

Process Optimization for Preparing High Performance PAN-based Carbon Fibers

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Optimum process conditions were investigated for maximizing the mechanical properties of the carbon fiber by from wet spun polyacrylonitrile (PAN) fiber precursors. The process variables chosen were treatment temperature, applied tension in stabilization process. The temperature profile of the stabilization was set on the basis of exothermic peaks of the differential scanning calorimetry (DSC) result. Both tensile strength and modulus increased with holding at onset temperatures of the exothermic peaks for extended duration, and with a higher heating rate up to the onset temperatures at a given applied tension among the experimental conditions. The increase in load monotonously increased the tensile modulus, on the other hand, the tensile strength was maximum at the load of 15 mg/filament (T15). The load 20 mg/filament (T20) was considered to be exceeded to form oriented crystalline structure, possibly introducing more defects in the fiber than under load of T15. The sample CP3-T15 O5 H30 showed the best tensile properties among the samples experimented whose tensile properties are compatible with the commercialized grade of general purpose carbon fibers even at low carbonization temperature such as 800 °C (the carbonization temperature in the commercial process. 1300 ~ 1500 °C).

Key Words: Carbon fiber. Stabilization. Carbonization. Tension. Tensile strength

Introduction

Carbon fibers are mainly used for reinforcement in advanced composite materials in the area of "lighter but stronger", such as those with applications in the aeronautics, aerospace, sports and leisure industries.¹⁻⁵ The carbon fibers are produced from various fibrous precursors such as polyacrylonitrile (PAN)-based, pitch-based, and vapor-grown fibers, but mainly produced from PAN fibers. Today, PAN-based carbon fibers dominate consumptions, accounting for nearly 90% of all sales worldwide⁶ because they have established a lot of impressive advantages as reinforced material for the advanced composites.

The conversion of a PAN precursor fiber to a carbon fiber involves stabilization and carbonization processes. The establishment of the morphological structure during the conversion process determines the physical and mechanical properties of the carbon fibers, which are dependent on the precursor material, heat treatment condition and applied tension. The stabilization converts the thermoplastic PAN into a nonplastic cyclic compound that can withstand at high temperatures during carbonization process.⁷ The stabilization process, i.e., oxidative thermal treatment of the PAN material is bottle neck in process and the most influential step in determining mechanical properties of the carbon fibers.⁸⁻¹¹ This study tempted to optimize the stabilization process to maximize the mechanical properties of the carbonized fibers. The shrinkage is another component related to a loss of molecular alignment leading to deterioration of the mechanical properties of the carbon fibers. In this work, we also investigated the effect of applied tension to shrinkage which would be affecting factor to modulus and tensile properties of the fibers.

Thermal Analysis. As the stabilization is occurred by cyclization reaction of the PAN, the information of the reaction temperature and the heat of reaction are the definite parameter to be considered. The DSC results give us useful information of chemical reactions, such as dehydration, intra- and intermolecular cyclizations. Figure 1 shows the thermal behavior of the PAN precursor in air or nitrogen atmosphere.

Two distinct exothermic peaks were observed at 260 and 300 °C in the air atmosphere, on the other hand, a single exothermic peak is observed at 260 °C in nitrogen atmosphere. It is understood that Peak I appears due to the intramolecular cyclization/thermal stabilization reactions, and Peak II is related to oxygen

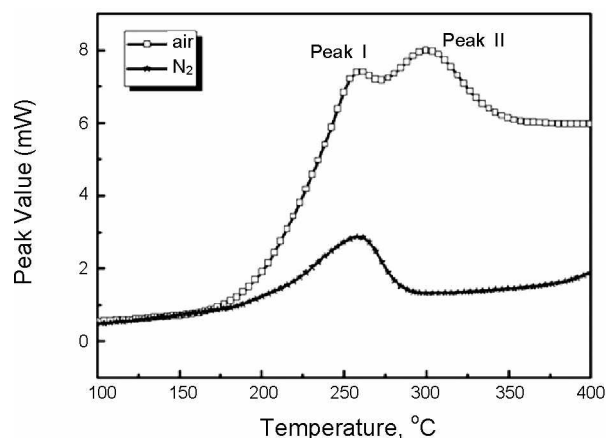


Figure 1. DSC plots of PAN precursor fiber in air and nitrogen heating at 2 °C/min.

molecules which introduce dehydration reaction leading to intermolecular cross-linking (Figure 2).¹²⁻¹⁴

Stabilization. According to the information from DSC curves, three specific temperatures were selected, onset temperature of the exothermic peak I at 190 °C and two other temperatures from the exothermic peaks at 259 °C and 300 °C. The PAN precursor fibers were under tension to keep the molecular orientation during the stabilization step.

