{\partial T}{\partial r}\right)_{R,x} = -\dfrac{(T_R - T_C)\alpha^*}{\lambda} \end{cases} \tag{8}$$

Where, T_0 is the melt temperature at the orifice outlet; T_R is the surface temperature of PEEK filament; T_C is the coolant's temperature; C_P is the specific heat of the melts; α^* is the convection heat transfer coefficient; λ is the conductivity factor.

Take V=60m/min, T_0=380℃, T_C=20℃, we can calculate the L_K of PEEK screw melt spinning by difference method. The result is L_K=0.26m. It shows clearly that the cooling distance needn't to be too long if natural cooling is taken for PEEK filaments. In general, the distance between the spinneret and the first feeder-beater is 4~6m for continuous filament fiber spinning. This cooling distance is too long for high performance plastics PEEK, and it should be modified.

Control of melt fracture and draw resonance

In practical production, people often come across a phenomenon called melt fracture. When the extrusion velocity surpasses a certain value, the surface of the extruded substance begins worsening in quality, gradually loses luster and appears "shark skin", then becomes unevening and changes into spiral or corrugated shape. Through primary experiment, we found that the instability phenomenon appeared when the screw speed was more than 38rpm for the 0.3mm-12-orifice spinneret. When the screw speed increased more, the filament of PEEK became big spiral shape, and then became small spiral shape. When the shearing rate is very high, the irregular melt fracture appeared in the end.

Melt fracture phenomenon depends on the melt flowing state in front of and inside the spinning die. The melt slip inside the spinning die has main influence on melt fracture. However, the melt slip is in close relationship with the elasticity and molecular structure of the polymer melts, as well as the cohesive property between the melts and the metal die. For the definite PEEK spinning melts under a certain condition, raising the wall fineness of the metal die is an effective way of lessening melt fracture. As for the irregular flow at the inlet of the die, melt fracture phenomenon will occur if the elastic deformation of the melts at the inlet surpasses the limitation. By means of designing a die of big L/D ratio and cone inlet, we can make the melt full relaxation, reduce the dead zone and cut down the chance of dead zone melts entering the streamlines, and thus lessen the melt fracture phenomenon. Besides, we can obtain smooth and uniform fibers through controlling the melt temperature, reducing the elasticity of the melts and using spinning die drawing method so as to eliminate the influence resulting from melt fracture in the end-filament.

Draw resonance depends to a large extent on the elongation flow after the extrusion die. On one hand, the occurrence of draw resonance has something to do with the elastic deformation of the filaments extruded from the spinneret plate. Namely, the more the elastic deformation the filament has, the more the energy of elastic deformation will be saved, the easier the draw resonance will occur, and the lower the critical value of draw-down ratio $(V_L/V_0)_{crit}$ will be. On the other hand, draw resonance has a relationship with the relaxation behavior of the material. If the elasticity is low and the plasticity is high as it being drawn, the relaxation time will be short, and the draw resonance phenomenon can be lessened.

The value of critical drawdown ratio is under the influence of the geometry shape and processing parameter of the die. Draw resonance makes the fiber’s diameter irregular, and the fiber’s breakage possibility increases. It’s possible that melt distortion will occur after the melt is extruded from the spinneret plate, but the melt distortion can be lightened by suitable drawing. Raising the drawdown ratio can obtain fine PEEK fibers. In the case of draw resonance, which is not like melt fracture, once the drawdown ratio surpasses the critical value $(V_L/V_0)_{crit}$, the filament fluctuation will occur. Raising the drawdown ratio again can only aggravate the filament fluctuation and thus cause the filament to break at the end. In order to avoid occurrence of draw resonance, we should pay attention to suitable orifice shape in the design to reduce die swell, raise the melts temperature to a certain extent, and use slow cooling method in the filament quench.

Primary analysis of experiment results of domestic PEEK screw spinning

The melt spinning experiments of screw extrusion for domestic high performance plastics PEEK were conducted in National Key Laboratory of Advanced Composites in Beijing. The experiments tested and verified the above-mentioned theoretical analysis and turned out to be successful.

According to the melt mechanism, there is a best barrel temperature for the biggest melt rate. In correspondence with this, there is a best spinning temperature. The experiment showed that the best spinning temperature of domestic PEEK screw spinning is a little lower than that of the firegrate spinning which is about 380~400C^0. [4] This might be due to the interface renewal of the screw spinning, which makes PEEK melts melt fully, and its temperature distribute well.

In the experiment, we found that the obvious melt fracture phenomenon didn't appear on the filament surface of domestic PEEK when the screw extrusion velocity surpassed a certain critic value for a definite spinneret structure. Instead, the melt filament showed big spiral shape at first and then small spiral shape. Only until the shearing rate was very high did the irregular melt fracture appear in the end. This is different from the melt fracture phenomenon of general polymer that appears "shark skin" and then its surface becomes uneven.

The experiment also verified the above L_K computation result. The natural cooling distance L_K of domestic PEEK spinline is greatly shorter than that of document [3], which is about 1.5~2m long. This is possibly relative with the different cooling condition and processing parameters.

Reference

1. Sylvie Beland, High performance thermoplastic resin and their composites, Technonic Publishing Co., 1991,pp201-202
2. S. Middleman, Fundamentals of polymer processing, MeGraw Hill, London, 1977,pp249-250
3. S. S. Song, J. L. White, and M. Cakmak, Structure development in melt spinning and drawing PEEK fibers, SEN-1 GAKKAISHI, 1989,v45,no.6,pp243-251
4. Yu Jianming, Bian Dongcai and Zhou Xiaofeng, Development of PEEK fiber, Journal of textile, 1995, v16,no.5,pp260-263
5. Yu Jianming, Bian Dongcai and Zhou Xiaofeng, The effects of melt-spinning process on the properties of as-spun PEEK fibers, China synthetic fiber industry, 1996, v19,no.3,pp5-8
6. Liu Qixian and Zhang Xiaoming,A study of rheological properties of PEEK, 38th SAMPLE symposium, May10-13, 1993, pp.1594-1599.