Effects of Fiber Processing Conditions on the Yield, Carbon Content, and Diameter of Lignosulfonate-based Carbon Fibers

Shih-Hsuan Yen and Feng-Cheng Chang*

The use of a hardwood lignosulfonate (HLS) precursor along with electrospinning technology was studied to produce HLS-based carbon fibers. The production of the fibers helped to determine the appropriate processing parameters in the HLS carbon fiber production process. The processing parameters examined were the heating rate (POR) and the treatment temperature (POT) in the preoxidation process; the heating rate (C_1R) and the treatment temperature (C_1T) were in the low-temperature carbonization phase; and the carbonization temperature (C_2T) and temperature holding period (C_2t) were in the high-temperature carbonization phase. The results revealed that preoxidation with a POR of 1 °C/min and a POT of 250 °C generated favorable properties, particularly enhancing the fiber mat integrity and the fiber carbon content. The designed two-phase carbonization process was found to be satisfactory in increasing carbon fiber yields and enhancing fiber mat integrity. A C_1R value of 1 °C/min and C_1T of 400 °C facilitated favorable properties in the produced carbon fibers. Furthermore, a prolonged C_2t increased the fiber carbon content but reduced the carbon fiber yield. The highest fiber carbon content occurred with a C_2t of 3 h and a C_2T of 1200 °C.

Keywords: Carbon fiber; Carbonization; Electrospinning; Lignosulfonates

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INTRODUCTION

Carbon fibers are high-performance materials that are lightweight and have favorable mechanical properties (*i.e.*, strength, modulus of elasticity, dimensional stability, and creep resistance). Moreover, carbon fibers can resist high temperatures, acids, and fatigue, and they can be used as heat and electrical conductors.

Carbon fibers were first used in military and aerospace fields in the 1950s. During this time, carbon fibers gained increased attention, with many countries and manufacturers endeavoring to develop high-performance carbon fiber products. In the 1980s, carbon fibers were primarily applied in high-technology fields such as aviation and aerospace technologies. The continued advance of manufacturing technologies has since elicited an increasing demand for carbon fiber products.

Appropriate precursors (*e.g.*, polyacrylonitrile, rayon, and pitch) for carbon fibers and the preoxidation process to enhance carbon fiber yields have been investigated. Due to many product development efforts, most carbon fiber types in current markets are light weight, high strength, and are resistant to high heat and acid (Savage 1992; Donnet 1998).

Industrial applications of general-purpose and high-performance carbon fibers have been widely explored. In particular, researchers have attempted to develop bio-based carbon fiber precursors that are low-cost and environmentally friendly. Among such precursors, lignin is inexpensive and has a favorable structure as a precursor for the production of carbon fibers. Lignin has long been used as a fuel source. To achieve value-added applications of technical lignin as precursors of carbon fibers, many studies have explored various types of lignin produced from different pulping processes (Kubo and Kadla 2005; Lallave *et al.* 2007; Huang 2009; Baker and Rials 2013; Frank *et al*. 2014; Rosas *et al*. 2014).

Lignin-based carbon fibers were first developed in 1969. Blending lignin with certain polymers in a fiber spinning processes can lower the glass transition temperature (T_g) of lignin, thereby enhancing its spinnability. However, high percentages of polymers in lignin/polymer blends lead to low carbon fiber yields. The T_g increases in response to increasing cross-linking reactions and the incorporation of oxidized groups; therefore, the heating rate in the preoxidation processes must remain low. Lignin outperforms conventional pitch precursors when used to improve carbon fiber yields (Otani *et al.* 1969; Kadla *et al*. 2002).

Carbon fiber production generally entails three processing steps: fiber spinning, preoxidation with carbonization, and graphitization (Buckley and Edie 1993). There are several fiber spinning methods commonly used, such as: melt spinning, wet spinning, dry spinning, freezing-gel spinning, and electrospinning. Of the fiber spinning methods, electrospinning is advantageous because of the simple equipment that can be used to produce fibers from various polymers and the minimal solvent recycling and pollution discharge (Okutan *et al.* 2014). Generally, reducing fiber diameters minimizes defects and improves the mechanical properties and uniaxial structures of the fibers, resulting in high specific surface areas. However, if the miscibility of a lignin/polymer blend is low, the polymers melt from the blend prior to pyrolysis. This reaction forms pores on fiber surfaces and thus influences the mechanical properties of produced fibers (Braun *et al*. 2005).

Preoxidation is a crucial step in carbon fiber production because it determines the structural and mechanical properties of the produced carbon fibers (Bailey and Clarke 1971; Norberg 2012). During preoxidation, lignin is heat treated in an oxygen atmosphere to promote oxygen bonding reactions with lignin, and reactions occurring during oxidation would increase the glass transition temperature (T_g). As the temperature increases at a slow heating rate the T_g can increase faster than the temperature, maintaining the material in the glassy state (Kadla *et al*. 2002; Braun *et al.* 2005), thereby preventing fiber melting while increasing carbon fiber yields in the subsequent carbonization step. The preoxidation heating rate (POR) is a crucial fiber-processing factor; for instance, high PORs result in unfavorable fiber shrinkage and fusion. Lower PORs may lead to higher thermal stability in preoxidized fibers (Mathur *et al.* 1992; Braun *et al.* 2005).

The heating rate during carbonization also affects the properties of the produced carbon fibers. The carbonization process can be divided into two phases based on carbonization temperatures, *i.e*., low and high temperatures. Thermal decomposition and volatile material production primarily occur in the low-temperature carbonization phase; therefore, high heating rates can induce volatile gases and form irregular pores on fiber surfaces. However, high heating rates in the subsequent high-temperature carbonization phase can effectively minimize fiber structure fractures caused by the exothermic process, ensuring favorable fiber mechanical properties (Baker 2011; Luo *et al.* 2011).

This study investigated a process for producing lignosulfonate (HLS)-based carbon fibers using HLS as the precursor. Electrospinning technology and carbonization treatment were integrated to produce carbon fibrous materials. In addition, a preoxidation process and a two-phase carbonization process were examined to evaluate the effects of particular processing parameters on selected properties of the produced carbon fibers.

EXPERIMENTAL

Materials

Lignosulfonates (hardwood lignosulfonic acid sodium salt (HLS), Borregaard, Sarpsborg, Norway; weight-average mass M_w = 8000 g/mol) were used as the raw material. Polyethylene oxide (Acros, Livingston, NJ, USA; $M_w = 6 \times 10^5$ g/mol) was selected as the facilitator for HLS fiber formation because Dallmeyer *et al.* (2010) suggested that lignin can bond to the chain structure of polyethylene oxide (PEO) through hydrogen bonding, thereby improving the spinnability of lignin solutions and facilitating production of continuous fibers during the electrospinning process.