The samples were identified on the basis of the temperature profile and the load applied. The sample ID of CP3-T15 O5 H30 represents the carbonized sample(C) after stabilization of three steps (P3) temperature profile, holding for 30 minutes (H30) at each step, 5 °C/min heating up to onset temperature (O5) and the applied load of 15 mg/fiber (T15). Temperature profiles used for this work are shown in Figure 10 (see Experimental section).

The stabilization conditions and the properties of the stabilized fibers were summarized in Table 1 and Table 2, respectively. According to the results in Table 2 and Figure 3, the stabilization process of heating program 2 turned out to be better mechanical properties than that of heating program 1. During the stabilization, shrinkage is observed, which is attributed to entropic recovery of the drawn and quenched material (physical), and nitrile cyclization reactions and subsequently formation of ladder

polymer (chemical). At relatively low temperature (80 ~ 100 °C), the shrinkage of the fibers begins from reverting the oriented amorphous polymeric chains to a random coil configuration.^{13,18} This physical shrinkage can be reduced or even eliminated by keeping the fibers under tension during the oxidative thermal treatment.^{18,19} But chemical shrinkage starts from 168 °C, which independent on the applied stress but increases with low cyclization rate.

As shown in Figure 4, the higher the tension applied, the lower the shrinkage was observed. The extent of shrinkage from the chemical reaction of PAN precursor fibers can be ranged from minimum 10% to maximum 30%, depending on the ratio of intermolecular to intramolecular cyclization reactions which produce the different types of ladder polymer sequences.^{15,21-22} It was calculated that the shrinkage is expected to be around 30% when ladder polymer structure with approximately symmetric sequences. The shrinkage reduces molecular alignment in the fibers and subsequent deterioration of the mechanical properties of the carbon fibers. Thus, the shrinkage must be optimized in developing highly ordered and defect free carbonized fibers.²³⁻²⁵

The tensile properties of the stabilized fiber depend on the treatment conditions such as temperature profile, holding time and stress applied which accompanying physical and chemical changes in the fiber.¹⁷ The results are summarized in Table 2

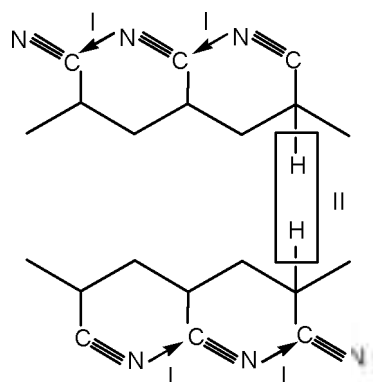


Figure 2. Model of the chemical shrinkage during stabilization.¹⁵⁻¹⁷ I, intramolecular cyclization; II, intermolecular cross-linking reaction.

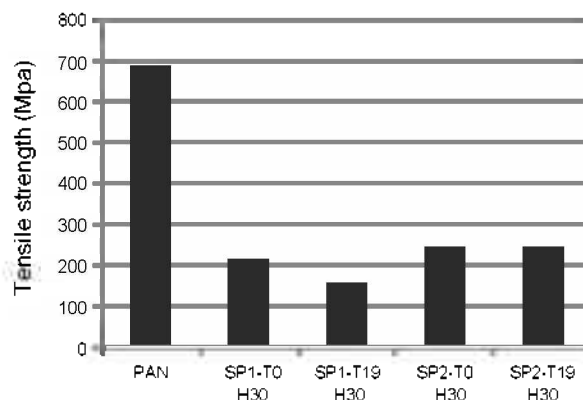


Figure 3. Tensile strength of the stabilized samples.

