JOURNAL OF MATERIALS SCIENCE **38** (2003) 2149–2153

Melt spinning of fine and ultra-fine PEEK-filaments*

H. BRÜNIG‡, R. BEYREUTHER, R. VOGEL, B. TÄNDLER
Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Hybrid yarns of PEEK and Carbon fibres are attractive as reinforcing materials. In an optimized hybrid yarn PEEK and Carbon fibres possess similar diameters. But the melt spinning of fine and ultra-fine thermoplastic filaments is a processing technique which makes great demands on the polymer and its elongational flow. The paper deals with theoretical and experimental investigations of the melt spinning process of fine and ultra-fine PEEK filaments up to finenesses of 1 dtex and lower. With a special spinning equipment finest filaments of lower than 0.1 dtex were reached.

1. Introduction

Poly(ether ether ketone) (PEEK) is a high performance thermoplastic material that retains its good mechanical properties even at high temperatures. The melting temperature and the glass transition temperature are 342°C and 143°C, respectively. The continuous service temperature of PEEK is up to 280°C, for a short time even a higher temperature is possible. The material shows also good chemical resistance. Because of these properties a hybrid yarn of PEEK and Carbon fibres (CF) becomes attractive as reinforcing material for heavy strained but light weighted industrial applications. Such hybrid yarns of reinforcing filaments (CF) and non consolidated thermoplastic matrix filaments (PEEK) show good conditions for the design of reinforcing semifinished products which are flexibly adaptable to complex structures.

The melt spinning process of PEEK has been investigated well [1–5]. The authors reported the structure development, crystallinity and orientation parameters [1], the draw mechanism [2], also the mechanical properties of PEEK fibres [3], the effect of molecular weight [4], and the heat transfer and its effect to the spinning course [5]. The main goal of these papers was the investigation of the structure development in the PEEK fibre forming process, therefore there was no attempt to fine or ultra-fine filaments.

The current paper deals with theoretical and experimental investigations of the melt spinning process of fine and ultra-fine PEEK filaments up to finenesses of 1 dtex and lower.

The motivation to produce fine PEEK filaments results from efforts to optimize the PEEK-CF-hybrid-yarn. The general spinning conditions and possibilities for the melt spinning process of PEEK filaments were estimated by means of the "Fiber Formation Model" developed in our institute. It is shown that for the goal of a 1-dtex-PEEK-filament a short distance between the spinning die and the take-up device is essential to minimize the spinline stress tension and to prevent filament breakages. Experiments were made with the PEEK-polymer Victrex® 151G by means of a laboratory high temperature extruder spinning device. To check the theoretical predictions, the spinline filament velocities and temperatures in dependence on the distance from the die were measured and compared with the theoretical values. The conditions for a stable spinning process of 1-dtex-filaments were determined. To test the limits of fibre formation, experiments with a self-constructed piston-type melt spinning device for low mass-throughputs were carried out. Finally, ultra-fine PEEK filaments with finenesses lower than 0.1 dtex were spun. It is assumed, that the limits of the melt spinning process have not been reached yet.

2. Fine PEEK-filaments as basis for optimized hybrid yarns

The investigations are part of the project "Textile reinforcements of high end components," promoted by the German Research Association (Deutsche Forschungsgemeinschaft). The goal of this project part is the own production of fine PEEK filaments with reduced filament diameter to get optimized hybrid yarns. A hybrid yarn PEEK/CF which is designed from a commercial PEEK-yarn (Zyex) with 95 dtex f6 and a commercial CF-yarn (Toray) with 198 dtex f300, shows a yarn cross section area similar to Fig. 1 at a mixture of 40/60 vol%.

Fig. 1 also shows a partly of a cross section for the typically used commercial components of a commingled hybrid yarn with diameters of 39 μm for the PEEK-filaments and 7 μm for the CF-filaments.

It can be easily seen that such a mixture would not be able to produce defectless reinforced thermoplastics.

*After a lecture at the POLYMER FIBRES 2002 Conference, Manchester, UK, 10–12 July, 2002.
‡Author to whom all correspondence should be addressed.