HLS is a water-soluble polymer; therefore, reverse osmosis water was used as the solvent in the precursor preparation. The HLS and PEO solutions were prepared by mixing the appropriate solutes with a HLS-to-PEO ratio of 97/3 (w/w) and then dissolving this HLS/PEO blend in reverse osmosis water. The concentration of the prepared sample solution was 20 wt.%. Vials containing the solutions were sealed tightly, vortexed for approximately 1 min, heated in an oil bath at 80 °C until the solutes were dissolved completely, and allowed to cool to room temperature before electrospinning.

Methods

Electrospinning

Electrospinning was used to produce HLS-based fibers by mounting a syringe filled with the aforementioned sample solution onto a syringe pump (NE-1000HP, New Era Pump Systems Inc., Farmingdale, USA). The syringe pump was connected to a high voltage power source (EL50P0, Glassman High Voltage Inc., High Bridge, USA) which was produced by connecting an 18 G needle and a collector to the positive and negative electrodes of the power supply, respectively. The operating voltage was 15 kV.

The syringe was placed so that the needle tip was 20 cm away from the collector, and the syringe pump was operated at a flow rate of 0.03 mL/min to ensure that the solution was extruded steadily from the syringe to form fiber samples on the collector. The roller collector was operated at 720 rpm and covered with release paper to enable the easy release of fiber samples from the collector. The above-mentioned electrospinning processing conditions were selected based on a previous study (Chang *et al.* 2016).

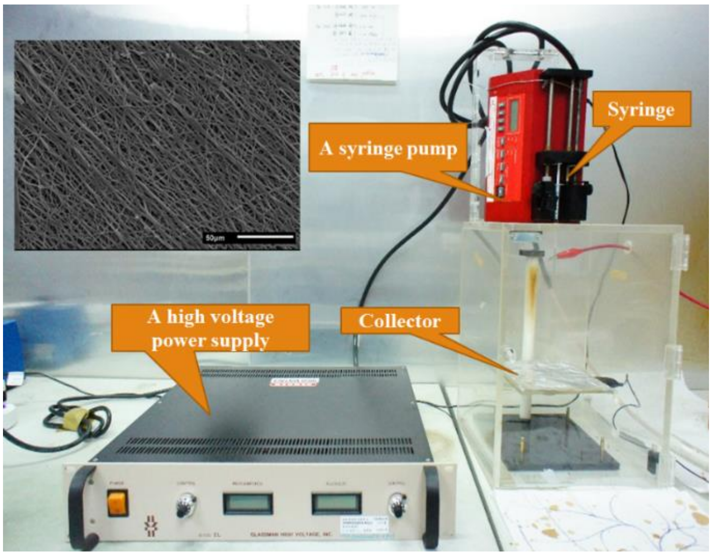

Fig. 1. Electrospinning setup and electrospun HLS-based fibers (inset)

Fiber mats with an average thicknesses of 44 µm were made by using 20 mL of the aforementioned HLS/PEO solution for each mat. The average diameters of the electrospun fibers were 1611 nm (Fig. 1), which were similar to the average fiber diameter reported in Dallmeyer *et al.* (2010). However, different formulations may result in different average diameters of the electrospun fibers (Chang *et al*. 2016). The carbon content of the produced fibers was 43.22 wt.%, as measured by an elemental analyzer (Perkin Elmer 2400 CHN, Waltham, USA), which was higher than that of pure HLS (38.88 wt.%), indicating a carbon contribution from the added PEO.

Preoxidation and carbonization

To determine the effects of particular fiber processing parameters on the produced carbon fibers, the prepared electrospun fiber samples were randomly divided into groups (A to F) according to the subsequent processing conditions presented in Table 1. Five processing parameters were investigated: the preoxidation temperature (POT), treatment temperature (C_1T) and heating rate (C_1R) in the low-temperature carbonization (C1) phase, and treatment temperature (C_2T) and temperature holding period (C_2t) in the high-temperature carbonization (C2) phase.

Table 1. Processing Parameters

Group	Parameters				
	POT (°C)	C_1R (°C/min)	C_1T (°C)	C_2t (h)	C_2T (°C)
A	250	1	400	1	700, 800, 900, 1000, 1200 and 1500
B	250	1	300	1	
C	250	3	400	1	
D	250	5	400	1	
E	250	1	400	3	
F	200	1	400	1	

In the preoxidation process, the electrospun fiber samples were clamped to a sample holder and then heated to a POT of 200 to 250 °C, at a heating rate of 0.5 to 5 °C/min. The samples were maintained at the POT for 1 h and then allowed to cool to room temperature.

After preoxidation, the fiber samples went through a two-phase carbonization process in a nitrogen (N_2) atmosphere inside of a tube furnace (Barnstead Thermolyne F59300, Conroe, USA). Figure 2 illustrates the carbonization process. In the C1 phase, the samples were heated at a rate of 1 to 5 °C/min until it reached the C_1T with a holding period of 5 min.

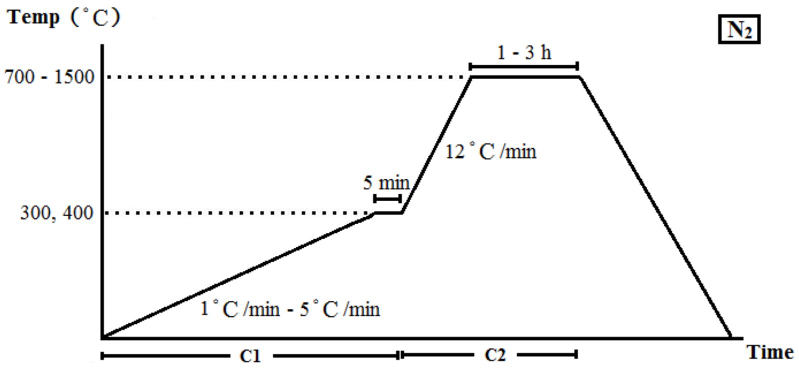

Fig. 2. Carbonization process

The samples were then treated in the C2 phase, in which the heating rate was 12 °C/min and the C_2T was between 700 and 1500 °C with a holding period of 1 to 3 h. The carbonized fibers were allowed cool to room temperature in the N_2 atmosphere.

Fiber analyses

Thermogravimetric analysis (TGA) with a thermogravimetric analyzer (TGA-851, Mettler-Toledo, Greifensee, Switzerland) was utilized to estimate appropriate C_1T and C_2T values in the carbon fiber production process. The preoxidized HLS-based fiber samples were heated from room temperature to 900 °C in N_2 with a heating rate of 5 °C/min.