Table 1. Stabilization conditions of the PAN precursor fibers.

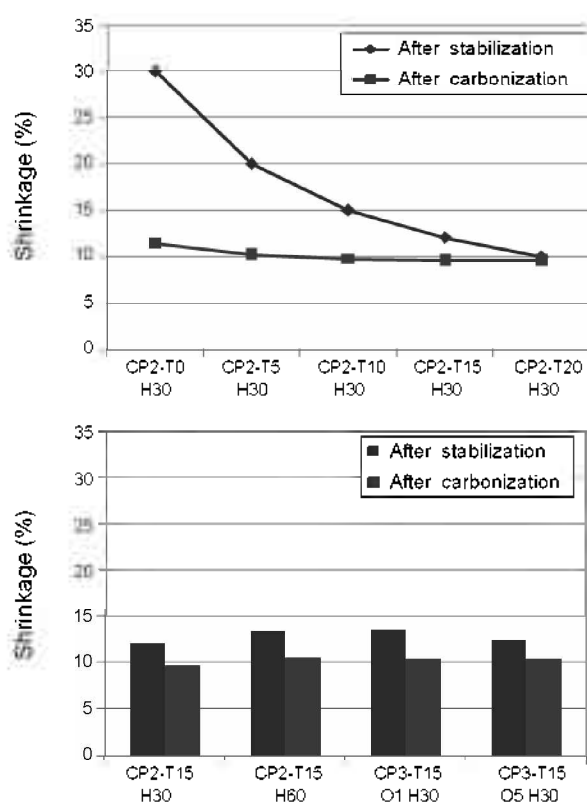
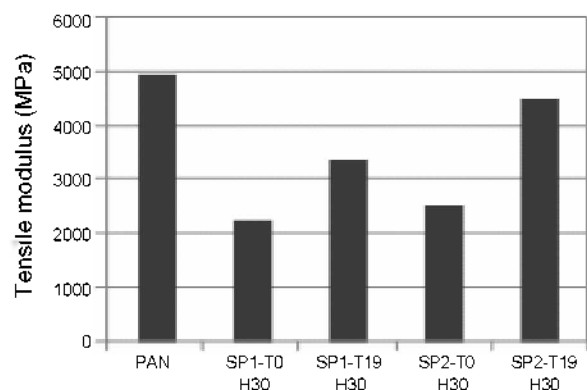
Stabilized Samples	Time-temperature condition
SP1-T0 H30	Stabilized with program 1 under no tension and 30 min holding
SP1-T19 H30	Stabilized with program 1 under tension 19 mg/fiber and 30 min holding
SP2-T0 H30	Stabilized with program 2 under no tension and 30 min holding
SP2-T19 H30	Stabilized with program 2 under tension 19 mg/fiber and 30 min holding

Table 2. Properties of the PAN precursor fiber and its stabilized PAN fibers.

	PAN precursor	SP1-T0 H30	SP1-T19 H30	SP2-T0 H30	SP2-T19 H30
Diameter (μm)	13.9	13.5	11.0	12.4	11.0
Cross sectional area (10 ⁻⁹ cm ²)	1025.8	967.6	642.4	816.4	642.4
Elongation (%)	13.9	9.4	4.5	9.5	5.4
Tensile strength (MPa)	688.3	212.8	152.7	240.2	244.3
Tensile modulus (MPa)	4951.8	2263.8	3393.3	2528.4	4524.1

Table 3. Stabilization conditions of the PAN precursor fibers.

Carbonized Samples	Time-temperature condition
CP2-T0 H30	Carbonized sample after stabilization with program 2 under no tension and 30 min holding each steps
CP2-T5 H30	Carbonized sample after stabilization with program 2 under tension 5 mg/fiber and 30 min holding each steps
CP2-T10 H30	Carbonized sample after stabilization with program 2 under tension 10 mg/fiber and 30 min holding each steps
CP2-T15 H30	Carbonized sample after stabilization with program 2 under tension 15 mg/fiber and 30 min holding each steps
CP2-T20 H30	Carbonized sample after stabilization with program 2 under tension 20 mg/fiber and 30 min holding each steps
CP2-T15 H60	Carbonized sample after stabilization with program 2 under tension 15 mg/fiber and 60 min holding each steps
CP3-T15 O1 H30	Carbonized sample after stabilization with program 3 under tension 15 mg/fiber, heating rate of 1 °C/min to onset temperature and 30 min holding each steps
CP3-T15 O5 H30	Carbonized sample after stabilization with program 3 under tension 15 mg/fiber, heating rate of 5 °C/min to onset temperature and 30 min holding each steps


Figure 4. Shrinkage dependence of the sample on the load and temperature after stabilization and carbonization.

