Macromolecular Research, Vol. 23, No. 1, pp 79-85 (2015)
DOI 10.1007/s13233-015-3007-3

www.springer.com/13233
pISSN 1598-5032 eISSN 2092-7673

Study on the Stabilization of Isotropic Pitch Based Fibers

Jiadeng Zhu[1,2], Sang Wook Park[3], Han-Ik Joh[1], Hwan Chul Kim[2], and Sungho Lee*[,1,4]

[1]Carbon Convergence Materials Research Center, Korea Institute of Science and Technology,
San 101 Eunha-ri, Bongdong-eup, Wanju-gun, Jeonbuk 565-905, Korea
[2]Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonbuk 561-756, Korea
[3]Chemical and Polymer Lab, GS Caltex R&D Center, 104-4 Munji-dong, Yusung-gu, Daejeon 305-380, Korea
[4] Department of Nano Material Engineering, Korea University of Science and Technology,
217 Gajeong-ro, Yuseong-gu, Daejeon 305-350, Korea

Received July 10, 2014; Revised August 29, 2014; Accepted September 28, 2014

Abstract: Evolution of chemical structure and out gases of isotropic pitch fibers were studied in terms of stabilization. As stabilization plays an important role in the mechanical properties of carbon fibers (CF), thermogravimetric analysis was performed to optimize the duration and temperature of stabilization in this study. Fourier transform-infrared spectroscopy was applied to investigate chemical structure and formation of O_2 containing functional groups during the stabilization. In addition, mass spectrometry showed that O_2 uptake started at around 150 °C along with formation of various gases such as CO, CO_2, and H_2O. The longer stabilization resulted in higher tensile strength of the pitch fiber with higher strain-to-failure due to intermolecular crosslinking reactions leading to a network formation of pitch molecules. The stabilized fibers were carbonized at 1500 °C in a furnace under nitrogen atmosphere. Maximum tensile strengths of ~900 MPa were obtained from CF stabilized for 60 min at 280 °C.

Keywords: isotropic pitch, mass spectroscopy, TGA, infrared spectroscopy, mechanical properties, carbon fiber.

Introduction

Carbon fibers (CF) have attained a great attention in various applications such as sporting goods, aircraft, aerospace, wind energy, as well as the automotive industry because of their unique properties, such as high modulus, dimensional stability, excellent thermal and electrical conductivities.[1] Union Carbide in 1964 had started to manufacture the rayon-based CFs, Thornel 25, with tensile strength and modulus of 1.25 and 170 GPa, respectively. Polyacrylonitrile (PAN) and pitch-based CFs also have been produced in Japan and US in 1970's.[1] In 1965, Otani reported a general purpose pitch-based CFs using pyrolyzed polyvinylchloride.[2] Nowadays, coal tar and petroleum residue oil are used for preparing pitches. Two kinds of pitches as precursors have been used for preparing CFs: isotropic and mesophase pitches. Isotropic pitches cannot be converted into a high performance CF whereas it can be derived from mesophase pitch fibers which have a highly oriented molecular orientation in melt spinning due to their liquid crystalline characteristics. Preparation of mesophase pitches requires special and complicated processes such as polymerization of aromatic hydrocarbons using aluminum chloride as a catalyst,[3] supercritical fluid extraction of petroleum pitch,[4] and high temperature centrifugation.[5] The processes require a high manufacturing cost of mesophase pitches, which is the limitation for mass production of high performance CFs. Therefore, isotropic pitch based CFs are attractive due to a reasonable manufacturing cost even though moderate properties are expected.[6]

Pitch based CFs experience melt-spun, stabilization, and carbonization (or graphitization) steps, and it is well known that the stabilization and the carbonization are thermal treatment processes which determine properties of resulting CFs.[7-11] The thermal stabilization of as-spun pitch fibers is firstly conducted in air atmosphere to have them suitable for subsequent carbonization. During the stabilization, an oxygen bridge structure is formed *via* various reactions: oxidation, dehydrogenation, crosslinking and cyclization releasing gases such as H_2O, CO, and CO_2.[1,12] An isotropic pitch has the properties responsible for long duration of stabilization: lower degree of condensation, high hydrogen content and a lower softening point. Systematic analysis on gases released during stabilization is necessary because the type and the amount of gases can be an important evidence to verify the chemical reaction involved. Furthermore, these provide details of process temperature and residence time for optimizing manufacturing conditions because gas removal is one of the factors responsible for structural and textural development of fibers, which contribute to mechanical

