Effect of Heating Rate and Temperature on the Carbonization Process of Commercial Viscose fibers

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Abstract

Effect of heating rate and temperature on the carbonization process of commercial Viscose (cellulosic based precursor) fibers are investigated in the present study. Several carbonization experiments are conducted on stabilized fibers with carbon content of 59.72 wt% and diameter of about 13.3 μm. The Viscose fibers are stabilized with the catalyst of mixture urea/diamonium hydrogen phosphate in air at temperature of 250 °C. The stabilized fibers are then carbonized in argon at temperature ranging from 600°C to 1200 °C with the heating rate of 5 °C.min^{-1}. Experimental results show that the obtained fibers have carbon content above 94 wt% and diameters of about 8μm. These fibers are potential to produce activated carbon fibers.

Keywords: Carbonization, carbon fibers, Viscose, cellulose based precursor

1. Introduction

Viscose rayon fiber (Cellulosic based precursor), PAN fiber (Polyacrylonitrile) and Pitch based precursor are widely used materials to manufacture carbon fibers [1, 2]. Among them, Viscose rayon fiber is the most common precursor for commercial carbon fibers production. Developing carbon fiber from Viscose fiber is generally subjected to three processes namely stabilization, carbonization, and graphitization to structural materials or activation to activated materials.

The experimental works on stabilization of Viscose fibers have recently been reported in litteratures [3, 4], in which suitable catalyst contents and dehydration temperature of cellulose have been determined. The objective of this study is to investigate carbonization process of Viscose fibers after stabilization step, and effective factors on carbon-cellulose transformation process.

Carbonization is a pyrolysis process at a temperature higher than that of the cellulosic based precursor. During the carbonization process, the cellulose mainly transforms into carbon. Pyrolysis of cellulose is an oxidation process in air at temperature below 350 °C to stabilize fibers, which improves carbon fibers properties and to prevent the undesirable formation of pitch. During the pyrolysis process of cellulose, suitable catalyst is used in order to increase dehydration rate, lower stabilization temperature, and prevent the elimination of carbon in residual fibers. In this stage, several chemical reactions take place at the same time, which brings out a significant reduction of fibers's weight. The formation of pre-structure proceeds subsequently at elevated temperatures to make carbon matrices [2, 5, 6].

After stabilization, residual fibers possesses about 60 – 70 wt% carbon. When the fibers are carbonized at temperatures 900 – 1500 °C, the carbon content increases continuously to reach of 90 – 95 wt%. In this stage, all physical and mechanical properties of fibers have been changed, therefore, it can be controlled to make carbon fibers with desirable characteristics.

This paper presents experimental results of carbonization processes of commercial Viscose fibers. The effects of heating rate and temperature on the carbonization process are investigated.

2. Experiment

2.1. Material preparation

Cellulosic based precursor is commercial Viscose fibers with diameter of about 18 μm possessed carbon content of 40.70 wt% (Fig 1). Cellulose pyrolysis, dehydration and stabilization of Viscose fibers are firstly done [3, 4]. Fibers are immersed into solution of mixtured urea/diamonium hydrogen phosphate (weight ratio of 2/1), then heated at temperature of 250 °C for 60 min in air.

After stabilization, the fibers possess 59.72 % carbon content, have diameter of 13.35 μm (Fig 2) and

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reduce 25.23 wt%. The stabilized fibers are then used in carbonization experiments as starting materials.

2.2. Experimental procedures

Carbonization experiments are conducted in tube furnace system of Nabertherm RSRC, Germany. Its maximum temperature can reach 1300 ^oC.

Experimental conditions are provided in tables 1 and 2. Carbonization process is conducted in 99.99 % argon at temperature ranging from 250 to 1200 ^oC. Carbon content is analyzed by LECO CS230CSH equipment, USA.

Viscose fibers and carbonized fibers are observed by SEM. The fiber diameter is measured based on the SEM images.