Figure 5. Tensile modulus of the stabilized sample.

and the mechanical properties are presented in Figures 3 and 5. The applied tension reduced fiber diameter and increased fiber modulus, on the other hand, the tensile strength was increased by the tension in the case of two step process (SP2) but it was reduced in the one step process (SP1). Accordingly, the two step process (SP2) is better than one step process (SP1) for tensile property under tension of T19. The results could be explained that there exist optimization conditions to obtain the maximum tensile property through development of the highly oriented crystallized structure.

Carbonization. After searching the proper conditions of stabilization, the stabilized samples were carbonized up to 800 °C holding for 60 minutes in a furnace under nitrogen atmosphere in the absence of tension. The carbonization introduced additional 10% of shrinkage from the stabilized fibers (Figure 4). There carbonized samples prepared at various conditions are summarized in Table 3 and their properties are in Table 4 and Figure 6. The sample CP3-T15 O5 H30 showed the best tensile properties among the samples experimented whose tensile properties are compatible with the commercialized grade of general purpose carbon fibers even at low carbonization temperature such as 800 °C (the carbonization temperature in the commercial process, 1300 ~ 1500 °C). The results imply that the improved tensile properties can be obtained from the conditions as follows; keep the molecular orientation of the precursor fiber as much as possible by rapid heating up to the cyclization reaction temperature (O5 rather than O1), hold at the reaction temperatures for the completion of the reactions (H30), apply optimum tension for building up crystalline structure aligned more perfectly (T15 rather than T20), etc.²⁶⁻²⁹

The data in Table 4 and Figure 6 represent that the prolonged heat treatment around the structure development improved the tensile strength, such as holding at onset temperature of 190 °C of the peak I. The increase in tension increased the tensile modulus, on the other hand, the tensile strength was maximum at the load of 15 mg (T15). The tension T20 is considered to be exceeded to form oriented crystalline structure, possibly introducing more defects in the fiber than under load of T15.³⁰⁻³³

Scanning Electron Microscopy (SEM). Figure 7 shows the cross sections of the stabilized and carbonized fibers, that is, the size of stabilized fiber was reduced by carbonization by 20%.

Figure 8 shows the rupture surface differences between the

Table 4. Properties of carbon fibers prepared at various conditions.

Sample name	Diameter (μm)	Elongation (%)	Area (10^{-9}cm^2)	Tensile strength (MPa)	Tensile modulus (GPa)
PAN	13.9	13.9	1025	688	5
CP2-T0 H30	9.40	0.71	469	339	51
CP2-T5 H30	9.20	0.72	449	321	43
CP2-T10 H30	8.50	0.49	383	284	57
CP2-T20 H30	7.40	0.79	290	459	76
CP2-T15 H30	7.60	0.62	306	520	65
CP2-T15 H60	8.10	0.92	348	704	76
CP3-T15 O1 H30	8.40	0.95	374	627	66
CP3-T15 O5 H30	8.50	1.09	381	801	73