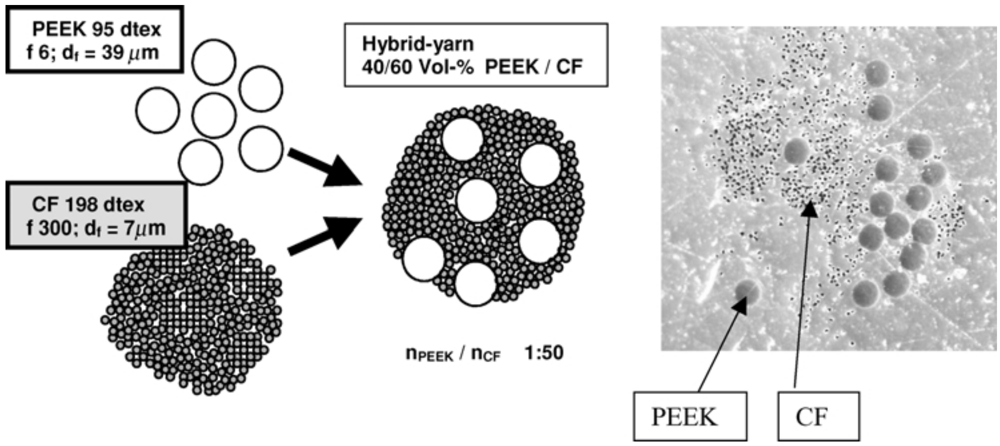

Figure 1 Schematic mixture of available PEEK/CF fibres to hybrid yarn (left), Microphotograph of a commingled PEEK/CF hybrid yarn (right, with kindly permission by Mr. B.-D. Choi, University of Technology, Dresden).

The reason is that the filament diameters of the hybrid yarn components are too different, so that the molten PEEK matrix filaments cannot reach each reinforcing CF-filament during the hot press molding procedure. This results in more or less less unbonded reinforcing filament clusters within the material.

There are mainly two criterions [6] for an optimum mixture of the filament components. In dependence on the mixture ratio and the diameter ratio it is possible to use the

- Filament Surface/Volume Ratio Criterion or the
- Each Other Touch (EOT) Criterion.

The EOT-Criterion determines the relation between the numbers n, the diameters D, and the volume ratio VR of the PEEK matrix filaments to the reinforcing CF filaments:

$$\frac{n_{\mathrm{PEEK}}}{n_{\mathrm{CF}}} = VR \cdot \frac{D_{\mathrm{CF}}^2}{D_{\mathrm{PEEK}}^2} \tag{1}$$

Fig. 2 shows the ratio $n_{\mathrm{PEEK}}/n_{\mathrm{CF}}$ in dependence on the diameter D_{PEEK} of the PEEK matrix filaments assuming a fixed diameter of the Carbon fibres $D_{\mathrm{CF}} = 7\ \mu$m and different volume ratios VR.

Simply spoken, both criterions show that an optimum mixture can only be reached if the diameters of the matrix filaments approach to the diameters of the reinforcing filaments. Therefore the first goal of our project was to produce fine PEEK-filaments with a fineness of 1 dtex and with filament diameters of about 10 μm to get optimized hybrid yarns for the used 7 μm Carbon-filaments. Of course, an ideal mixture should consist of the PEEK filaments with even lower diameters.

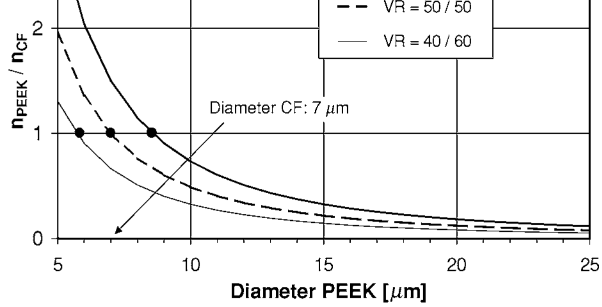

Figure 2 Example for the Each-Other-Touch (EOT) criterion, fixed diameter of 7 μm for CF.

3. Theoretical considerations

PEEK-yarns are commercially available, also the melt spinning process is well investigated [1–5]. But for the development of a technology to produce microfiber-like yarns the following simple considerations are usefull. The fineness Tt of a melt spun and drawn filament depends on the relation of the capillary mass throughput Q, the spinning velocity (take-up velocity) v_{spin} , and on the possible draw ratio DR:

$$Tt = \frac{Q}{v_{\mathrm{spin}}} \cdot \frac{1}{DR} \tag{2}$$

To get very fine filaments high take-up velocities are needed as well as a very low mass throughput, and a high value of the draw ratio, simply spoken. The parameters are not independent of each other, especially the maximum possible draw ratio DR is a function of the spinning conditions: $DR = f(v_{\mathrm{spin}}, \mathrm{Q}, \ldots)$. High take-up speed and low throughput cause high spinning stress and provoke filament breakage, also the draw ratio may tend to unity. An adapted melt spinning simulation software was employed to get an imagination about the expected spinning stress tension and the length of the fibre formation zone for very low throughputs. This melt spinning simulation software was developed in our institute. Originally it is applied for the typical melt spinning polymers like poly(ethylene terephthalate) (PET), polyamides (PA), or polypropylenes (PP). The model [7] bases on the well known balance equations for mass, energy, and momentum [8]. It is completed by a constitutive equation describing the polymer deformation behaviour in the molten state. Because there is not enough knowledge yet about the elongational rheological behaviour of PEEK for high deformation

