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Optimization of Curing Process for Carbon Fiberpreparation from Wood-Phenol Liquefaction Product

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Abstract

In this study, China fir was liquefied in phenol, and liquefactionproduct was used to produce carbon fiber precursors by curing process. The effect of heating rate, curing temperature, curing time and hydrochloric acid concentration on curing processwas investigated by orthogonal experimentsin term of the crystallinityof carbon fiber precursors produced.According to experiment results, the primary and secondary relation of the four variables is: curing time>curing temperature>hydrochloric acid concentration >heating rate. The optimal conditions of curing technology are as follow: heating rate of 15 °C/h, curing temperature of 90 °C, curing time of 2 h with hydrochloric acid concentration of 18.5%. Using the optimal conditions, carbon fiber precursors could obtain the highest crystallinity of 36.96%.

Key words: Carbon fiber precursors; Curing; Crystallinity; Liquefaction; Phenol

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INTRODUCTION

Carbon fiber, as a new kind of fibrous carbon materials, has become an essential material in space flight (aviation) industry and civilian industry for its light weight, superior mechanical strength, corrosion resistance, high temperature resistance and conductivity. Carbon fiber production from lignocelluloses has become more and more popular, because traditional manufacturing processescould convert lignocelluloses to high quality carbon fibers, meanwhile lignocelluloses is a kind of cheap and abundant materials. The replacement of oil refinery with biomass refinery is vital for sustaining the growth of the chemical industry and society, and biomass liquefaction is a potential way of biomass refinery, which is also a new way of carbon fiber production.

The crystallinity specified as a percentage of the volume of carbon fiber that is crystalline refers to the degree of structural order in carbon fiber precursors. The degree of crystallinity has an influence on the physical and chemical properties of fibers to some extent. Therefore crystallinity is always used to assess the physical and chemical properties of biomass materials. In the present study, wood-phenol liquefaction product was used to produce carbon fiber precursors by curing process. Orthogonal experiment design experiment was carried out to investigate the effect of heating rate, curing temperature, curing time and hydrochloric acid concentration on curing process in term of the crystallinity. The results of this study could provide some useful information to realize cost-efficient carbon fiber production from biomass.

MATERIAL AND METHODS

1. Raw Material and Liquefaction

China fir was smasher and sieved, and the particle at 40-80 mesh was dried at 100°C for above 12 h before

being used.Phenol, vitriol (99%), formaldehyde (37%), urotropine and HCl (37%) used were of analytical grade. Liquefaction was carried out in 8% vitriol with a solid-to liquid ratio (wood flour/phenol) of 1:5 in a 500 ml three-neck flask.Liquefaction experiment was performed at 170 °C with a agitation rate of 1000 rpm for 2 h. Cooled liquefied wood was then filtrated, and filter liquor was kept in glass container until it was used forcarbon fiber production.

2. Carbon Fiber Production and Optimization of Curing Technology

Synthetic agent (5%) was added into 7 g liquefied wood in a reactor. With agitation, temperature of reactor was increased from 60 °C to 150 °C by a rate of 1.5°C/min, and then it was maintained at 150 °C for 10 min to get spinning solution. Spinning solution was then used for spinning by melt spinning techniques to get initial fiber. The conditions for spinning are as follow: spinneret diameter (1mm), take-up roller speed (180-200r/min), the distance between spinneret and take-up roller (150 mm), spinning temperature (110°C to 120 °C).

Initial fibers were added into mixture of certain concentration HCl solution (ranged from 11% to18.5%) and 18.5% formaldehyde solution. The temperature of the mixed solution was increased at a certain heating rate (range from 6°C/min to15°C/min) to a certain curing temperature (ranged from 80°C to 95°C), and then the temperature was maintained constant for a certain hour (ranged from 1.5 h to 3 h) for curing. Carbon fibers produced by curing process were water-rinsed, and then dried at 85 °C for 40 min to get carbon fiber precursors.

Table 1
The Results of Orthogonal Design Methodology Experiment

Number	heating rate (°C/h)	curing temperature (°C)	curing time (h)	hydrochloric acid concentration (%)	Relative crystallinity (%)
1	6	80	1.5	11.0	34.93
2	6	85	2	13.5	36.03
3	6	90	2.5	16.0	35.69
4	6	95	3	18.5	36.05
5	9	80	2	16.0	36.30
6	9	85	1.5	18.5	35.86
7	9	90	3	11.0	35.04
8	9	95	2.5	13.5	33.95
9	12	80	2.5	18.5	34.80
10	12	85	3	16.0	35.80
11	12	90	1.5	13.5	36.26
12	12	95	2	11.0	35.07
13	15	80	3	13.5	35.82
14	15	85	2.5	11.0	35.60
15	15	90	2	18.5	36.96
16	15	98	1.5	16.0	35.17
K1	35.675	36.463	35.555	35.160	
K2	35.288	35.823	36.090	35.515	
K3	35.483	35.988	35.010	35.740	
K4	35.888	35.060	35.678	35.918	
Range	0.60	0.93	1.08	0.76	

As showed in table 1, four curing factors such as hydrochloric acid concentration, heating rate, curing temperature and curing time were selected to be optimized by using aL16 (44) orthogonal table in term of the crystallinityof carbon fiber precursors.

