

Structure and Properties of Thermotropic Liquid Crystalline Polyarylate Fibers

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Abstract. Thermotropic liquid crystalline polyarylate fiber is a kind of high performance fiber with high strength and modulus, high temperature and chemical resistance. In this paper, TLCPAR fibers were prepared by melt spinning and then heat-treated. The effects of spinneret draft ratio, heat-treatment temperature on aggregate structure and mechanical properties of the fibers were investigated.

1. Introduction

Thermotropic liquid crystalline polyarylate (TLCPAR) fiber is a kind of high-performance fiber with high strength and modulus, excellent dimensional stability and high temperature, chemical, radiation resistance. Therefore, TLCPAR fiber has wide potential application in the fields of aerospace, military, electronics and industry.

Commercially available TLCPAR can be classified into three categories according to the heat-distortion temperature (HDT, load of 1.86 MPa). They are high temperature resistant (model I), medium temperature resistant (model II) and low temperature resistant (model III) [1], respectively. Commercial TLCPAR fiber, Vectran[®], is of model II with excellent mechanical properties, chemical resistance, and low hygroscopicity. However, HDT of Vectran is below 280 °C which limits its application in high temperature environment. While HDT of Model I is above 300 °C, therefore it has wider application due to better temperature resistance and cheaper raw materials. SUMIKASUPER LCP of Sumitomo in Japan is one of representative samples.

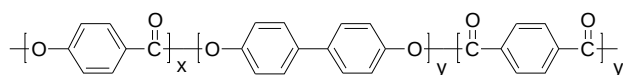
In this paper, fibers of SUMIKASUPER LCP were prepared by melt-spinning and subsequent heat-treatment. The changes of aggregate structure and mechanical properties of fibers were studied.

2. Experimental

2.1. Materials

SE6000 of Model I TLCPAR pellets was kindly provided by Sumitomo in Japan. It is copolyester of *p*-hydroxybenzoic acid (HBA), 4, 4'-Dihydroxybiphenyl (DOD) and *p*-terephthalic acid (PTA). The chemical formula is as follows.





2.2. Spinning process

The pellets were dried at 150 °C in vacuum. As-spun fibers were obtained by melt-spinning. The spinning temperature was 360 °C. During the spinning process, take-up velocity was varied to prepare fibers with different spinneret draft ratios (SDRs) at certain pump delivery.

2.3. Heat-treatment process

As-spun fibers were heat-treated at the heating rate of 5 °C/30min to the final temperature in nitrogen atmosphere. The heat-treated fibers were cooled to room temperature under the N₂ atmosphere.

2.4. Characterization

Wide-Angle X-ray Diffraction (WAXD) was carried out using D8 Discover 2D X-ray diffractometer. The fiber axis is parallel to the scattering plane. Thermal analysis was carried out using DSC Q20-TA at the heating rate of 20 °C/min. Mechanical properties was carried out using fiber tensile tester.

3. Results and discussion

3.1. Structures and properties of as-spun fiber

The effects of SDR on crystallinity and orientation of TLCPAR fibers are shown in Figure 1. Crystallinity of as-spun fibers without winding reaches 26.8 %, and increases to 34.0 % with SDR to 54. The rigid molecular chains limit the movement of molecular chains during crystallization, so they cannot fully organized [2]. On the other hand, fully crystallized structure cannot occur due to random sequence of the polymer chains. Therefore, the crystallinity of as-spun fiber is not very high.

It can also be seen that the crystal orientation of the fibers is very high and has no evident change with the SDR. Due to the liquid crystallinity of the TLCPAR, the orientation behavior is different from that of conventional flexible chain polymers. It is easy to orientate at small tensile force [3]. Therefore TLCPAR fiber's orientation is very high.

