

Research of Factors Affecting Orientation of PAN Precursor used in Carbon Fiber

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Abstract. In the process of producing PAN precursor used in carbon fiber, applying orthogonal experiment method and a dry-wet spinning technology, the main systematical study are the influence of coagulation bath, jet stretch, pre-draft and water-bath draft on degree of orientation. Results show that under applying dry-wet spinning technology, in smaller jet velocity, and to give fiber appropriate pre-draft ratio and high water-bath draft ratio, degree of orientation is higher, and high fiber strength also can be obtained.

Introduction

Carbon fiber is a kind of fiber material with more than 90% of carbon content, possessing the high strength, high specific modulus, conductive and heat resistant and self-lubricating excellent comprehensive performance, applied in aviation, aerospace, automotive, electronics, machinery, chemical industry, sports equipment and other fields widely. After oxidation carbonization and surface treatment of PAN precursor, the carbon fiber based on PAN is produced one of the most widely used high performance fiber materials and is also currently the fastest growing^[1].

The quality of the carbon fiber to a large extent depends on the quality of PAN, and the orientation degree of PAN is the main factors influencing the mechanical properties of PAN^[2-3]. In the process of the carbon fiber based on PAN production, it is necessary to improve the quality of carbon fiber to explore the influence factors of the original silk orientation degree and to improve the quality of PAN. This paper adopts a certain molecular weight PAN spinning solution and the application of dry-Jet wet spinning, as well as explore the influence of the coagulation bath, shower and the pre-tension and hot water draft on orientation degree of the original silk, at last speculating the best conditions of orientation degree of the original silk.

Experimentation

Spinning solution and the spinning forming. With DMSO as solvent and AIBN as initiator, choose AN acrylic acid solution to polymerize to get good composite spinning solution^[4].

Slurry filter after metering pumps measurement, and then jet through nozzle. Apply dry-Jet wet spinning. The whole process is as follows: Homogeneous solution of polymerization, polymerization, filter, reaeration, metrology, dry-wet spinning, pre-draft, wash, water-bath stretch, heat-setting, silk.

Test. Coagulation bath concentration can be got through measuring refractive index under 20°C by Abbe refractometer.

Fineness of fibers can be determined by conventional weighing method of fixed-length.

Strength of fibers can be measured by YG021-A, a type of single wire electronic tonometer. Measurement conditions: length 10mm, speed 10mm/min.

Sonic orientation can use Som-ii type sonic orientation Analyzer. Measurement conditions: length 40cm, tension about 0.1cN/dtex.

Outcome and discussion

Determine the forming process parameters. Orthogonal design method can be utilized to determine the parameters. By selecting jet speed, jet draft ratio, pre-draft ratio and water-bath draft velocity as four factors, orthogonal experiment of four factors and three levels will be available as shown in Tab. 1.

Tab.1 Element level table

	jet speed (m/min)	jet draft ratio (times)	pre-draft ratio (times)	water-bath draft velocity (m/min)
1	14.12	0.8	1.2	40.06
2	20.04	1	1.5	60.12
3	25.18	1.2	1.8	80.03

Orthogonal test result and analysis is shown in Tab.2.

By Visual analysis on T value from test results, the best level of jet rate, Jet stretch ratio, pre-draft ratio and water-bath draft rate is respectively 1,3,3,3. Seeing from results of range R, these factors of effects on degree of orientation rank according to the strength: water-bath stretch rate > jet speed > jet stretch ratio > pre-stretch ratio. With improve of and water-bath rate, degree of orientation rises, when jet speed increases, degree of orientation declines. Effect of pre-draft on degree of orientation is compared complex, existing a minimum value. Above shows that to obtain a high degree of orientation, it is necessary to high jet draft ratio, water-bath stretch rate, lower jet speed, as well as proper Pre-stretch ratio. Besides when degree of orientation grow, the fiber strength also rise, which indicate this analysis is reasonable.

Tab.2 Orthogonal test result and analysis

	jet velocity	jet draft ratio	pre-draft ratio	water-bath draft velocity	fiber strength (cN/dtex)	Degree of orientation (%)
1	1	1	3	2	3.65	61.25
2	1	2	2	1	2.92	55.05
3	1	3	1	3	4.96	68.37
4	2	1	1	1	2.86	49.10
5	2	2	3	3	3.78	64.64
6	2	3	2	2	3.26	58.45
7	3	1	2	3	3.14	55.85
8	3	2	1	2	3.27	57.62
9	3	3	3	1	3.02	52.01
T1	184.67	166.20	175.09	156.16		
T2	172.19	177.31	169.35	177.32		
T3	165.48	178.83	177.90	188.86		
R1	12.48	-11.11	5.74	-24.16		
R2	6.71	-1.52	-8.55	-11.54		

Temperature and concentration of coagulating bath. In this experiment, addition to temperature and concentration of coagulating bath, other terms refer to the orthogonality condition 5# to set. Firstly by changing Temperature rating of coagulation bath the influence of temperature on degree of orientation can be investigated. The results are presented in Tab.3.