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*Corresponding Author. E-mail: sunghol@kist.re.kr

properties of resulting carbon fibers. Miura *et al.* reported that oxygen up-taken during stabilization played a role in crosslinking of pitch fibers with the formation of -CH_2OH, =C=O, or -CH_2-O- when H_2O,CO, and CO_2 were produced as by-products.[12] In this work, Fourier transform-infrared spectroscopy (FTIR) and *in situ* mass spectrometer were used to observe an evolution of chemical structure and released gases in stabilization of isotropic pitch fibers, respectively. In addition, tensile properties were measured to investigate the relationship between the degree of stabilization and mechanical performance. The resulting stabilized fibers were carbonized and tensile properties of CF were determined by a single filament test.

Experimental

Materials. Pitch was synthesized using naphtha cracking bottom oil by following procedures; bromination, debrominated condensation, thermal treatment, and distillation, which is known as halogen derived polymerization.[13] The softening point was measured using the Mettler Toledo FP-83 and FP-90 universal controller according to ASTM D3104-99. The synthesized pitch showed the softening point of 276 °C. For preparing pitch fibers, the resulting pitch was loaded in barrel at 300 to 310 °C, and melt-spun by nitrogen pressure of 5 bar through spinneret with diameter of 500 μm. The winder speed was 300 rpm.

Oxidation and Carbonization of the As-Spun Fibers. For stabilization, as-spun fibers were placed in a convection oven under air atmosphere. Temperature was increased with a rate of 5 °C/min to 280 °C and held at 280 °C for 10-120 min. The stabilized fibers were taken out from the oven as soon as it reached to a certain stabilized time and naturally cooled down to room temperature. After stabilization, the fibers were carbonized at 1500 °C with a heating rate of 5 °C/min under nitrogen atmosphere in a furnace.

Characterization. The weight change during the stabilization was measured by a thermogravimetric analyzer (TGA Q50, TA instruments, USA) with a heating rate of 5 °C/min to 280 °C in air atmosphere. After reaching 280 °C, samples were held for 10 h. The weight of sample used for each test was ~10 mg.

FTIR Spectroscopy (Nicolet IS10, USA) was performed to investigate the change of the oxygen functional groups through the stabilization using the KBr pellet technique. The mixed pellet was prepared with 400 mg of spectrometric grade KBr and 2 mg of sample. The mixture of the sample and the salt was crushed using a pestle and a mortar. The mixture powder was placed in a KBr die kit and pressed with a hydraulic laboratory press. Each sample was scanned 16 times at a resolution of 16 cm^{-1} with a range of 4000-400 cm^{-1}. All spectra were collected in the absorbance mode with an automatic baseline correction and then transferred to transmittance.

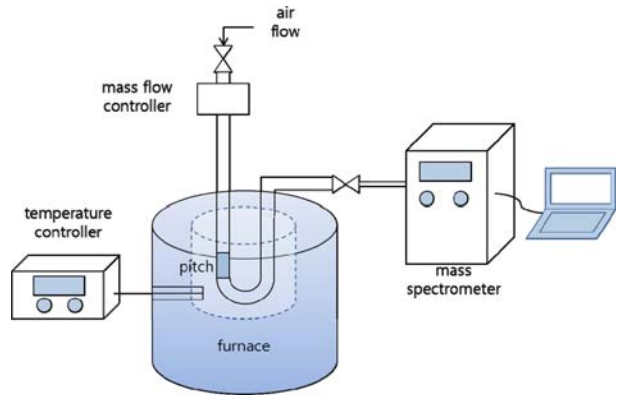

Figure 1. A scheme for *in situ* mass spectroscopy experimental set-up.

Mass spectrometer system (Hiden Analytical HPR-20, UK), shown in Figure 1, was used for *in situ* analysis of the product gas during the stabilization. Crushed fibers of 500 mg were loaded in a vertical type quartz reactor. A mixture gas of N_2 and O_2 (4:1) flowed into the reactor at 100 sccm regulated by the mass flow controller. The reactor with samples was heated at a rate of 5 °C /min to 280 °C and held for 2 h to mimic stabilization condition in convection oven. The mass spectra were collected in the two modes: Faraday and multiple ion detection (MID) mode. First, all kinds of gaseous species were analyzed by the Faraday mode, which gives a high scan rate of mass-to-charge (m/z) numbers from 1 to 100. On the basis of the Faraday result, detected m/z numbers of 12, 16, 17, 18, 32, and 44 were selectively measured in the MID mode. Before the measurement, N_2 and O_2 flowing test without samples was carried out to eliminate the delay of the gas analysis in profile mode. Pure N_2 went through a mass spectrometer and then a few minutes later pure O_2 started to flow. The time difference between pressure decrement point of N_2 and the appearance of O_2 peak was obtained. The delay time was used to calibrate the mass spectroscopy analysis.