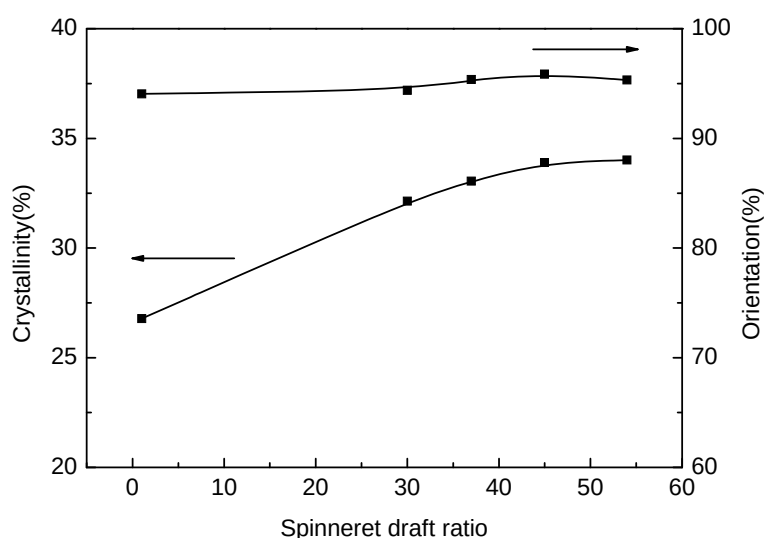


Figure 1. Effects of SDR on crystallinity and orientation of TLCPAR fibers

The mechanical properties of fibers under different SDRs are shown in Table 1. When the spinneret draft ratio increased from 30 to 54, the strength of the fibers increased from 4.2 cN/dtex to 4.8 cN/dtex

and modulus from 391.4 cN/dtex to 452.8 cN/dtex with small increase. At low spinneret draft ratio, the crystal orientation of as-spun fibers is already very high. With the increase from 30 to 54 of SDR, crystallinity become larger slightly. So the mechanical properties of as-spun fibers increase slightly with different spinneret draft ratio.

Table 1. Structure and mechanical properties of fibers under different SDRs

No.	Take-up velocity (m/min)	SDR	Fineness (dtex)	Diameter (μm)	Strength (cN/dtex)	Modulus (cN/dtex)
1	0	1.5 ^①	349.5	205	0.3	72.7
2	275	30	20.7	48	4.2	391.4
3	345	37	16.4	44	4.2	398.5
4	415	45	13.6	40	4.3	399.8
5	500	54	12.1	33	4.8	452.8

Note ①: Sample No. 1 is fiber without winding. The spinneret draft ratio of 1.5 was calculated from its diameter.

3.2. Structures and properties of heat-treated fiber

Heat-treatment is generally set at the temperature near but lower than the melting point. On the one hand the temperature provides energy for movement of molecular chain ends; on the other hand it must prevent the adhesion among fibers. The heat-treatment mechanism of TLCPAR fibers is complex. It is considered that heat-treatment can provide opportunity for the movement of molecular chain ends, and solid-state polycondensation occurs as a result.

WAXD pattern analysis of as-spun (SDR is 54) and heat-treated fibers (heat-treatment temperature 325 °C) is shown in Figure 2. The crystalline peak of (001) plane at $2\theta=20^\circ$ tends to disappear, while the (110) plane becomes sharper. This indicates that the crystal plane perpendicular to the fiber axis rotates after heat-treatment.