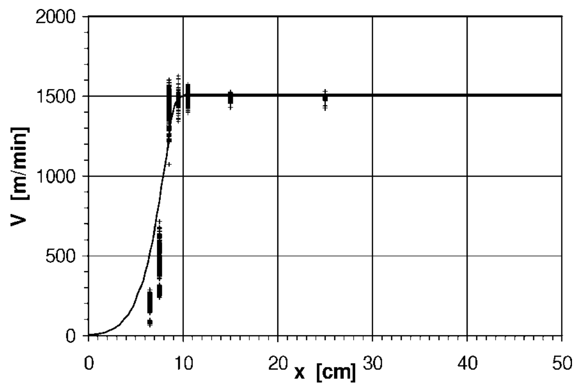

Figure 3 Filament velocity v vs. distance x, mass throughput 10.8 g/min (total), take up velocity 1500 m/min, fineness 7.2 tex f48; solid line: computer simulation, points: measured values by means of Laser-Doppler-Anemometry (LaserSpeed).

rates, some simple approximations were used, especially for the course of the elongational viscosity (e.g., Newtonian-behaviour). The software allows to calculate the courses of fibre velocity v, temperature T, spinline stress tension σ, and other physical parameters in dependence on the distance x from the spinning die. The model uses correlations to the structure development within the spinline for the well investigated and known polymers PET, PA, and PP, to determine textile properties like elongation to break, draw ratio, or tenacity. But in the case of PEEK these correlations are unknown yet and an estimation of the expected draw ratio after spinning based on a software simulation is not possible. At least we learned that the fibre formation is finished after a very short distance from spinneret and the air drag force is the main contribution to spinning stress for longer distances. An example for the calculated filament velocity v in dependence on the distance x is shown in Fig. 3.

4. Experimental

4.1. Fine PEEK filaments

Spinning experiments were carried out by means of a laboratory high temperature extruder spinning equipment with the PEEK polymer Victrex® 151G. A moveable winder was arranged at a distance of about 1 m below the spinneret to minimize the spinline stress and to prevent filament breakages (see Fig. 4). The equipment is characterized by the following limitations:

Maximum possible temperature:	450°C
Maximum mass throughput:	50 g/min
Minimium mass throughput:	5 g/min
Maximum take up speed of the winder:	2500 m/min

Several runs were made with different combinations of take up velocities and mass throughputs to get stable spinning conditions for the goal of 1.5 and 1.0 dtex filament fineness. The possible draw ratio was estimated by means of force-elongation-experiments. At first, the effect of increasing take up velocity on the spinnability was investigated. Fig. 5 shows the reached filament fineness, the draw ratio, and the expected fineness after drawing in dependence on the take up velocity for a constant mass throughput. For the possible mass throughput per hole, the extruder limitation of minimum 5 g/min has to be noticed. Above 2000 m/min more and more filament breakages were observed, the spinning process became unstable. The goal of 1-dtex-filament-fineness could not be reached this way. The other option is the further reduction of the mass throughput per hole. Fig. 6 shows the filament

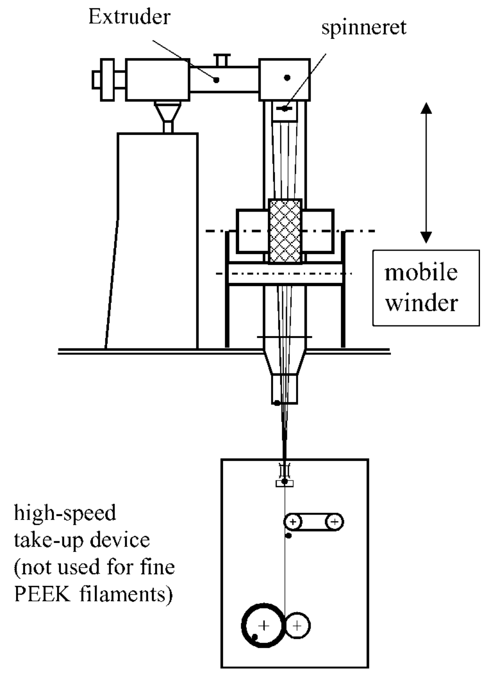

Figure 4 Melt spinning equipment.