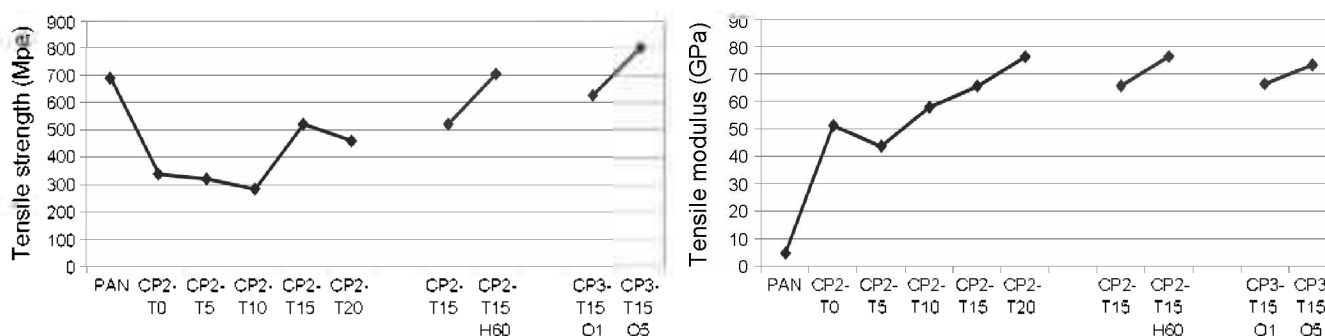


Figure 6. Tensile strength and modulus of the carbonized samples.

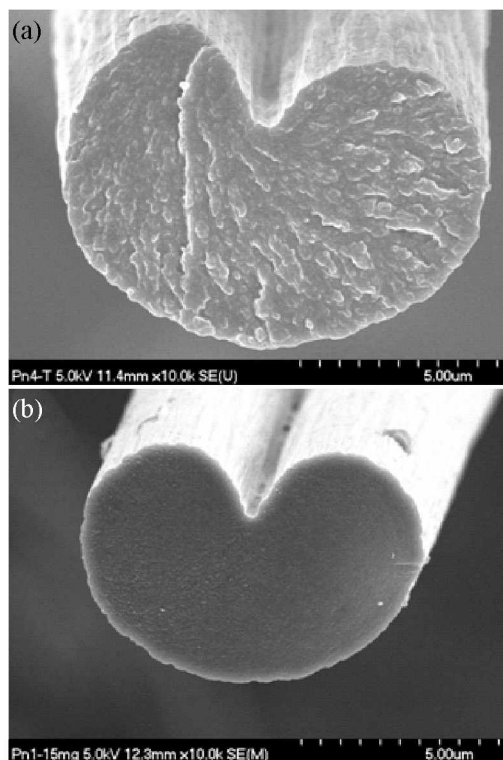


Figure 7. SEM of cross sections of carbon fibers: (a) stabilized fiber (SP2-T15 H30) (b) carbonized fiber (CP2-T15 H30).

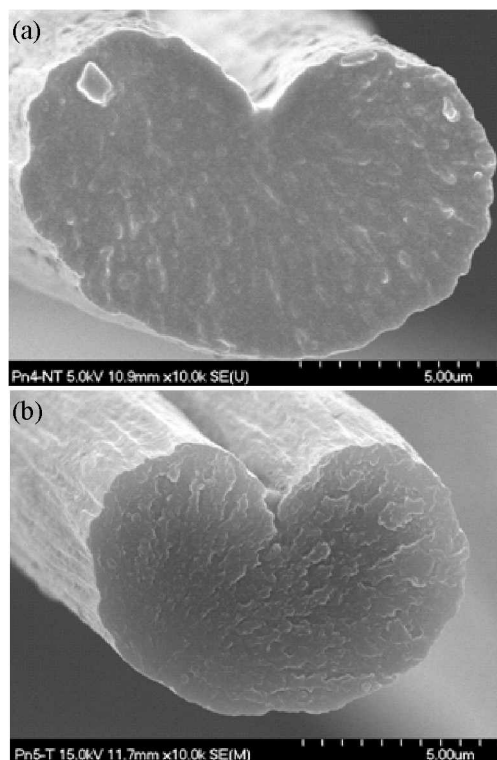


Figure 8. Cross section of stabilized fiber: (a) without tension (b) with tension.

stabilized fibers with and without tensions. The fiber processed under tension shows smoother fiber (less pull-off structure due to the higher modulus) surface and reduced fiber diameter than the fiber under no tension.

Conclusion

The high performances of PAN-based carbon fibers can be achieved by optimum process conditions. The data represent



Figure 9. Tube furnace apparatus.