An elemental analyzer (Perkin Elmer 2400 CHN, Waltham, USA) was used to measure the carbon contents of the fiber samples. The ash contents of the produced carbon fiber samples were measured according to ASTM D2866-11 (2011). Subsequently, the yields of the produced carbon fibers were calculated based on yield (wt.%)= [(weight of fiber mat after carbonization) / (weight of electrospun fiber mat)]*100, and the diameters of the fibers were measured using a scanning electron microscope (SEM; JSM-5410, JEOL, Tokyo, Japan). Comparisons of the different groups were performed through the analysis of variance (ANOVA, $\alpha = 0.05$) to investigate the effects of the processing conditions. A Tukey test (confidence level of 95%) was also conducted to evaluate differences among the test groups.

Linear regression analyses were conducted to determine the effects of formulations on the properties of the products. Specifically, five processing variables were examined: POT (preoxidation temperature), C_1T (C1-phase temperature), C_1R (C1-phase heating rate), C_2T (C2-phase temperature), and C_2t (C2-phase holding period). The interactions between two of these variables were also investigated.

The explicit response function of these variables is unavailable; therefore, a multiple regression method was employed to approximate the actual response by using a second-order polynomial function (Eq. 1).

$$\begin{aligned} \mathrm{Y} = {} & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_5 + \beta_{11} x_1^{\,2} + \beta_{22} x_2^{\,2} + \beta_{33} x_3^{\,2} + \beta_{44} x_4^{\,2} + \beta_{55} x_5^{\,2} \\ & + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{15} x_1 x_5 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{25} x_2 x_5 + \beta_{34} x_3 x_4 + \beta_{35} x_3 x_5 + \beta_{45} x_4 x_5 + \varepsilon \end{aligned} \tag{1}$$

where Y is the property of interest; x_1, x_2, x_3, x_4, and x_5 are the POT, C_1T, C_2T, C_1R, and C_2t variables, respectively; β_0, β_i , and β_{ij} are unknown coefficients for defining the response surface; and ε is the error term.

RESULTS AND DISCUSSION

High heating rates in the C1 phase often triggered a fast release of a large volume of gaseous products due to lignin pyrolysis, resulting in the generation of pores on fiber surfaces. In the C2 phase, physical activation in the released water (H_2O) and carbon dioxide (CO_2) could prompt the development of porous structures in the fibers.

Ferdous *et al.* (2002) investigated the pyrolysis of kraft pulping process produced lignin in a N_2 atmosphere with a heating rate of between 5 and 15 °C/min and a pyrolysis temperature of 800 °C. Their study determined that the gaseous products mainly consisted of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and hydrogen (H_2). They also found that, during pyrolysis, weak bonds broke at low temperatures (< 500 °C), eliciting the release of CO_2 and CH_4; whereas at high temperatures (> 500 °C), aromatic rings were rearranged and condensed, releasing H_2 (19).

In the present study, the results of the TGA/derivative thermogravimetric analysis (DTG) indicated that when the treatment temperature was lower than 170 °C, the mass loss of the treated samples was primarily caused by water evaporation because no chemical reactions occurred at this stage. When the treatment temperature was increased from 250 to 500 °C, the samples mass decreased by approximately 25%. The next substantial mass loss was 15%, which occurred when the treatment temperature increased from 650 to 720 °C, resulting in a total mass loss of about 78%.

The TGA/DTG results (Fig. 3) revealed that the first and second lignin pyrolysis reactions occurred when the temperature went higher than 350 °C and around 700 °C, respectively. The first pyrolysis reaction produced a large volume of gases, which created irregular pores on the surfaces of the fibers that were treated at high heating rates. The second lignin pyrolysis reaction was associated with the release of noncarbon materials. The results indicated favorable C_1T and C_2T values of 400 °C and > 700 °C, respectively.

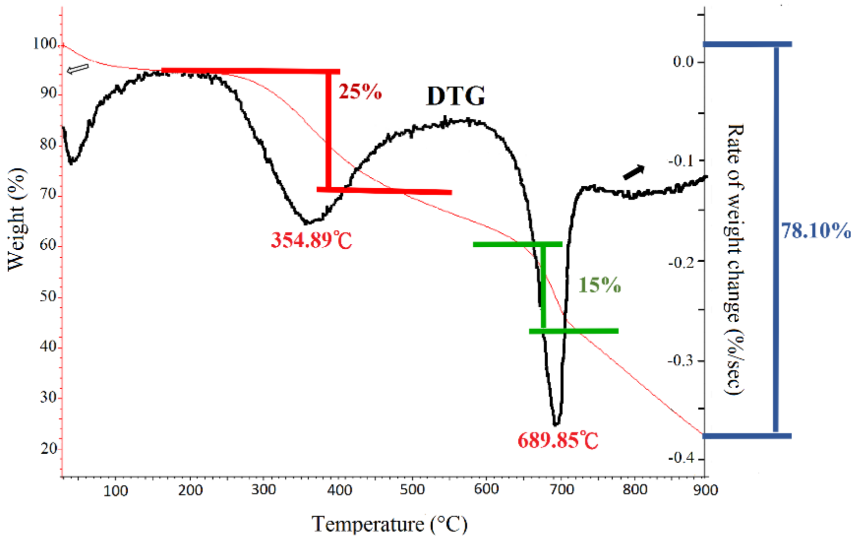

Fig. 3. TGA-DTG results when the heating rate was 5°C/min

To investigate the effect of the heating rate in the preoxidation step, various PORs in a range of 0.5 to 5 °C/min were explored. The rate of 1 °C/min enabled high carbon fiber yields, with the produced fibers exhibiting obvious layered structures (Fig. 4A). When the POR was greater than 1 °C/min, fiber fusion occurred (Fig. 4B). When the POR was less than 1 °C/min, the produced fibers had an average diameter of only 323 nm and were brittle (Fig. 4C).

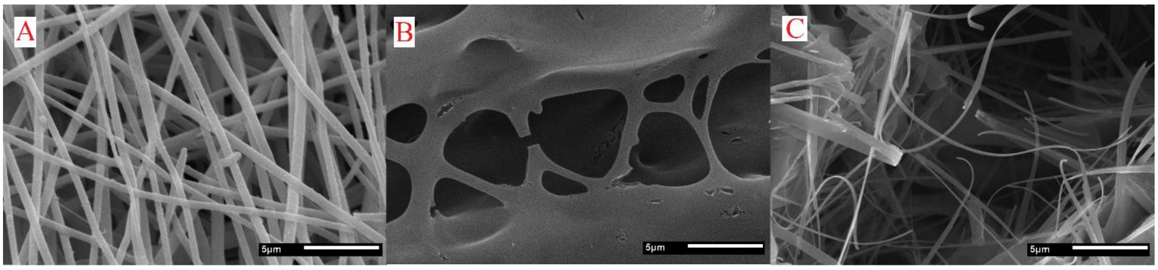

Fig. 4. Fibers produced by preoxidizing lignin at heating rates of A) 1 °C/min, B) 5 °C/min, and C) 0.8 °C/min

These results can be attributed to the slower rate of increase in the T_g when the POR is higher than 1 °C/min, prompting fusion and the rubbery state of the treated HLS fibers. The preoxidation at high PORs can cause incomplete oxidation reactions, thereby reducing carbon fiber yields. In contrast, low heating rates prolonged the preoxidation process and prompted oxygen to bond with carbon, forming CO and CO_2. In this case, the produced fibers had small diameters and brittle structures. The carbon fiber yields in Groups A to F suggested that a POT of 250 °C was associated with a higher carbon fiber yield and fiber carbon content compared with those of a POT of 200 °C.