The mechanical properties of stabilized and carbonized fibers were examined by a universal tensile machine (Instron Universal Tester 5567, USA) with a cross head speed of 2 mm/min. The length of the specimen was 2.5 cm and the diameter of each specimen was measured by optical microscope (Olympus BX51, Germany). At least 30 specimens were prepared for each tensile test and the average value was reported in this work.

Field-emission scanning electron microcopy (FE-SEM, Hitachi S-4700) with an acceleration voltage of 10 kV was used to observe the morphology of cross-sections.

Results and Discussion

TGA Analysis. For thermogravimetric analysis (TGA), samples were heated at a rate of 5 °C/min to 280 °C, and held for 10 h in air atmosphere. In Figure 2, TGA thermogram showed

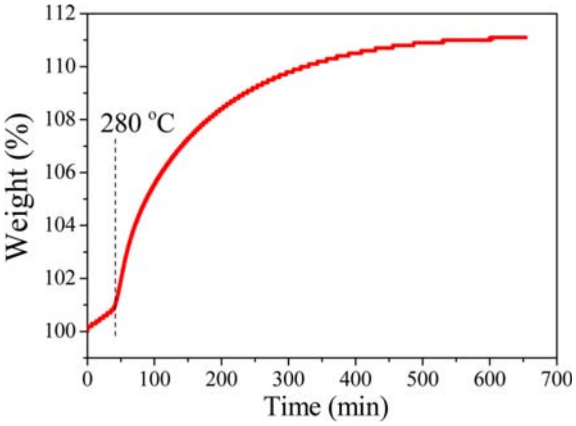

Figure 2. TGA thermograms of as-spun fibers at 280 °C under air.

less than 1 wt% of weight gain during non-isothermal thermal treatment, and a significant weight gain was observed in isothermal holding at 280 °C due to various chemical reaction. 2 h holding resulted in the weight gain of ~9% from O_2 up-take. After then, the monotonous weight gain up to ~11% was observed. From the TGA result, as-spun pitch fibers were stabilized for 2 h in maximum after non-isothermal heating for ~52 min from 20 to 280 °C to investigate gas evolution in a given stabilization and the effect of stabilization on tensile properties.

FTIR Analysis. The reaction of as-spun pitch fibers with oxygen at various stabilized times was investigated by FTIR. Figure 3 represents FTIR spectra of pitch fibers before and after stabilization in a convection oven. Note that it took ~52 min to reach 280 °C because the heating rate was 5 °C/min. Therefore, an assigned time in Figure 3 is an exposed time only at 280 °C. Pure isotropic pitch fibers showed distinct bands at 1439, 2918, and 3042 cm^{-1} which corresponds to the aliphatic C-H bending, aliphatic C-H stretch, and aromatic C-H stretch, respectively.[14,15] The bands in the region 900-700 cm^{-1} are generally ascribed to the out of plane C-H and ring bends,[14,15] which indicates hydrocarbon and oxygen-containing functional groups in pitch fibers. With stabilized fibers for 10 min, a decrease of these absorption bands was observed, indicating a chemical structural evolution due to the evaporation of gases such as CO, CO_2, and H_2O during the stabilization.[12] In addition, two bands appeared at 1190 and 1702 cm^{-1}, attributed to various C-O-C and O-C-O stretches and carbonyl C=O stretching, respectively, resulting from the formation of ketones, carboxylates, and carbonates due to oxygen up-take.[15] It should be noted that as-spun pitch fibers were stabilized when they were exposed not only at 280 °C for 10 min but also in heating from room temperature to 280 °C for ~52 min. As expected, intensities of hydrogen related bands decreased while those of newly appeared bands in stabilization significantly increased with increasing stabilization time up to 2 h.