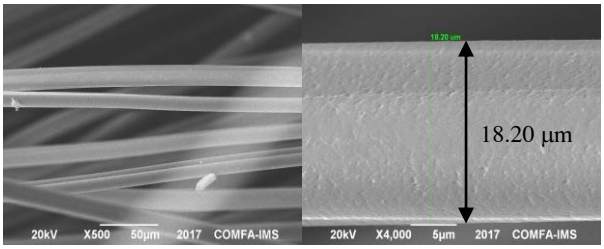

Fig. 1. SEM image of commercial Viscose fiber

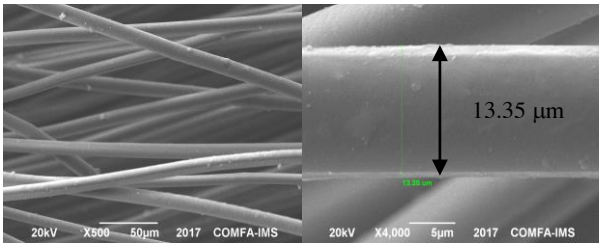

Fig. 2. SEM image of stabilized Viscose fiber

Table 1. Experimental modes and results at different carbonization heating rates

Samples	Stabilization temp, ^oC	Heating rate, $^oC.min^{-1}$		Carbonization temp, ^oC	Temp holding time, min	Carbon content, wt%	Weight loss, %
		250 to 600^oC	above 600^oC				
VC11	250	1	5	1200	60	94.90	55.97
VC12	250	2	5	1200	60	94.40	56.34
VC13	250	3	5	1200	60	94.15	56.43
VC14	250	4	5	1200	60	92.95	56.80
VC15	250	5	5	1200	60	92.65	56.82

Table 2. Experimental modes and results of various carbonization temperatures

Samples	Stabilization temp, ^oC	Heating rate, $^oC.min^{-1}$		Carbonization temp, ^oC	Temp holding time, min	Carbon content, wt%	Weight loss, %
		250 to 600^oC	above 600^oC				
VC250	250	-	-	250	60	59.72	25.23
C600	250	3	5	600	60	77.10	45.69
C650	250	3	5	650	60	78.65	46.56
C700	250	3	5	700	60	79.95	46.89
C750	250	3	5	750	60	80.50	47.62
C800	250	3	5	800	60	83.30	49.50
C850	250	3	5	850	60	84.45	49.72
C900	250	3	5	900	60	86.65	50.65
C950	250	3	5	950	60	89.05	52.04
C1000	250	3	5	1000	60	90.00	52.62
C1050	250	3	5	1050	60	92.35	54.18
C1100	250	3	5	1100	60	93.05	55.53
C1200	250	3	5	1200	60	94.15	56.43

3. Results and disscusion

3.1. Carbonization at different heating rates

In the carbonization, as the temperature is below 600 ^oC, it is necessary to control the heating rate to manipulate pyrolytic elimination of oxygen and hydrogen. The quick elimination may bring about a reduction of fiber's strength because the elimination of carbon will weaken new C-C bonds.

As the temperature is above 600 ^oC, a small remaining amount of oxygen continues to be eliminated, however, the removal of hydrogen and aromatization of C-C bonds are still significant and are the main processes before reaching perfect structure [6]. Thus, in this stage, it can increase carbonization rate in order to reduce the cycle time of carbonization.

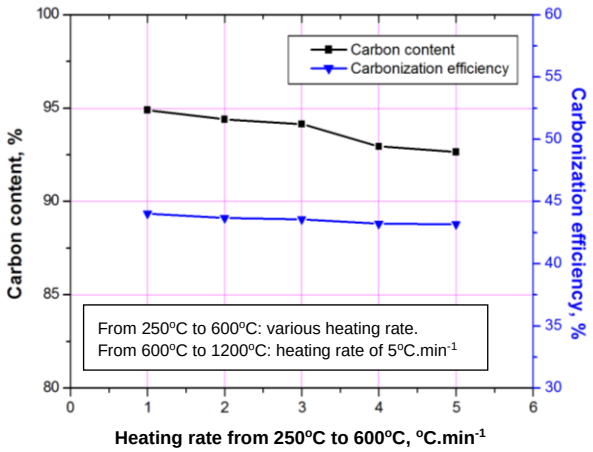

Fig. 3. Final carbon content and carbonization efficiency as functions of heating rate when carbonizing Viscose fibers at 1200 °C