According to the measurement of the elemental analyzer, the carbon contents of carbon fibers produced at a POR of 1 °C/min, and POTs of 250 °C and 200 °C, were 43.39 and 47.73 wt.%, respectively. This result indicated that elevating the POT reduced the fiber carbon content. Similar findings were reported in Braun *et al.* (2005). The heating process in the preoxidation process enabled complete oxidation of toluene, inducing an increase in the release of H_2O, CO_2, and CO. Therefore, the produced carbon fibers had relatively stable structures that could resist high carbonization temperatures.

The comparisons of different POT values revealed that the HLS fibers preoxidized at 200 °C were vulnerable to high carbonization temperatures, thereby influencing fiber morphology in the HLS fibers. As displayed in Fig. 5, the incremental rate of the carbon content along with the carbonization temperature was lower in Group F (POT of 200 °C) than in Group A (POT of 250 °C), signifying that higher POTs enabled higher fiber carbon content. The diameter values of the carbon fibers in Group F exhibited a minor fluctuation with the change in the carbonization temperature.

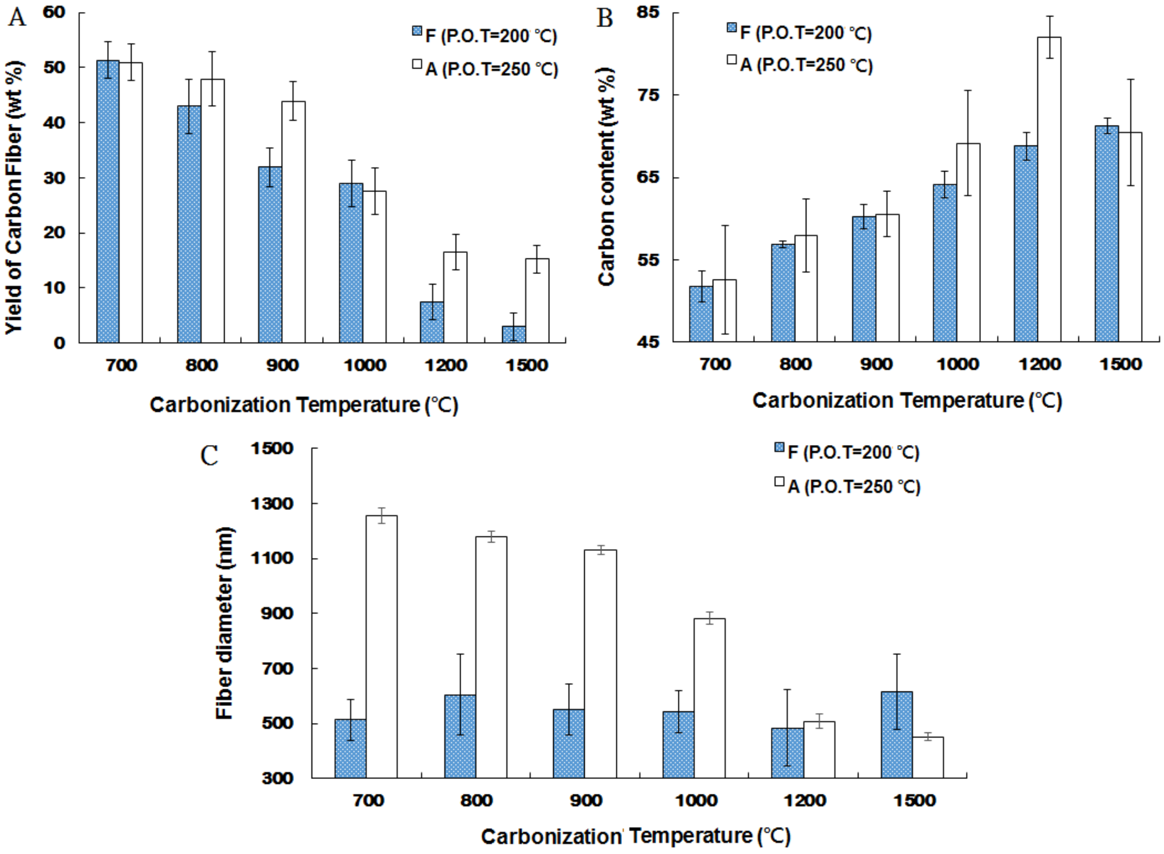

Fig. 5. Effects of the POT on the properties of HLS-based carbon fibers

Ruptures in the carbon fibers and fiber mats were observed using a microscope. When the POT was as low as 200 °C, insufficient preoxidation occurred, making the produced carbon fibers prone to rupture at high carbonization temperatures, and thus lowering the carbon fiber yields. Therefore, a POT of 250 °C was considered more favorable for producing HLS-based carbon fibers.

In the carbonization process, high heating rates in the C1 phase (C_1Rs) led to the formation of pores on fiber surfaces, due to the release of a large volume of gaseous products (Ferdous *et al.* 2002). The results showed that prolonged temperature holding periods in the C2 phase (C_2t values) caused fiber rupture. Because the investigation discovered that HLS-based carbon fibers that were produced by using a one-phase carbonization process, resulted in brittle fibers and low fiber yields. This study employed a two-phase carbonization process.

The results of this study also indicated that a C_1R of 1 °C/min was suitable for carbon fiber production, because carbon fibers created at a C_1R of more than 1 °C/min were brittle. According to observations of fiber mat ruptures, the ruptures were located in the surface layers of the produced carbon fiber mats. When the C_2T was 1000 °C, the comparison among the carbon fiber mat samples, which were treated at C_1R values of 1, 3, and 5 °C/min, indicated that higher C_1Rs were associated with more severe fiber ruptures (Fig. 6).