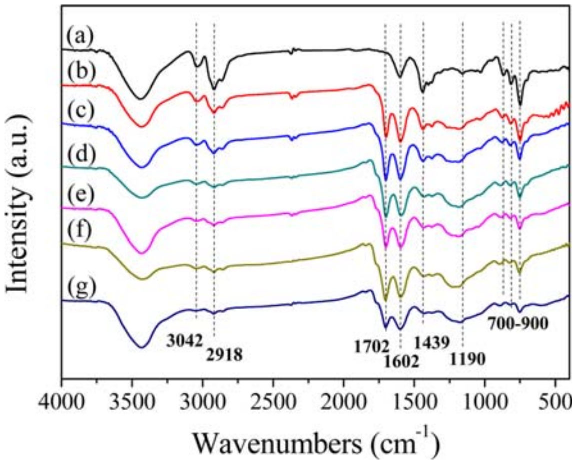

Figure 3. FTIR spectra of (a) as-spun fibers and their stabilized fibers at 280 °C for (b) 10, (c) 20, (d) 30, (e) 60, (f) 90, and (g) 120 min, respectively.

Mass Spectroscopy in Stabilization. Figure 4(a) exhibited *in situ* mass spectrum in Faraday and MID mode when as-spun pitch fibers were stabilized at 280 °C, and it was evident that H_2O, CO, and CO_2 were produced during the

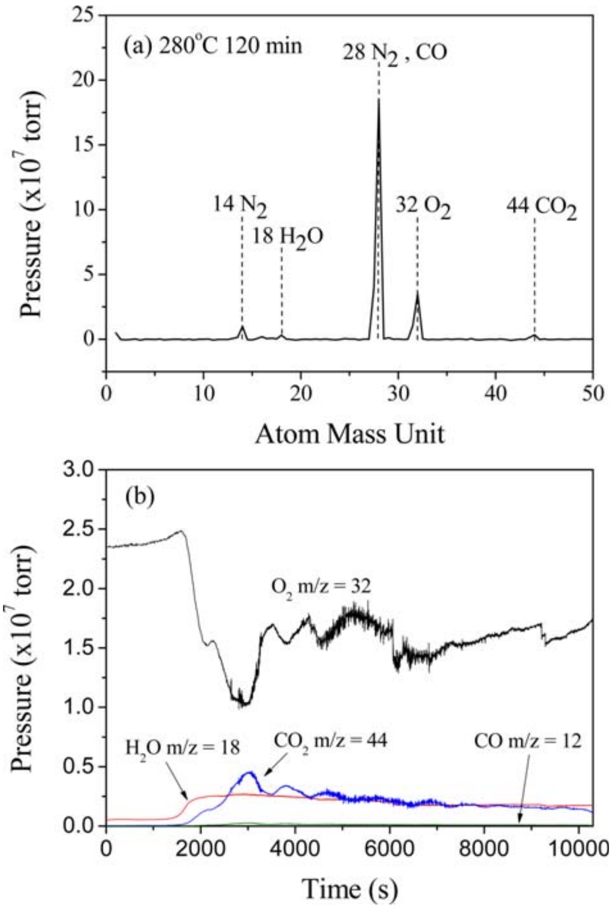

Figure 4. Mass spectra of gases generated during stabilization of pitch fibers (a) in Faraday and (b) MID mode. Samples were heated at a rate of 5 °C/min to 280 °C and held for 120 min.