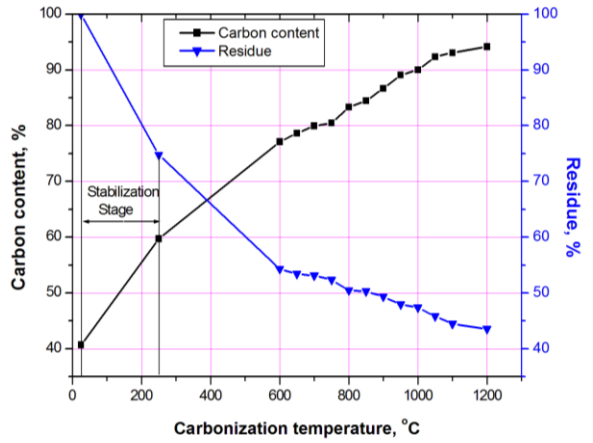

Fig. 4. Relationship between carbonization temperature and carbon content, residue

Experimental results are provided in table 1 and presented in figure 3. They show that the weight loss increases slightly (55.97 to 56.82 %) when the heating rate increases from 1 to 5 °C.min^{-1}. In addition, the carbonization efficiency slightly decreases (44.03 to 43.18 %) with respect to the increase of heating rate. The fibers carbon content significantly decreases at the rate above 3 °C.min^{-1} (94.15 to 92.65 wt%) while it reduces slightly at the rate ranging from 1 – 3 °C.min^{-1} (94.90 to 94.15 wt%).

The results proved that VC13 sample which is carbonized at heating rate of 3 °C.min^{-1} kept carbonization efficiency approximately 44 % and carbon content above 94 %. Furthermore, carbonization cycle time of VC13 sample is shorter than that of VC11 and VC12 samples. Therefore, the heating mode of VC13 sample is selected for subsequent experiments at different carbonization temperatures.

3.2. Carbonization at various temperatures

Experimental modes and results of various carbonization temperatures are listed in table 2 and illustrated in figure 4.

The results show that the highest weight loss would occur in stabilization stage (25.23 %), while the carbon content in residue enhances quickly (40.70 to 59.72 wt%). Oxygen and hydrogen are largely eliminated in pyrolysis stage from 250 °C to 600 °C, in which the weight loss (25.23 to 45.69 %) and the enhancement of carbon content (59.72 to 77.10 wt%) are still significant. In stages of higher temperatures from 600 to 1200 °C, the rate of weight loss and carbon enhancement become slower because of the small amount of oxygen in residue. The elimination of hydrogen, aromatization and polymerization occurred during these stages. After carbonizing at temperature of 850 °C, the fibers weight reduces a half (49.72 %) and carbon content in residue is as twice (84.45 wt%) as that in starting fibers.

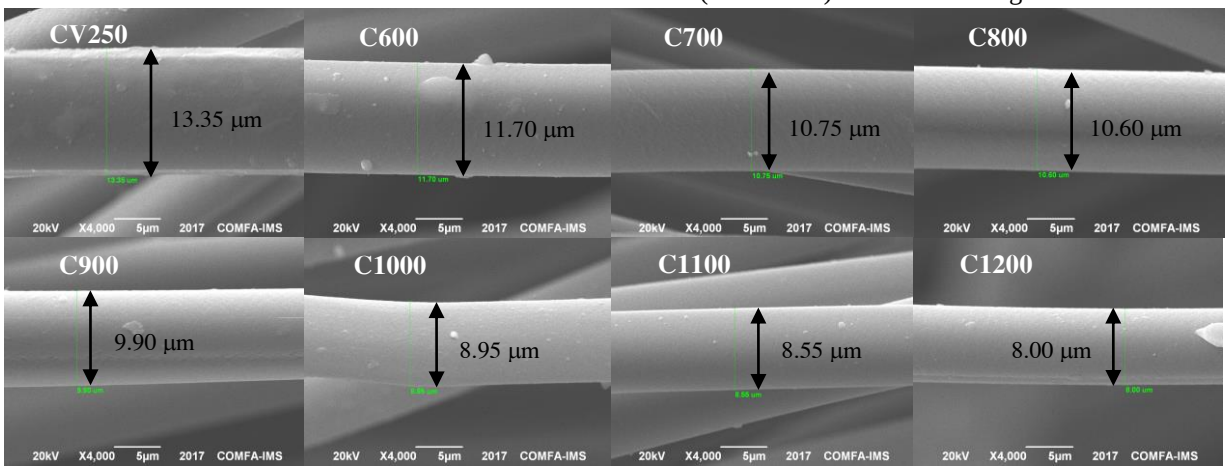

Fig. 5. SEM images of fiber at various carbonization temperatures.