3. Characterization of Carbon Fiber Precursors

The crystalline structure of carbon fiber precursors was analysed by X-ray diffraction on an XRD-6000 instrument (Shimadzu, Japan) with 5omin−1 scan speed 2θranged from 5o to40o. The total diffracted area and the areas under the crystalline peaks were determined by integration after correcting the data for absorption. The ratio of the crystalline area to that of the total diffracted area was used to determine the relative crystallinity.

RESULTS AND DISCUSSION

1. The Results of Orthogonal Design Methodology Experiment

Table 1 showed the results of orthogonal design methodology experiment. The primary and secondary relation of the four variables is: curing time > curing temperature > hydrochloric acid concentration > heating rate. The optimal conditions of curing technology are as follow: heating rate(15 °C/h), curing temperature (90 °C), curing time (2 h) and hydrochloric acid concentration (18.5%). Carbon fiber precursors produced by using the optimal conditions could obtain the highest crystallinity of 36.96%. Experiment 15 in table 1 was performed at the optimal conditions, so extra experiment was not needed to test the optimal conditions.

2. The Effect of Heating Rate and Curing Temperature on the Crystallinity of Carbon Fiber Precursors

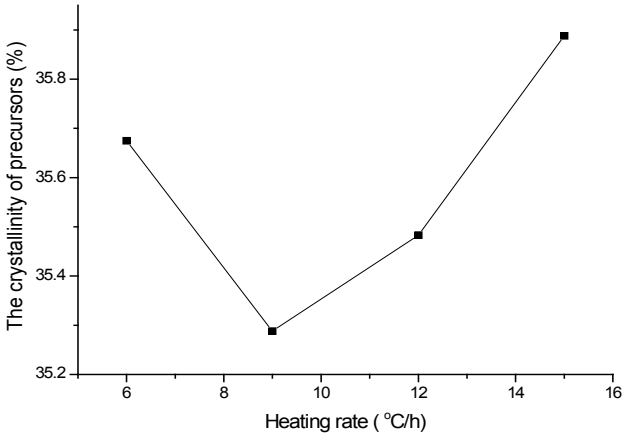

Figure 1
Effect of Heating Rate on Crystallinity of Precursors

Figure 1 showed the effect of heating rate on the crystallinity of carbon fiber precursors. With increasing heating rate, the crystallinity of carbon fiber precursors

deceased firstly and then increased. When a heating rate of 15 °C/min was used, the highest crystallinity was obtained. Using low heating rate, the accessibility of initial fibers for carbonium ions ($+CH_2OH$) is low. However using low heating rate means that reactor will be heated for a long time to reach the set temperature, and a long heating time is supposed to have active effect on the reaction between carbonium ions ($+CH_2OH$) and initial fiber. This could explain that using low heating rate also obtains high crystallinity. High heating rate increased the accessibility of initial fibers for carbonium ions ($+CH_2OH$), which maybe the reason for that the highest crystallinity was obtained by using a heating rate of 15 °C/min. According to Orthogonal design methodology experiment, heating rate has little effect on the crystallinity, so heating rates, which would not lead melting of carbon fibers, were supposed to be suitable.