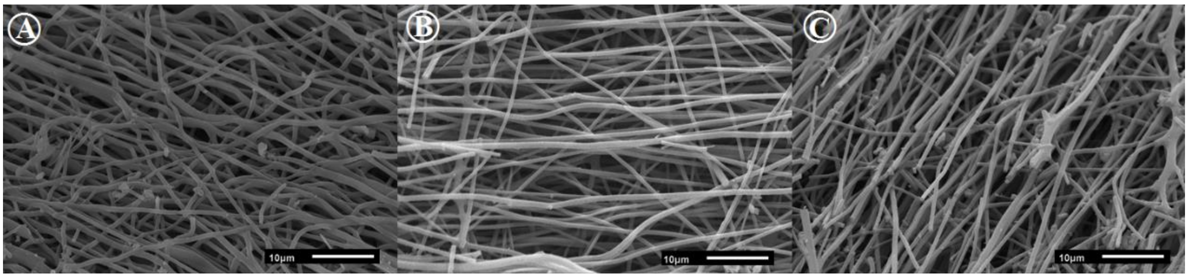

Fig. 6. Fibers carbonized at C_1R of A) 1 °C/min, B) 3 °C/min, and C) 5 °C/min

Figure 7 demonstrates the effect that the C_1R had on the properties of the carbon fibers. When the C_1R was greater than 1 °C/min, the carbon fiber yield displayed no particular trends with changes in the carbonization temperature. This phenomenon was attributed to the fact that high C_1R values cause incomplete pyrolysis, which in turn leads to the formation of unstable fiber structures. Furthermore, the shorter carbonization period caused by the high C_1R of Group D resulted in higher carbon fiber yields, but lower fiber carbon contents than those of Group A. The carbon fibers in Group D had small fiber diameters and brittle structures. High C_1Rs were unfavorable for the production of HLS-based carbon fibers; this finding was confirmed by other studies (Mathur *et al.* 1992; Baker 2011).

The investigation of the effect of the C_1T on the properties of the produced carbon fibers suggested that, in response to the change of the carbonization temperature, the samples treated at C_1Ts of 300 and 400 °C demonstrated similar trends in the carbon fiber yield, fiber carbon content, and fiber diameter (Fig. 8). However, when studied at the same carbonization temperatures, the carbon fiber yield and fiber carbon content of Group B were lower than those of Group A. When the C_1T was 300 °C, the release of gaseous products primarily took place in the C2 phase, leading to incomplete pyrolysis, and thus created a negative influence on the carbon fiber yield and fiber carbon content.