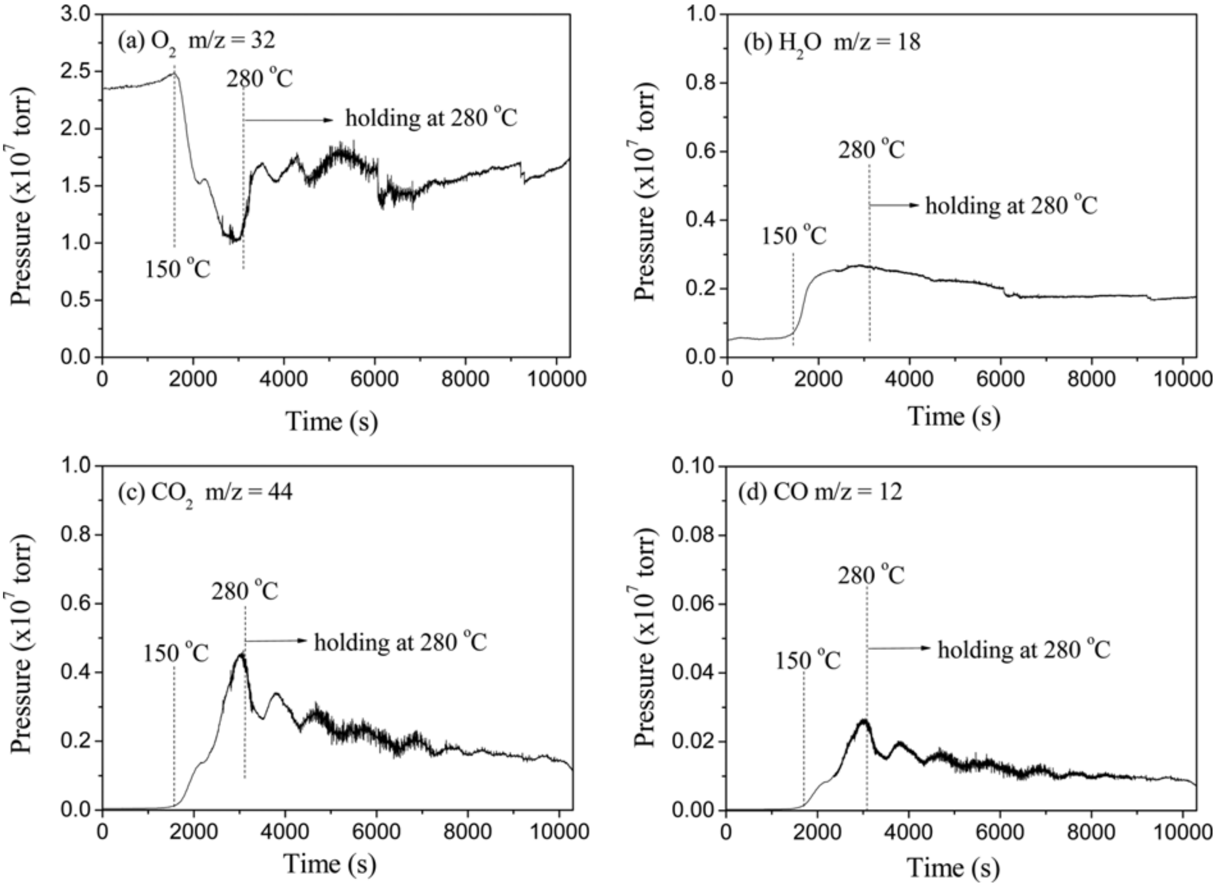

Figure 5. Detail mass spectra for pressure changes of out gases during stabilization of pitch fibers in MID mode: (a) O_2, (b) H_2O, (c) CO_2, and (d) CO.

stabilization. The m/z number of 28 exhibited a sharp peak compared to other peaks because the primary m/z number of CO is identical with N_2. Therefore, m/z number of 12 as a cracking number was analyzed in the MID mode in order to detect the produced CO. It should be noted that an intensity of the cracking number (m/z=12) is only 5% of the intensity of the primary number (m/z=28), resulting in the very low intensity of CO as shown in Figure 4(b). Figure 5(a)-(d) show detail pressure changes of out gases such as O_2, H_2O, CO_2, and CO, respectively, in MID mode. It is recalled that non-isothermal treatment was applied to as-spun pitch fibers until ~3120 s (~52 min), and then temperature was held at 280 °C. From Figure 5(a), after a small increase, a significant pressure drop of O_2 started at 150 °C, indicating O_2 up-take of as-spun pitch fibers. The decrease of O_2 continued from 2.5×10^{-7} down to 1.0×10^{-7} torr when temperature reached at 280 °C, which is the fact that isothermal treatment started. After then, a sudden increase of O_2 pressure back to half of initial level was observed. Till the end of experiment, O_2 pressure level was maintained between 1.3×10^{-7} torr to 1.8×10^{-7} torr. In Figure 5(b), a dramatic increase of H_2O pressure from 5.0×10^{-9} down to 2.5×10^{-8} torr was observed from 150 to 230 °C, and the pressure slowly reached to the maximum at 280 °C. In isothermal period, a gradual decrease was observed. It is suggested that H_2O is the first gas produced from as-spun pitch fibers at 150 °C, indicating that in an early stage, oxygen atom in H_2O is from O_2 up-taking atmosphere. CO_2 and CO gases started being produced at 160 °C, and maximum values, 4.5×10^{-8} and 2.7×10^{-9} torr for CO_2 and CO, respectively, were observed at 280 °C. After then, gradual decreases of pressure were observed. The amounts of the produced CO may be similar to those of the CO_2 because the detected pressure of the CO with m/z number of 12 is very low as described in Figure 4(b). The up-taking O_2 plays a role in cross-linking as a part of stabilization as well as, reducing yield of CF after carbonization. It is recalled that a continuous weight gain observed from TGA after 2 h holding at 280 °C indicates that O_2 uptake rate is higher than decomposition rate of pitch as formation of H_2O, CO_2, and CO in a given condition.