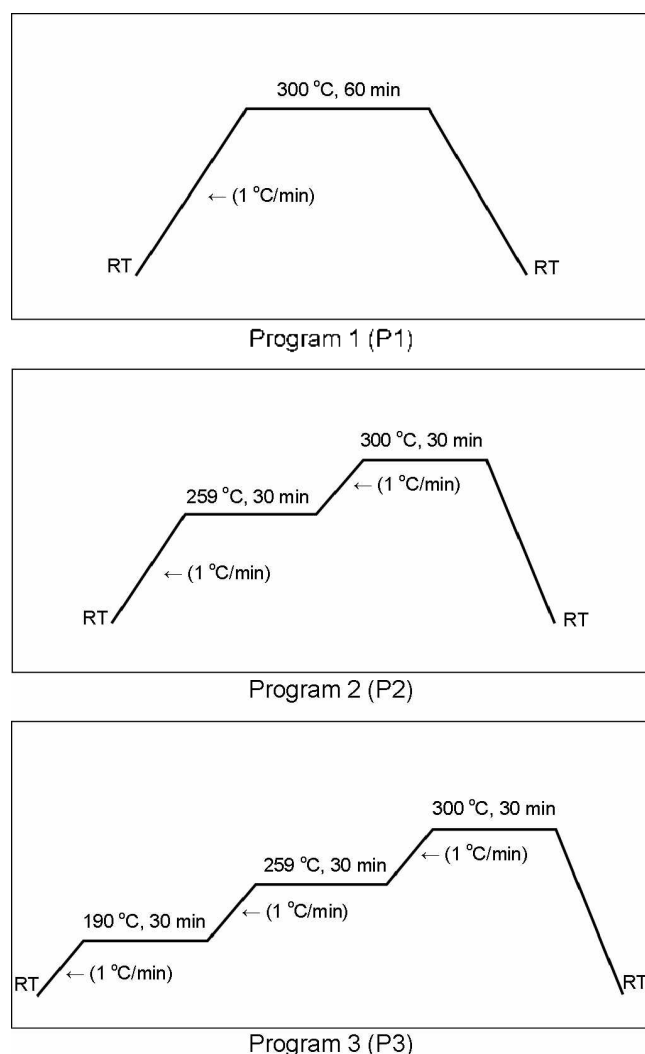


Figure 10. Heating profile of stabilization process.

that the prolonged heat treatment around the structure development improved the tensile strength, such as holding at on set temperature 190 °C of the peak I. An increase in tension leads to increase in tensile modulus but not in tensile strength, the over tension possibly starts to introduce defects in the fiber.

Experimental Section

Precursors. PAN precursor fibers used in the study were recei-

ved from commercial sources (China), and therefore the details of the precursor fibers are not available. The wet spun PAN fibers were supplied in tows of 12 K consisting of 12 μm fibers with a heart shaped cross section.

Stabilization and Carbonization. The heat treatment experiments were performed in a tube furnace furnished with gas regulators with 10 cm heating zone. The 10 cm sample fiber tied with commercial carbon fibers was located in the center of heating zone. A given weight was applied at one end of the carbon fiber bundle stretched out to the tube furnace and the other end was fixed as shown in Figure 9. The load applied to the individual fiber was calculated by dividing the total load by the number of fibers.

Three temperatures were selected on the basis of the exothermic peaks of the DSC curve, i.e., onset temperature of 190 °C of the first exothermic peak and two other temperatures at 259 °C and 300 °C of the two exothermic peaks. On the basis of the DSC plots, the temperature profiles of stabilization process were set with 3 programs (Figure 10).

All of stabilized fibers were carbonized up to 800 °C holding for 60 minutes in a furnace under nitrogen atmosphere with zero tension.

Analysis. Samples for DSC experiments were heated up to 400 °C under air or nitrogen atmosphere at a heating rate of 2 °C/min. The tensile tests of the samples were performed with a single filament using a universal testing machine (Instron 5565) with a load cell of 2.5 N, a gauge length of 20 mm and a strain rate of 1 mm/min. The tensile values were averaged from the 25 tests of the samples for the reliability of the data obtained. The specimen was prepared by fixing a single fiber on a paper frame,⁸ and the average value was obtained from 25 specimens. In order to calculate the tensile strength of the fibers, the mean monofilament cross-section area was determined by SEM.

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