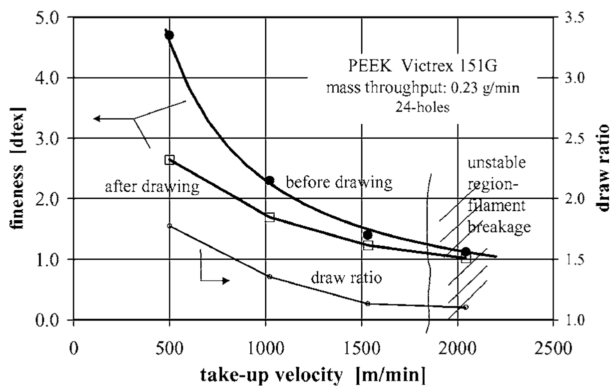

Figure 5 Fineness vs. take-up velocity.

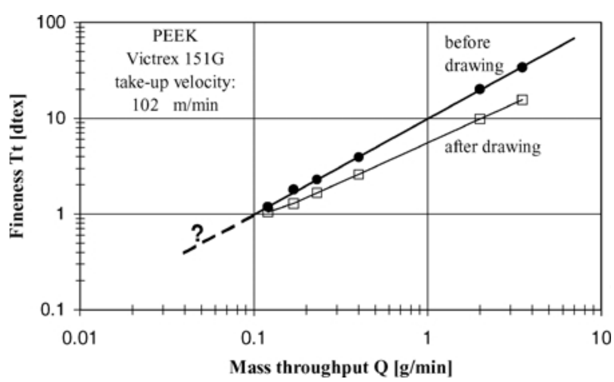

Figure 6 Fineness vs. throughput.

TABLE I Melt spinning conditions for 1.5 and 1.0 dtex filament fineness, PEEK Victrex® 151G

	Run 1	Run 2
Temperature	400°C	400°C
Take-up velocity	1500 m/min	1500 m/min
Mass throughput		
Total	10.8 g/min	7.2 g/min
Per filament	0.225 g/min	0.15 g/min
Fineness		
Total	7.2 dtex f48	4.8 dtex f48
Per filament	1.5 dtex	1.0 dtex
Diameter	12 μm	10 μm

fineness before and after drawing in dependence on the throughput per hole for a constant take-up velocity. The experiments suggest that a 48-hole-die must be used at least. As result we got the spinning conditions shown in Table I, which did not lead to any problems with the spinnability. To get fine filaments it is more effective to reduce the capillary mass throughput than to increase the take-up velocity. Take-up velocities higher than 2000 m/min were not practicable for the 1 dtex filament fineness. The filament velocity versus distance from spinneret was measured by means of a Laser Doppler Anemometry System (Laser-Speed LSM50, TSI Inc.), an example for the 1.5 dtex filament has been already shown in Fig. 3. The deformation rate is about 2000 s^{-1}. For further tests of the commingling properties several kilograms were produced.

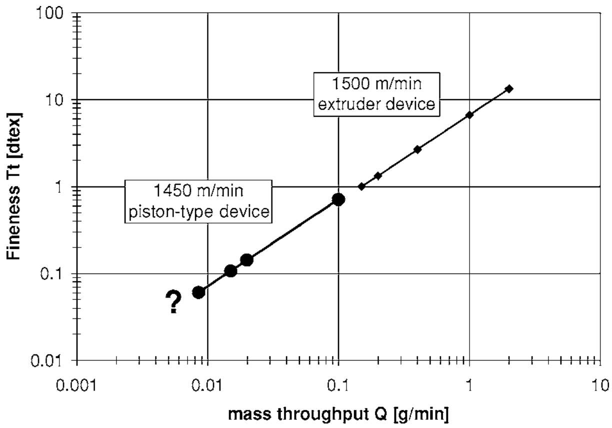

Figure 8 Experimentally realized finenesses *Tt* for ultra-fine PEEK filaments by reduction of throughput *Q*.

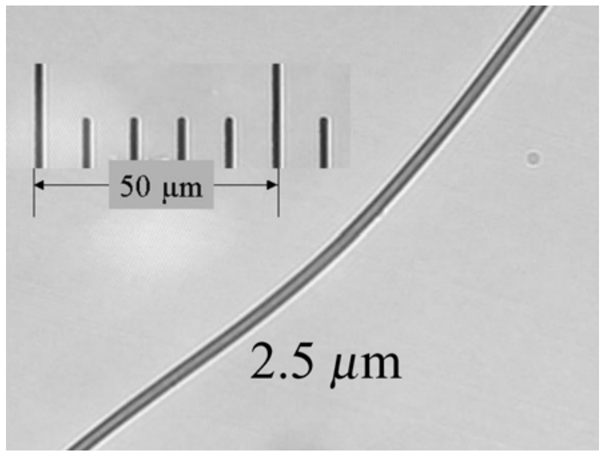

Figure 9 Ultra-fine PEEK filaments, Diameter ~2.5 μm.