Tensile Properties of Stabilized and Carbonized Fibers. Tensile properties of as-spun pitch and its stabilized fibers were measured by a single filament test in Figure 6. A diameter of as-spun pitch fibers was ~27 μm, and small increase was

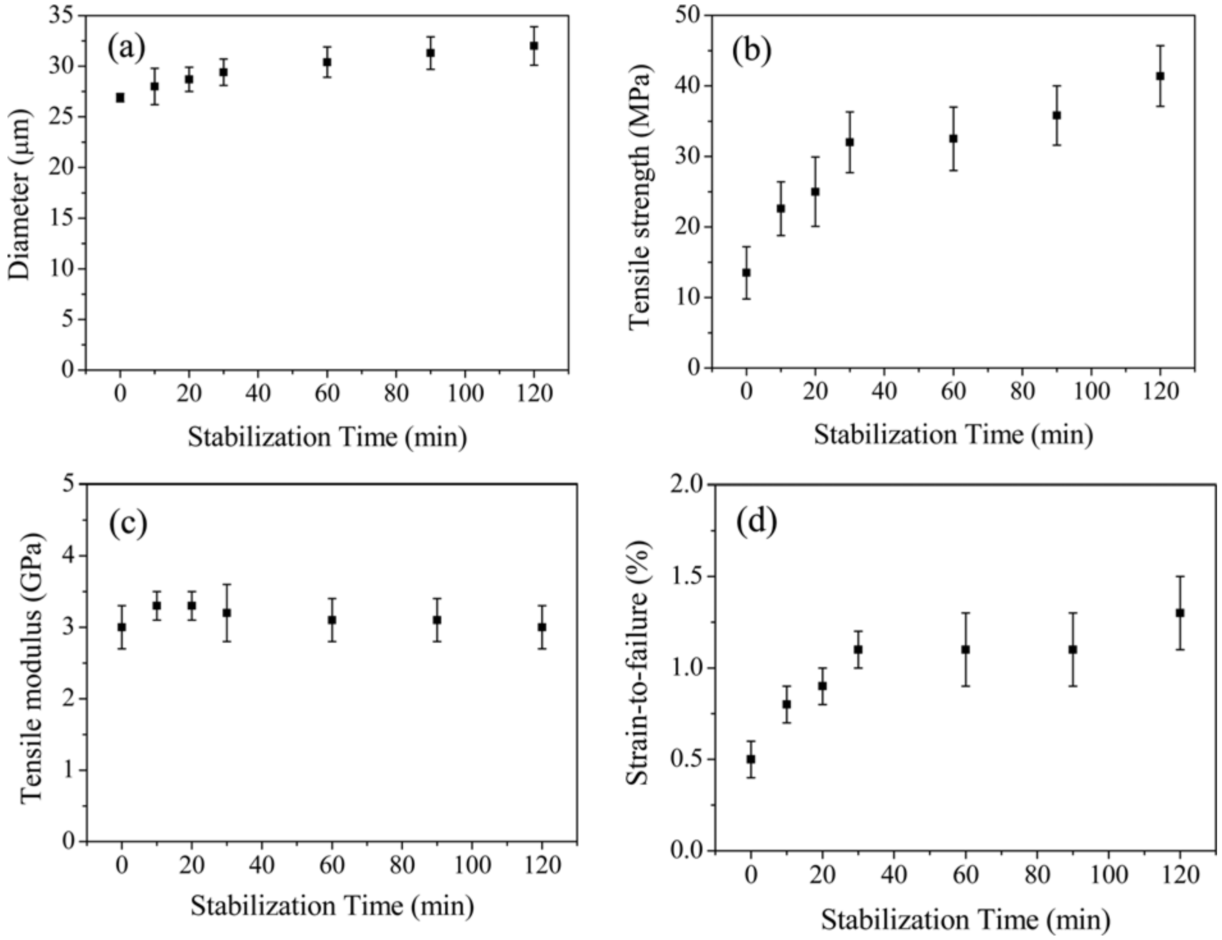

Figure 6. Tensile properties of as-spun fibers and their stabilized fibers as a function of stabilization time at 280 ºC: (a) diameter, (b) tensile strength, (c) tensile modulus, and (d) strain-to-failure.