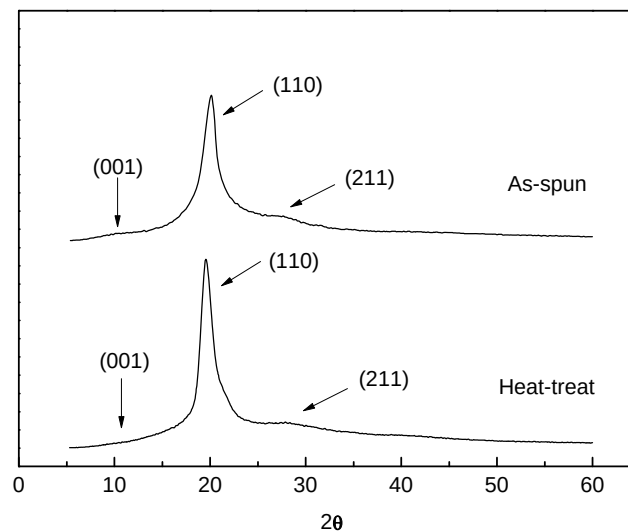


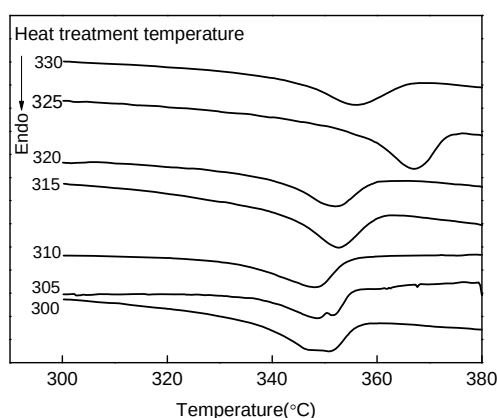
Figure 2. WAXD patterns of as-spun and heat-treated fibers

Crystalline parameters of as-spun and heat-treated fibers are shown in Table 2. It can be seen that the d-spacing and full width of half maximum (FWHM) of the fibers have no obvious change after heat-treatment, and the crystallite size (XS) and the crystallinity (Xc) become larger. Heat-treatment makes the crystal structure of the fiber more perfect, and therefore can improve the strength of fibers at the same time [4-5].

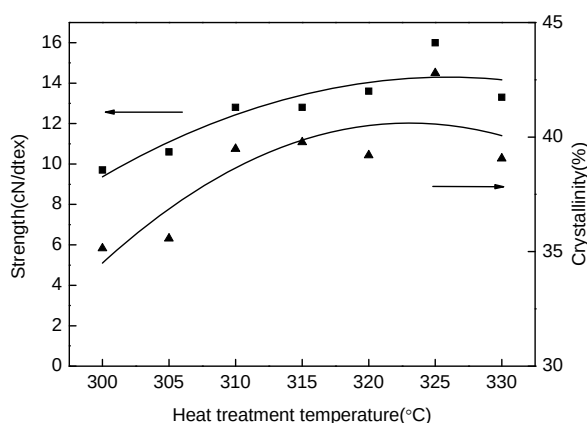
Table 2. WAXD extracted parameters for as-spun and heat-treated fibers

	2-Theta(°)	d(Å)	FWHM(°)	XS(Å)	Xc (%)
As-spun	20.2	4.4	0.91	90	34.0
Heat-treated	19.6	4.5	0.88	93	39.5

The DSC thermograms of the fibers at different heat-treatment temperature are shown in Figure 3. Melting point has no obvious increase at the temperature below 310 °C. While over 315 °C, the higher heat-treatment temperature is, the higher fiber melting point is. It is suggested that the higher temperature provides more opportunity for movement of molecular chain ends, and promotes solid phase polycondensation. With the increase of heat-treatment temperature, the degree of solid phase polycondensation increases, reflected in the increase of melting point [6]. When the heat-treatment temperature is set at 330 °C, the melting point of the fiber decreases on the contrary, and the melting peak broadens. It indicates that the regularity of the macromolecule is destroyed. Thus, the heat-treatment temperature must be set below 330 °C.

**Figure 3.** DSC thermogram of TLCPAR heat-treated fibers

The crystallinity and strength of the fibers at different heat-treatment temperature are shown in Figure 4. The strength of the fibers gradually enhances while the heat-treatment temperature increases. The optimal strength of the fibers reaches 16 cN/dtex at 325 °C. After that, higher heat-treatment temperature at 330 °C makes strength decrease, and adhesion occurs among the fibers. Comparing the curves of crystallinity and mechanical properties with temperature, it can be seen that increasing of crystallinity of the fibers can significantly improve the mechanical properties.

**Figure 4.** The crystallinity and strength of the fibers at different heat-treatment temperatures

4. Conclusion

As-spun fibers are prepared by melt spinning. The strength and crystallinity of the as-spun fiber are not high, and increase slightly with spinneret draft ratio. The degree of crystal orientation of as-spun fiber is very high at low spinneret draft ratio and almost independent on the spinneret draft ratio. Proper heat-treatment can improve significantly crystallinity and mechanical properties and increase the melting point obviously.

References

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