Tab.3 influence of temperature of coagulation bath on degree of orientation

temperature rating	1	2	3
fiber strength (cN/dtex)	4.16	3.42	3.21
Degree of orientation (%)	77.18	72.13	69.78

Tab. 3 shows that with rise of temperature of the coagulation bath, degree of orientation decrease, meanwhile fiber strength decline. This is because during process of solidification solvent with coagulant can generate a double diffusion effect^[5]. When the temperature rises, the diffusion

coefficient increases, and then double diffusion process is accelerated, with fiber forming speeding and average pore radius and average fiber radius soaring. These lead to uneven and severe defects in internal structure, and therefore degree of orientation and fiber strength decrease.

Next only change concentration rating of coagulation bath to explore and other terms refer to the orthogonality 5# to set. Results presented in Tab.4 show that in a certain range, increase of concentration of coagulation bath accompany rise of degree of orientation of fiber, but when the concentration is increased to a certain value, the influence will weaken. This is because as the concentration increase, filament silk get slowed or draft ratio of filament in coagulating bath lower, leading to diminution of diffusion coefficient of solvent or coagulant, with forming of double diffusion process eased, so fiber structures tend to be dense and evenly.

Tab.4 influence of concentration of coagulation bath on degree of orientation

Concentration rating	1	2	3
Fiber strength(cN/dtex)	3.24	3.96	3.91
Degree of orientation (%)	58.12	64.35	63.92

Pre-draft and water-bath draft. Thermal stabilization of tension stretch is the prerequisite for producing high performance carbon fiber^[6]. After setting that the overall draft ratio is 3.8 and jet stretch ratio is 1.5, and remaining the stretch ratio, as well as other conditions, the effect of pre-draft and water-bath draft on degree of orientation as shown in Tab 5. When degree of orientation falls,

Tab.5 the effect of pre-draft and water-bath draft on degree of orientation,

Pre-draft ratio	Water-bath draft ratio	Fiber strength(cN/dtex)	Degree of orientation (%)
1.4	2.71	5.39	69.44
1.5	2.53	3.95	63.82
2.0	1.90	2.57	51.25

Water-bath draft ratio drops down significantly, indicating water-bath draft have great effects on degree of orientation; After setting a certain pre-draft ratio, in order to improve degree of orientation and increase strength, water-bath draw ratio should be given maximum.

Dry heat draft. When proceeding hot drawing, firstly the fibers are put in dry heat air. Then under specific temperature and other conditions, the effect of stretching ratio on degree of orientation is detected, as shown in Tab.6. When the draw ratio increases, degree of orientation will rise, and strength also will increase. But after stretching ratio more than 1.7, degree of orientation will began to decline, the strength also will follow down, at the same time there appear. This is because when the draft ratio is too large, although the degree of orientation increase, due to that the stretching speed quickens, tensile time will be shortened under the high temperature, so it is difficult to relax the internal stress which comes from drawing, leading to the existence of internal stress that will decrease the strength of the fiber, and generate easily caused by local rift tow, which is not conducive to dry heat drawing^[7].

Tab.6 the impact of draft ratio on degree of orientation

Draft ratio	1.2	1.3	1.4	1.45	1.6	1.7	1.77	undrawn
Fiber strength(cN/dtex)	4.35	5.08	5.20	5.67	6.07	6.53	6.26	3.90
Degree of orientation (%)	73.50	76.40	76.95	78.35	80.04	84.36	83.24	66.65
remark	fuzziness							

After setting certain draw ratio, by changing the air temperature, there examine the influence of drawing temperature on the degree of orientation, as shown Tab.7, indicating that under the same stretching ratio, with the improvement of drawing temperature, degree of fiber orientation and strength increase. This is because there are CN groups containing strong polarity on the PAN macromolecular chain, besides between CN groups exist a great deal of repulsive force and gravity because of their difference of position inside and outside, which adverse to activity of the macromolecular chain, and then causes twists and turns in its local^[7]. Its strong polarity about CN groups also has great attraction between the molecules and forms many join points easily, granting the fiber larger rigidity which can reduce or disappear only at higher temperatures. Therefore, the strength of fiber showed dependence on the temperature in the process of heat draft.

Tab.7 the influence of temperature in the process of dry heat draft

Temperature grade	1	2	3
Fiber strength(cN/dtex)	5.62	6.07	6.35
Degree of orientation (%)	78.26	80.12	83.26

Water-bath draft. With the dry heat draft conditions, position the fiber in water bath, heat stretching is proceeded. By changing temperatures or stretch ratio, results of measured degree of orientation are shown in Tab.8, indicating that with the increase of temperature and stretch ratio, degree of orientation also increase.

Tab.8 the impact of temperature and draft ratio on degree of orientation in water-bath draft

Temperature	1	2	3
Draft ratio	1.8	2.0	2.5
Degree of orientation (%)	88.2	89.6	91.9

Summary

Under the condition of not influence on jet, jet speed should be as small as possible, and the relatively higher the jet draft ratio is, the better.

The temperature of coagulation bath should be appropriately reduced, and the concentrations should be appropriate elevated.

The pre-draft shouldn't be too large.

The fiber is suitable for dry and water-bath drafting, draft ratio can be relative the higher and the better, but also is unfavorable for excess, otherwise leading to easily appearance of fuzziness which affect the quality of PAN.

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