observed with stabilized fibers for 30 min to ~29 μm. A further stabilization led to an increase of diameters to ~31 μm. Tensile strength of as-spun pitch fibers was ~14 MPa (Figure 6(b)). Stabilized pitch fibers for up to 30 min showed an increase of tensile strength, indicating that non-isothermal treatment by a heating rate of 5 ºC/min and relatively short exposure time at 280 ºC led to enough stabilization for increasing tensile strength of pitch fibers (Figure 6(b)). Stabilization time for 30 min resulted in a significant increase of tensile strength to ~32 MPa, and a further increase of stabilization time up to 90 min showed a similar tensile strength. The maximum tensile strength of ~40 MPa was observed with stabilized fibers for 120 min. The most significant reaction in stabilization is oxidation. Initially, oxidation occurs on the surface of the fibers to form conjugated carbonyls, and oxygen diffuses into the pitch fibers, leading to crosslinking of aromatic compounds and increase of average molecular weight.[16] It is noted that pitch has low average molecular weight with a broad distribution observed by MALDI-TOF mass spectrometer.[17,18] Therefore, the stabilized fibers showed the higher tensile strength than as-spun pitch fibers, and the longer stabilization resulted in the higher tensile strength.

There was no significant change in tensile moduli shown for as-spun pitch and its stabilized fibers in Figure 6(c). Strain-to-failure of as-spun pitch was ~0.5%. Stabilized fibers for 30 and 120 min revealed strain-to-failure of ~1.1% and 1.3%, respectively, which is significant increase compared to as-spun pitch fibers (Figure 6(d)). Interestingly, tensile strength and strain-to-failure showed a similar increase with increasing stabilization time, suggesting that these result from structural change in stabilization because strain-to-failure is attributed to intermolecular crosslinking reactions to lead to a network formation of pitch molecules. This crosslinking helps the fibers maintain the shape, so they are able to be carbonized in the following process without inter-filament fusing. Figure 7 showed radial cross-sections of the as-spun and stabilized fibers for 10 to 120 min. As stabilization time increased, the diameter of fibers increased, but a significant morphological change was not observed.

Stabilized fibers were carbonized at 1500 ºC with a heating rate of 5 °C/min under nitrogen atmosphere. Figure 8 exhibited tensile properties of resulting CFs as a function of

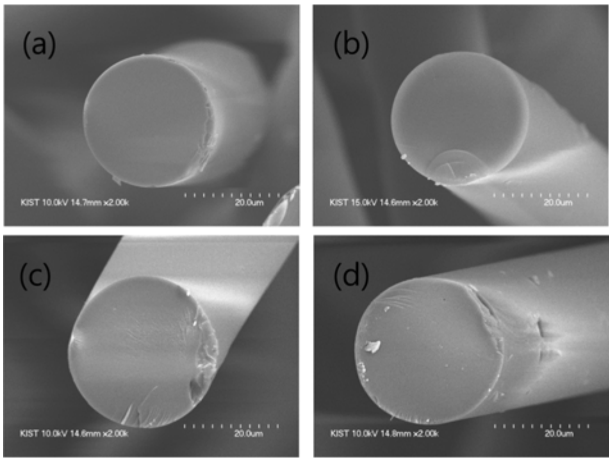

Figure 7. SEM images of (a) as-spun and stabilized fibers for (b) 10 min, (c) 60 min, and (d) 120 min.

stabilization time. A diameter of CF stabilized for 10 min was ~25 μm, but CF stabilized for 30 min showed a significant decrease (~19 μm) compared to stabilized fibers. Diameters increased with increasing stabilization time from 30 to 120 min, and CF stabilized for 120 min revealed a diameter of ~27 μm. It is recalled that diameters of stabilized fibers was similarly dependent on stabilization time. Even though carbonization resulted in the significant increase of tensile strength of stabilized fibers, values were found to be 480-740 MPa, which are lower than those of PAN based CFs, but comparable to isotropic pitch based CF reported by Mochida *et al*.[7] It is interesting that maximum strength as ~900 MPa was obtained from CF stabilized for 60 min, and a longer stabilization decreased strength, suggesting that optimal stabilization time existed in a given stabilization condition. Tensile modulus and strain-to failure values ranged from 35 to 37 GPa and from 2.0% to 2.3%, respectively, with similar trend to tensile strength as a function of stabilization time.

