PREPARATION AND MECHANICAL PROPERTIES OF MESOPHASE PITCH-BASED HOLLOW CARBON FIBERS

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Introduction

Mesophase pitch-based noncircular carbon fibers have higher mechanical properties than round carbon fibers. Up to now, different shaped carbon fibers have been prepared, including hollow, C-shaped, ribbon-shaped, Y-shaped and other shaped fibers [1,2]. Hollow carbon fibers are difficult to be prepared. Rhee [3] spun mesophase pitch-based hollow fibers with annulus type spinnerets, the outside diameter of the fibers is 55~60 μm and the fibers have big hollow ratio. In this paper, mesophase pitch hollow fibers were spun with a curved slot spinneret which owns a C-shaped capillary. After stabilization and carbonization the hollow carbon fibers possess smaller out diameter, more appropriate hollow ratio, and they show higher mechanical properties than round carbon fibers. The reasons of this improvement were analyzed by means of scanning electron microscope (SEM) and X- ray diffraction (XRD).

Experimental

Mesophase pitch was prepared by thermal condensation from petroleum based pitch. Some properties of the mesophase pitch are listed in Table 1.

The data of die-swell of melt is important to design curved slot spinnerets. It was measured with an XLY- II capillary rheometer in the conditions that is similar to the spinning conditions. The die-swell (e) is defined as follows:

$$e = D_{\max} / D_0 \qquad (1)$$

where $D_{\max}$ is the maximum diameter of the melt exiting capillary, D_0 is the diameter of capillary.

A C-shaped slot spinneret was used to melt-spin hollow pitch fibers and a round spinneret was utilized to spin round fibers. The pitch fibers were stabilized in oxygen flow, then carbonized in nitrogen flow up to 1000 ℃. The mechanical properties of carbon fibers were tested by mono-filament testing method, and the microstructure of fibers were observed by a scanning electron microscope. In addition, the orientation degrees of round and hollow pitch fibers were measured by X-ray diffraction [4].

Results and Discussion

The die-swell of melt pitch is about 1.3. According to this, the C-shaped slot ends were designed to be separated from each other with a gap about one times the width of the slot. With the help of this spinneret, hollow fibers were spun. The round fibers were spun with a round shaped spinneret.

Mesophase pitch is a sort of nematic liquid crystal. The orientation of pitch molecules is considered to be formed in spinning process. The orientation degrees of round and hollow pitch fibers prepared in this work are 79.8% and 82.4% respectively. It proves that higher orientation of hollow pitch fibers is related to the structure of spinneret.

Table 2 shows some characteristic dimensions of the spinnerets. D_e is the hydraulic diameter of spinneret, it is defined as follows:

$$D_e = 4A_0 / S_0 \qquad (2)$$

where A_0 is the cross-sectional area of capillary; S_0 is the perimeter of capillary. Apparently, the hydraulic diameters of round shaped spinnerets are equal to their diameters.

Although the C-shaped slot spinneret has bigger cross-sectional area, its hydraulic diameter is smaller than the round shaped spinneret's. With smaller hydraulic diameter, the C-shaped slot spinneret can exert more shear effect on the liquid crystal molecules than the round shaped spinneret. So hollow pitch fibers possess higher orientation degree than round fibers, and the higher orientation is helpful to improve the mechanical properties of hollow carbon fibers.

Table 3 shows properties of the carbon fibers. The hollow carbon fibers (Figure 1) are 27.2% higher than round carbon fibers in tensile strength, 14.4% higher in tensile modulus and 11.0% higher in strain to break. It means that the mechanical properties of hollow carbon fibers are improved on the whole.

SEM photographs show that the round carbon fiber is easy to form flaws and voids during stabilization and carbonization (see Figure 2). Hollow carbon fibers have

two surfaces and the decomposed components are easier to escape from fibers in carbonization process, so hollow carbon fibers can avoid obvious flaws.

Conclusions

Mesophase pitch-based hollow carbon fibers can be prepared with curved slot spinnerets which are designed according to the properties of mesophase pitch, such as the die-swell of melt pitch. Hydraulic diameter of spinnerets have influence on the orientation of pitch molecules. Hollow carbon fibers show higher mechanical properties than round carbon fibers, one reason is that the hollow pitch fibers possess higher orientation degree, another reason is their flaws are less and smaller.

References

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Table 1. Some analytical properties of mesophase pitch

Code	Softening point (℃)	Anisotropic content (vol%)	Solubility (wt%)		
			BS	BI-QS	QI
MP	295	1 00	5.46	10.91	83.63

Table 2. Characteristic dimensions of spinnerets

Capillary shape	Cross-sectional area $A_0(mm^2)$	Length of capillary $L(mm)$	Hydraulic diameter $D_e(mm)$	L/D_e
C-shape	0.208	0.5	0.191	2.62
Round shape	0.071	0.9	0.3	3

Table 3. Properties of carbon fibers

Fiber type	Cross-sectional area (μm^2)	Outer diameter (μm)	Inner diameter (μm)	Tensile strength (GPa)	Tensile modulus (GPa)	Strain to break (%)
Hollow	318	21.0	6.0	0.991	77.0	1.31
Round	283	19.0	----	0.779	67.3	1.18

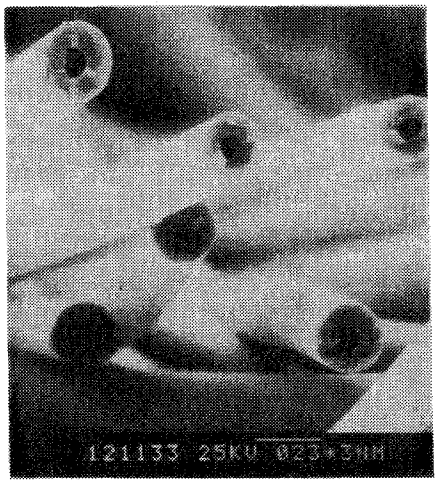

Figure 1. SEM photograph of hollow carbon fibers

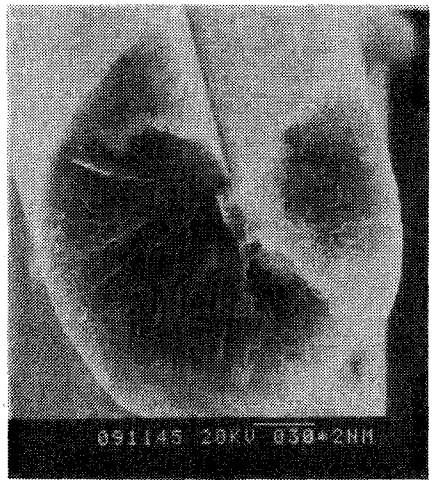

Figure 2. SEM photograph of round carbon fibers