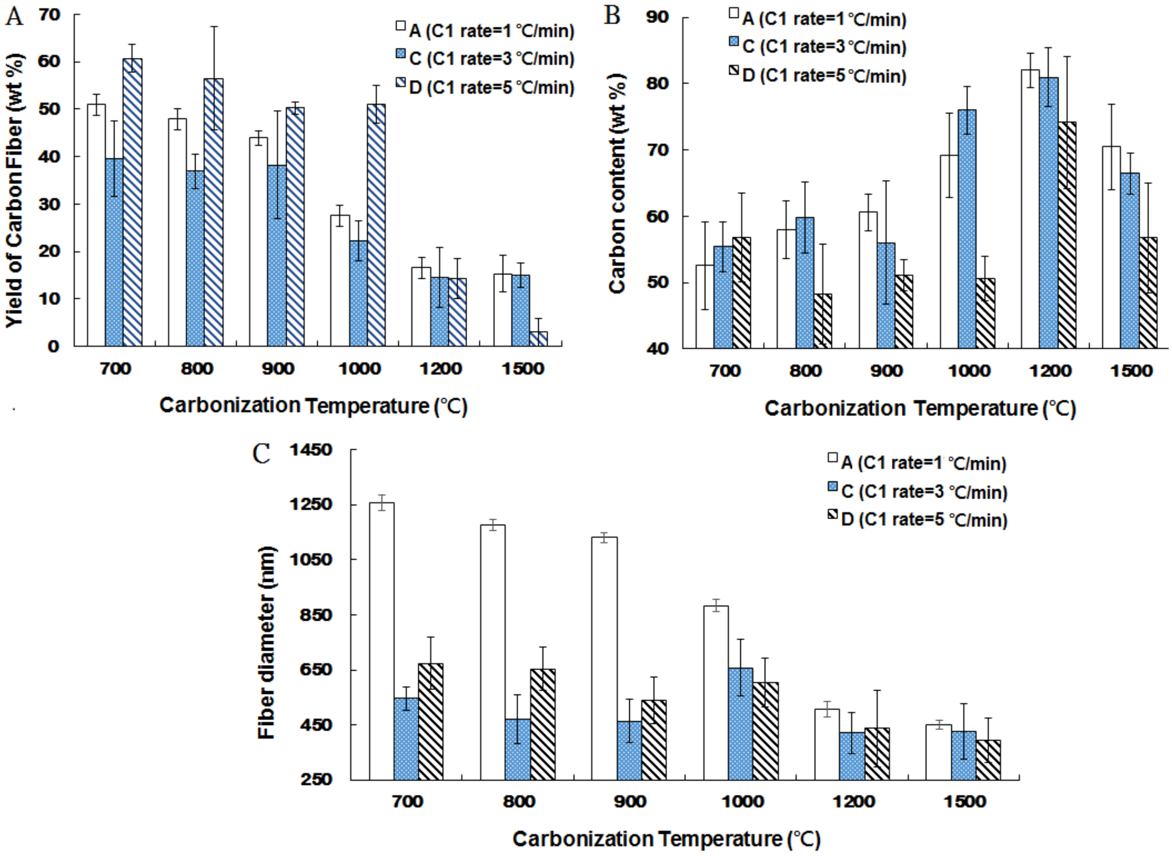

Fig. 7. Effects of C_1R on the properties of HLS-based carbon fibers

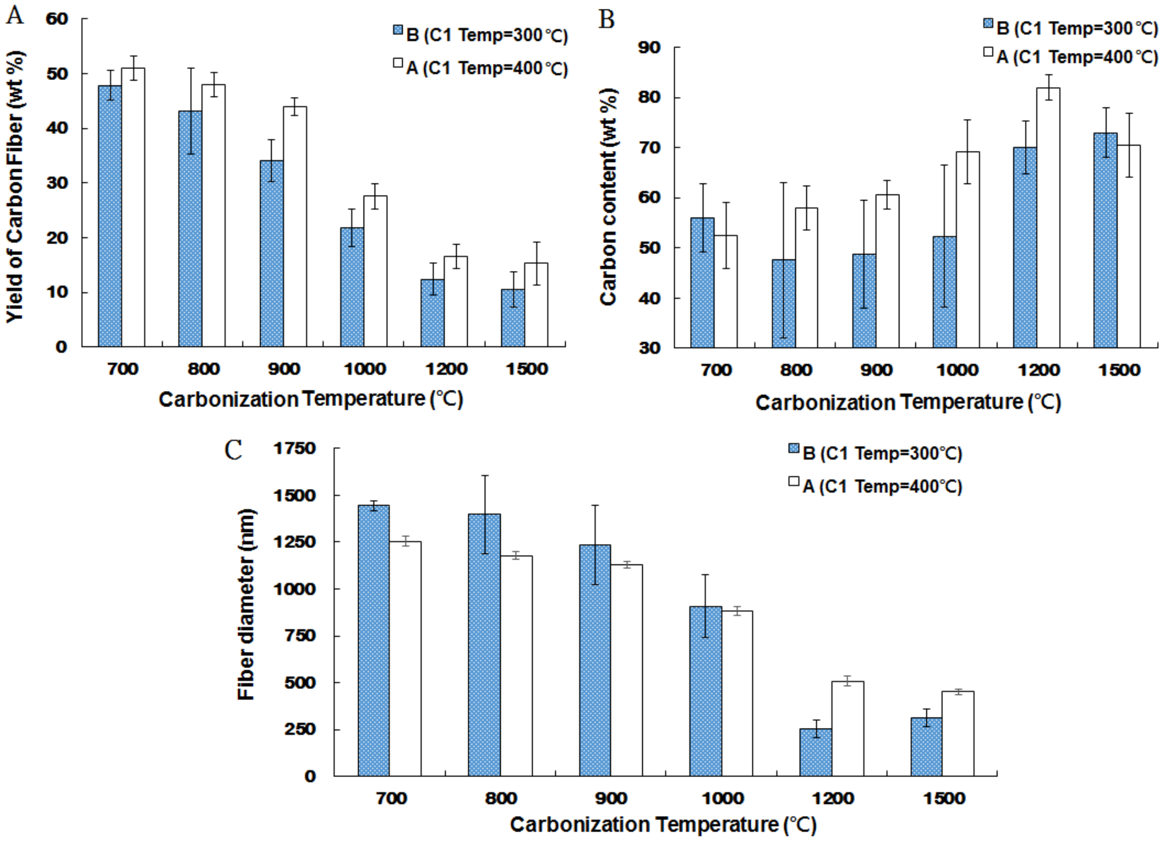

Fig. 8. Effects of C_1T on HLS-based carbon fibers

Higher C_2t and C_2T values were associated with lower carbon fiber yields but higher fiber carbon contents. For example, before the carbonization step, the carbon content of the pre-oxidized fibers was approximately 43 wt.%. Comparably, after carbonization at a C_2T of 1200 °C, the average carbon content of the produced carbon fibers reached approximately 85 wt.%. Despite the influence of C_1R, substantial fiber pyrolysis and shrinkage reactions occurred when C_2T was higher than 900 °C. This resulted in carbon fiber mat rupture. Moreover, the carbon fibers presented even rupture faces, signifying a brittle failure (Fig. 9).

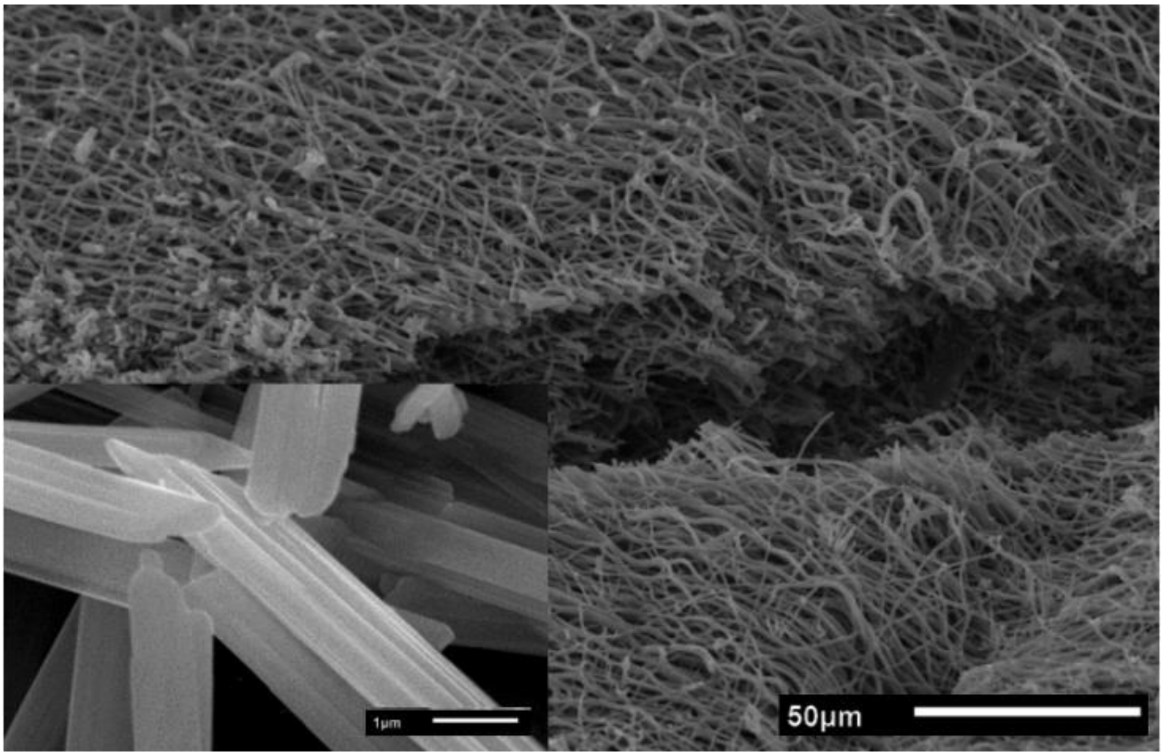

Fig. 9. Rupture of carbon fibers in Group B (C_2T = 700°C) and Group D (inset picture, C_2T = 800°C)

Figure 10 presents the effects of the C_2t on the properties of the produced carbon fibers. Under the same carbonization temperatures, Group E had a lower carbon fiber yield, but a higher fiber carbon content than Group A.

Ruptures were observed at the peripheries of the carbon fiber mats in Group E, implying that pyrolysis and cross-linking reactions progressed along with the heating process, and thus resulted in continuous fiber shrinkage. Figure 10C indicates that the average diameter of the produced carbon fibers in Group E was only 292 nm when C_2T was 1500 °C.

As shown in the SEM image of the produced carbon fibers in Group E in Fig. 11A, the fibers had rough surfaces and nonuniform fiber diameters along the fiber length, and the carbon fiber mats were severely ruptured.

Groups A and E shared the same values for most of the processing parameters, except that the temperature holding period was 1 h in Group A and 3 h in Group E. However, the carbon fibers in Group A presented relatively smooth surfaces and uniform fiber diameters. Therefore, a long C_2t is considered unfavorable for production of HLS-based carbon fibers.