At the highest temperature of 1200 ^oC, the carbon content reached 94.15 wt% and residual weight of 43.57 %, whereas the Viscose fibers possessed 40.70 wt% carbon. This shows a high carbonization efficiency and a small elimination of carbon amount.

3.3. Change of fiber diameter at various carbonization temperatures

Figure 5 shows SEM images of fiber samples after stabilization and carbonization at temperatures from 600 ^oC to 1200 ^oC. It can be seen that fiber diameter decreases strongly (18.20 to 13.35 μm) after stabilization stage at 250 ^oC, and thereby, a significant weight loss. The fibers are carbonized in unstrained condition. Diameter of the fiber decreases slowly when carbonization temperature increases. After carbonizing at 1200 ^oC, fiber diameter decreased of 56.05 % (down to 8.00μm), while it reduced of 26.65 % in stabilization stage and 29.40 % in 250 – 1200 ^oC stage. The reduction of fiber diameter in carbonization stage is slower than that in stabilization stage, which corresponds to a smaller weight loss. This is consistent with mechanism of carbon-cellulose transformation. A large amount of oxygen and hydrogen are removed in stages of dehydration at 250 ^oC and pyrolysis below 600 ^oC. The removal of hydrogen, aromatization and polymerization were the processes in elevated temperature stages.

4. Conclusions

- Commercial Viscose fibers (Cellulosic based precursor) had carbonized in argon at temperature of 1200 ^oC to get carbon fibers, which possess carbon content above 94 wt%.

- The suitable heating rate had chosen for carbonization process, as follow: 3$^oC.min^{-1}$ in the below 600 ^oC stages; 5 $^oC.min^{-1}$ in the above 600 ^oC stages. When carbonizing with this heating mode, carbonization efficiency reaches 43.57 % (precursor possessed 40.70 % carbon) and carbon content reaches 94.15 wt%.

- Carbon fibers have diameter of about 8.00 μm after carbonizing at 1200 ^oC in unstrained condition. It decreases of 56.05 % as one of Viscose fibers (18.20 μm). Fiber diameter decreases quickly of 26.65 % (down to 13.35 μm) in stabilization stage, subsequently it decreases slower in carbonization stages.

- Weight loss is larger and carbon content increases quickly in carbonization stages below 600 ^oC. In carbonization stages at temperatures in a range of 600 to 1200 ^oC, weight loss is smaller and carbon content enhancement is slower.

- Obtained carbon fibers are also used to produce activated carbon fibers.

References

[1] Peter Morgan, “Carbon Fibers and their Composite – Chapter 4: Precursor of Carbon Fiber Manufacture”, Taylor & Francis Group, 2005.

[2] D. D. Edie & R. J. Diefendort, “Carbon Fiber Manufacturing”, Carbon-Carbon Materials and Composite, Edited by John D. Buckley & Dan D. Edie, Noyes Publications, 1993.

[3] Nguyễn Hữu Sơn, Phạm Văn Cường, Vũ Lê Hoàng, Lê Thái Hùng, “Ổn định hóa sợi Viscose thương mại cho chế tạo sợi các bon”, Hội nghị Luyện kim và Khoa học vật liệu tiên tiến – Sự phát triển bền vững của nền công nghiệp, ĐH Bách Khoa Hà Nội, 10/2016, pp34-39.

[4] Nguyễn Hữu Sơn, Phạm Văn Cường, Vũ Lê Hoàng, Lê Thái Hùng, “Ảnh hưởng của hàm lượng chất xúc tác đến quá trình ổn định hóa sợi Viscose thương mại cho chế tạo sợi các bon”, Tạp chí Khoa học Công nghệ Kim loại, số 76, (2018), pp38-43.

[5] Peter Morgan, “Carbon Fibers and their Composite – Chapter 6: Carbon Fiber Production using Cellulosic based Precursor”, Taylor & Francis Group, 2005.

[6] Bacon, R. and M. Tang, “Carbonization of Cellulose Fibers-I: Low Temperature Pyrolysis, Pergamon Press Ltd, Carbon, vol 2, (1964) pp. 211-220.