4.2. Ultra-fine PEEK filaments

To get ultra-fine filaments lower than 1 dtex a further reduction of the mass throughput is necessary. But this is not possible with our extruder spinning equipment because of its limitation to a minimal mass throughput of ~5 g/min. For the following low throughput experiments a self-constructed piston-type device (Fig. 7) was used. It consists of a drive train with adjustable speed, a heated cylinder with piston, and a winder up to 1500 m/min. Several single-hole dies with different capillary diameters are available.

Fig. 8 is a continuation of the diagram shown in Fig. 6 and depicts the reduction of the throughput and the reached finenesses of filaments spun at a take up velocity of 1450 m/min. It was possible to realize ultra-fine PEEK filaments with a mass throughput of 30 mg/min—that is 0.2 dtex fineness- and also with finally 0.15 mg/min (0.1 dtex fineness). The draw down ratio *DDR*—the ratio between the cross section of the capillary die hole and the filament—is $DDR > 9000$ in this case. The finest possible filament we reached is shown in Fig. 9, its diameter is ~2.5 μm, the fineness is ~0.06 dtex. But the spinning process for this run was not stable, it took only a few seconds until the filament broke. There were also problems with the mechanical syncronization of the drive train. It is impossible to handle such fine filaments at the moment.

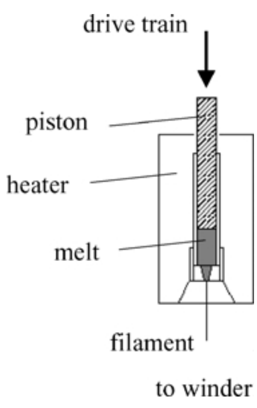

Figure 7 Self-constructed piston-type melt spinning device.

5. Conclusions

PEEK is a well spinnable polymer. Furthermore it can be advantageously used as the thermoplastic matrix component in hybrid reinforcing yarns. The PEEK/CF-hybrid yarn can be optimized by adapting the diameter of the PEEK filaments to the diameter of the used CF filaments. The general spinning conditions and possibilities for the melt spinning process of fine PEEK filaments were estimated by means of the (adapted) "Fibre Formation Model" developed in our institute. It was shown that for the goal of a 1-dtex-filament a short distance between the exit of the spinning die and the take-up device is essential to minimize the spinline stress tension. Experiments were made with the PEEK polymer Victrex® 151G by means of a laboratory high temperature extruder spinning equipment. The conditions for stable spinning processes for finenesses of 1.5 and 1.0 dtex were determined.

To get ultra-fine filaments lower than 1.0 dtex a self-constructed piston-type device for low mass throughputs was used. It was shown that filament finenesses <0.2 dtex until 0.1 dtex are possible to spin. Obviously, it is not the limit of spinnability and consequently further investigations are nessecary.

Acknowledgement

The authors thank the German Research Association (DFG) for the financial support of the project.

References

1. J. SHIMIZU, T. KIKUTANI, Y. OHKOSHI and A. TAKAKU, *Sen-i Gakkaishi* **43**(10) (1987) 507.
2. Y. OHKOSHI, H. OHSHIMA, T. MATSUHISA, K. TORIUMI and A. KONDA, *ibid.* **45**(12) (1989) 509.
3. Y. OHKOSHI, H. OHSHIMA, T. MATSUHISA, N. MIYAMOTO, K. TORIUMI and A. KONDA, *ibid.* **46**(3) (1990) 87.
4. Y. OHKOSHI, T. KIKUTANI, A. KONDA and J. SHIMIZU, *ibid.* **49**(5) (1993) 211.
5. Y. OHKOSHI, C. PARK, Y. GOTO, M. NAGURA, K. TORIUMI and T. KIKUTANI, *ibid.* **56**(7) (2000) 340.
6. R. BEYREUTHER, H. BRÜNIG and R. VOGEL, *International Polymer Processing* **XVII**(2) (2002) 153.
7. R. BEYREUTHER, H. BRÜNIG and R. VOGEL, in "Polymeric Material Encyclopedia: Synthesis, Properties and Applications" (CRC Press, Inc., Boca Raton, Florida, 1996) p. 4061.
8. A. ZIABICKI and H. KAWAI (eds), "High-Speed Fiber Spinning" (Wiley & Sons, New York, 1985).

Received 13 September
and accepted 12 November 2002