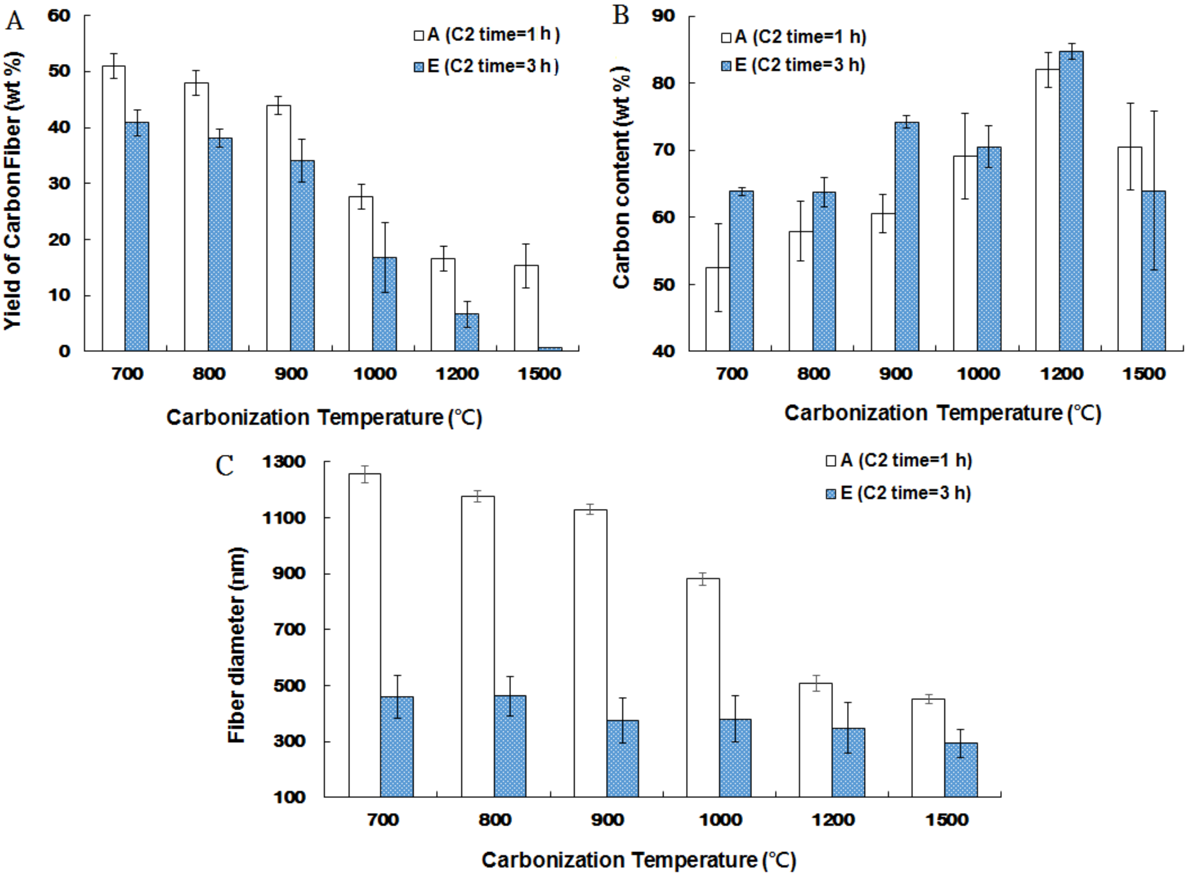

Fig. 10. Effects of C_2t on the properties of the produced carbon fibers

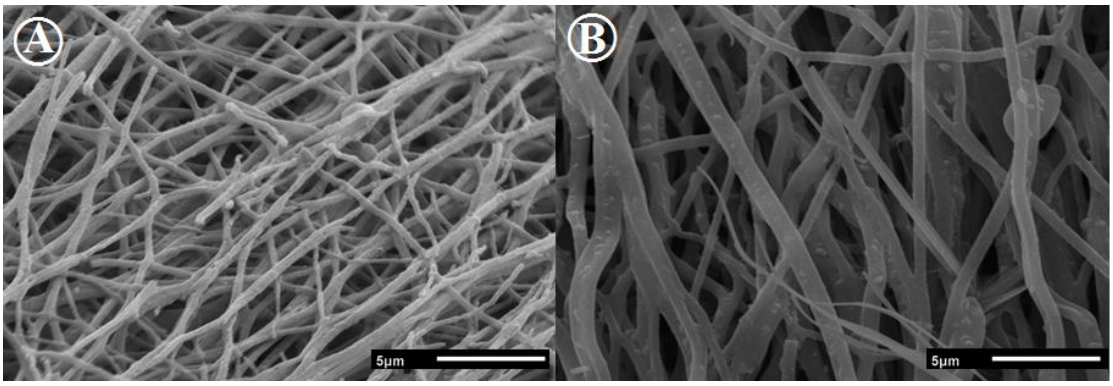

Fig. 11. Carbon fibers produced in A) Group E and B) Group A

According to Figs. 5, 7, 8 and 10, when the C_2T was less than 1200 °C, higher C_2Ts resulted in a higher fiber carbon content. However, when C_2T was greater than 1200 °C, a substantial decline in the fiber carbon content occurred in all fiber groups. This phenomenon may be attributed to the influence of the noncarbon components on the cross-linking reactions of the carbon fibers when the C_2T was more than 1200 °C. This influence resulted in the formation of amorphous carbon materials, the constant consumption of carbon, and the reduction of the fiber carbon content. However, further studies will be needed to confirm this point.

Before the carbonization step, the ash content of the HLS-based fibers was 14.98 wt.%. During carbonization, the components of ash may produce considerable noncarbon compounds, which remained in the final carbon fibers. The carbon content of the produced carbon fibers was lower than 90 wt.%, and the fiber carbon contents in each fiber group were widely distributed.

The average diameter of the untreated HLS fibers was 1611 nm. The fiber diameter decreased after treatment in the preoxidation and carbonization steps. For example, the average diameter of the pre-oxidized HLS fiber samples in Group A was 1298 nm. After the carbonization, the average diameter of the final carbon fibers was 1256 nm (C_2T of 700 °C) and 451 nm (C_2T of 1500 °C).

The carbon fiber yields in Group A presented a similar declining trend as the C_2T increased, and a substantial decline occurred when the carbonization temperature was greater than 900 °C. The declining trend indicated intense fiber shrinkage (Fig. 12). Therefore, the produced carbon fiber mat could not retain a nonruptured configuration.