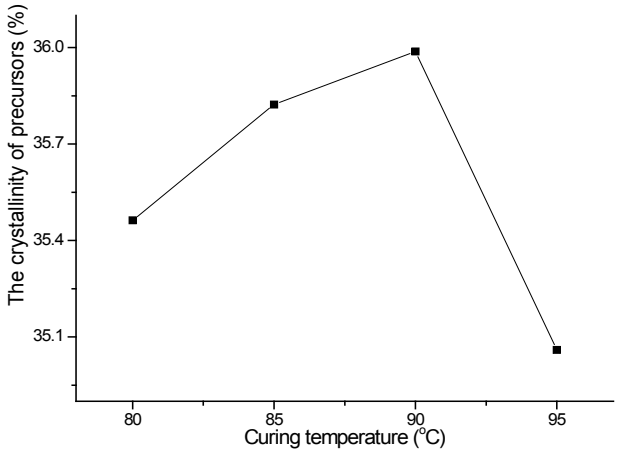

Figure 2
Effect of the Curing Temperature on Crystallinity of Precursors

Figure 2 showed the effect of curing temperature on the crystallinity of carbon fiber precursors. Increasing temperature could increase the crystallinity of carbon fiber precursors when temperature was lower than 90 °C. Increasing temperature could improve both of the diffusion velocity of carbonium ions ($+CH_2OH$) into initial fibers and the reaction rate of carbonium ions ($+CH_2OH$)/ surface fibers crosslinking reaction. The improvement of diffusion velocity of carbonium ions ($+CH_2OH$) is the reason for that the crystallinity increased with increasing curing temperature. Carbonium ions ($+CH_2OH$)/surface fibers crosslinking reaction will produce dense structure of peripheral region, which would prevent the diffusion of carbonium ions ($+CH_2OH$) into initial fibers. Therefore a high curing temperature could also lead a low crystallinity. The optimized curing temperature is 90 °C.

3. The Effect of Curing Time and Hydrochloric Acid Concentration on the Crystallinity of Carbon Fiber Precursors

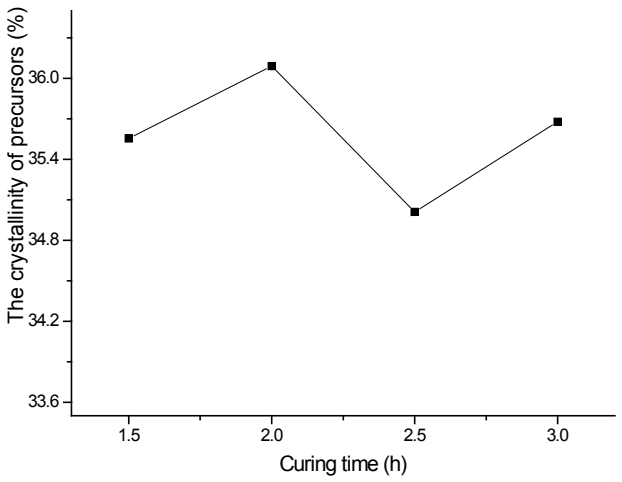

Figure 3
Effect of the Curing Time on Crystallinity of Precursors

Figure 3 showed the effect of curing time on the crystallinity of carbon fibers precursors. When curing time was increased from 1.5 h to 2.5 h, the crystallinity increased firstly and then decreased.The crystallinity of carbon fibers precursors produced by using 3 h was higher than that using 2.5 h, but lower than that using 2 h. Enough curing time could ensure a high crystallinity, but long curing time will also lead crystallinity decrease. More experiments are needed to explain that long curing time will lead crystallinity decrease. Using short curing time obviously could decrease the process cost. Therefore the optimized curing time is 2 h.

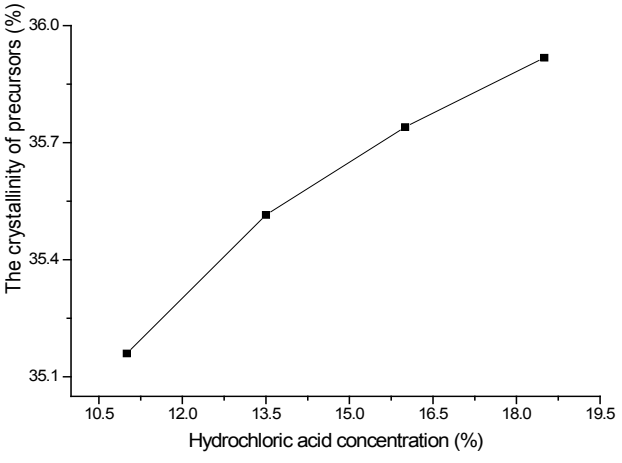

Figure 4
Effect of the Hydrochloric Acid Concentration on Crystallinity of Precursors

The effect of hydrochloric acid concentration on the crystallinity was illustrated in Fig 4. The results showed that the crystallinity of precursors monotonously increased with hydrochloric acid concentration increasing. Carbonium ions ($+CH_2OH$) was formed in the mixture of formaldehyde solution and hydrochloric acid solution. The

concentrationof carbonium ions(+CH_2OH) was supposed to be mainly depend on hydrochloric acid concentration, and increasing hydrochloric acid concentration would increase the concentration of carbonium ions (+CH_2OH), which may be the reason for that the crysatllinityincreases withincreasing hydrochloric acid concentration.

CONCLUSIONS

According to the results of orthogonal design methodology experiment, the primary and secondary relation of the four variables is: curing time>curing temperature> hydrochloric acid concentration> heating rate. Compared with heating rate and hydrochloric acid concentration, it has been indicated that curing temperature and curing time are the key-contribution to the crystallinity of carbon fiber precursors.The optimal conditions of curing process are as follow: heating rate15°C/h, curing temperature 90 °C, curing time 2 h and hydrochloric acid concentration 18.5%. Carbon fiber precursors produced under the optimal conditions could obtain the highest crystallinity of 36.96%.

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