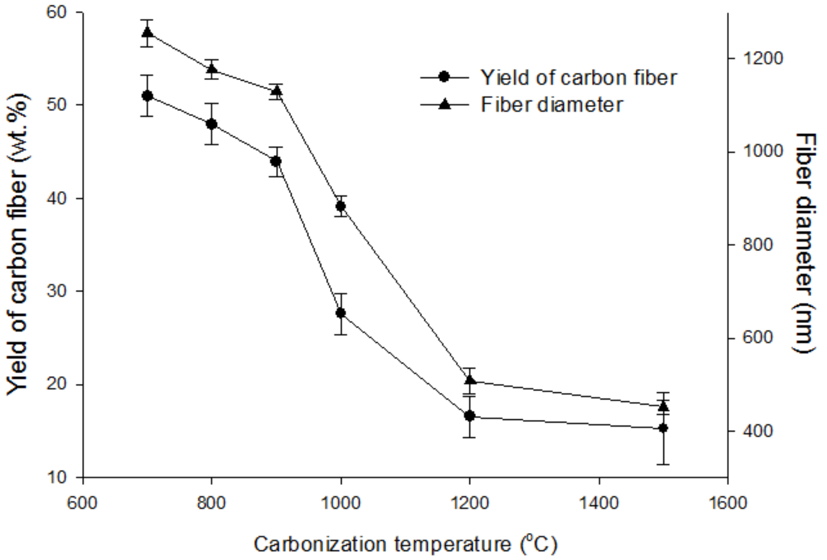

Fig. 12. Relationships of C_2T to the carbon fiber yield and diameter in Group A

In similar studies, Kadla *et al.* (2002) blended Kraft and organosolv lignins with PEO and produced carbon fibers with a carbonization temperature of 1000 °C. The resulting carbon fiber yields were 40 to 46% and fiber diameters were 30 to 55 μm. Similarly, Lallave *et al.* (2007) employed organosolv lignin and a carbonization temperature of 900 °C and obtained a carbon fiber yield of 31.6 wt.% and diameter of 200 nm. When carbonizing calcium HLS at 800 °C, Chen and Zhou (2012) attained a carbon fiber yield of 15 wt.%.

According to Robert *et al.* (1984), the carbon content of lignin sulfonate was 44.84 wt.%. Lü *et al.* (2011) employed a lignin sulfonate-polyaniline blend, with a heating rate of 3 °C/min and a carbonization temperature of 1200 °C to produce carbon fibers. The resulting carbon content of the produced fibers was 75.84 wt.%. Norberg *et al.* (2013) carbonized kraft lignin at 1000 °C and obtained carbon fibers with carbon content above 90 wt.%.

To evaluate the statistical effect of each processing parameter, a series of two-way ANOVAs were conducted. The results are summarized in Table 2 and indicate that the processing parameters had significant effects on the properties of final products, except for C_1T. However, some interaction effects were not significant, suggesting that the processing parameters need to be considered carefully.

Table 2. ANOVA Results

Parameters	Carbon Fiber yield	Fiber Carbon Content	Fiber Diameter
POT	*	*	*
C_1T	*	*	n.s.
C_1R	*	*	*
C_2T	*	*	*
C_2t	*	*	*
$POT*C_2T$	*	*	*
C_1T*C_2T	n.s.	n.s.	*
C_1R*C_2T	*	*	*
C_2t*C_2T	n.s.	*	*

Note: * means significant effect ($p < 0.05$), whereas n.s. means no significant effect ($p > 0.05$)

To further determine the relationships between the processing parameters and the properties of the produced carbon fibers (*i.e.*, carbon fiber diameter and yield and carbon content), multiple regression equations were evaluated based on the collected test data, with a confidence level of 95%. The derived regression equations are tabulated in Table 3. Some transformation was needed for several parameters to properly estimate the dependent variables. The fiber yields and diameters were associated with processing parameters, according to the high coefficient of determination (R^2) values. The R^2 value of the equation for fiber carbon content was not comparable because the carbon content values of the HLS-based carbon fibers fluctuated widely, influencing the estimation.

Table 3. Regression Equations

Property	Regression Equation
	$-13.64-3.28\times10^{-2}(C_2T)-3.05\times10^{-3}(POT)+5.23\times10^{-6}(C_2T)^2+1.47\times10^{-2}(C_1R)^2$
Carbon fiber yield (wt.%) =	$-664\times10^{-5}(C_2T\times C_1R)-6.6\times10^{-7}(C_2T\times C_2t)+36\times10^{-6}(C_2T\times POT)+1.31(C_2T)^{0.5}$ $6.42-9.695\times10^{-3}(C_2T)-1.1194\times10^{-2}(C_1T)+2.52\times10^{-6}(C_2T)^2-4.7585\times10^{-3}(C_1T)^2$ (R^2 = 0.88) $+2.50\times10^{-5}(C_2T\times C_1T)-2.18\times10^{-5}(C_2T\times POT)-10^{-8}\left[(C_1T)^2\times(C_2T)^2\right]+10^{-8}\left[(C_2T)^2\times(POT)^2\right]$
Fiber carbon content (wt.%) =	$-10^{-8}\left[(C_2T)^3\times(POT)^3\right]$ $-9.09+4.57\times10^{-2}(C_2T)-4.95(C_1R)+0.114(POT)-2.6\times10^{-5}(C_2T)^2+0.426(C_1R)^2$ (R^2 = 0.60) $-2.05\times10^{-4}(C_2t)^2-1.65\times10^{-3}(C_2T\times C_1R)-2.3\times10^{-5}(C_2T\times C_2t)+4.4\times10^{-5}(C_2T\times POT)$
Fiber diameter (nm) =	$+10^{-8}(C_2T)^3+0.408\left(\sqrt{C_2T}\times\sqrt{C_1R}\right)+4.54\times10^{-2}\left(\sqrt{C_2T}\times\sqrt{C_2t}\right)-0.144\left(\sqrt{C_2T}\times\sqrt{POT}\right)$ (R^2=0.86)

CONCLUSIONS

The electrospinning method was applied to produce HLS-based carbon fibers, and then effects of particular processing parameters were investigated relative to the yields, carbon contents, and diameters of the produced carbon fibers. The results revealed that:

1. The preoxidation step is crucial for the subsequent carbonization process. The application of a POR of 1 °C/min successfully prevented fiber fusion and rupture, thereby enabling the production of unruptured fiber mats, high carbon fiber yields, and clear fibrous layers. A POT of 250 °C prevented fiber mat rupture and increased the fiber carbon content.

2. In the carbonization process, higher C_1Rs induced fiber rupture. According to the TGA results, a C_1T of 400 °C prevented gaseous products from creating pores on the fiber surfaces, thereby retaining the structural integrity of the produced fiber mats and increasing the fiber carbon content.
3. Higher C_2Ts were associated with lower carbon fiber yields and fiber diameters, as well as higher fiber carbon contents. As the C_2t was prolonged, the carbon fiber yields and diameters decreased, but the fiber carbon contents increased. The highest fiber carbon content occurred with a C_2t of 3 h and a C_2T of 1200 °C.
4. The ANOVA results indicated that processing parameters such as POT, C_1R, C_2T and C_2t had significant effects on the carbon fiber yields, fiber carbon contents and fiber diameters; however, the C_1T had a significant influence on the carbon fiber yields and fiber carbon content but not on fiber diameters. Furthermore, some interaction effects between processing parameters were also observed.

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