Conclusions

Isotropic pitches from naphtha cracking bottom oil were melt-spun, stabilized and carbonized for preparing CFs. Thermogravimetric analysis of spun fibers showed a weight gain of ~9.0% after non-isothermal heating for ~52 min from

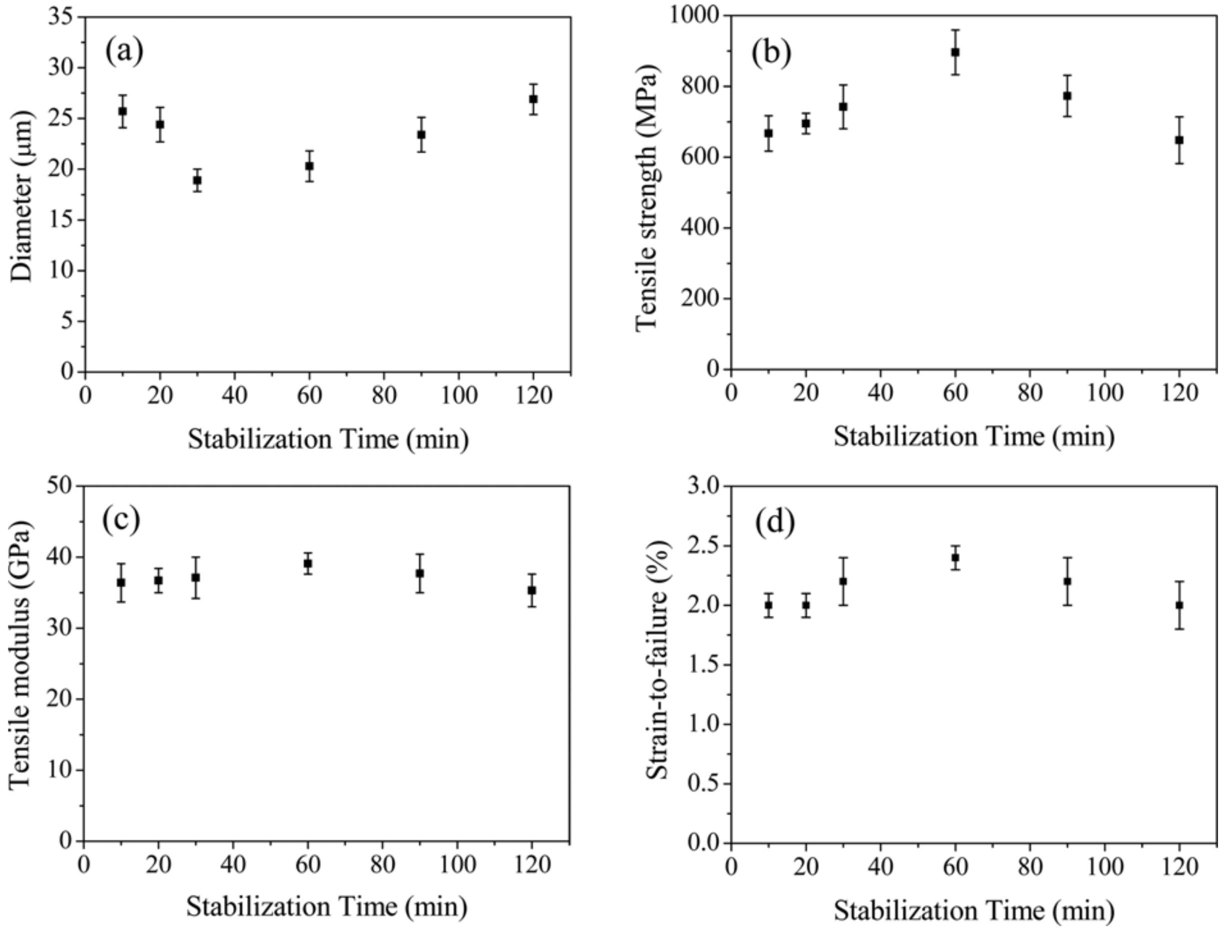

Figure 8. Tensile properties of carbonized fibers as a function of stabilization time at 280 ºC: (a) diameter, (b) tensile strength, (c) tensile modulus, and (d) strain-to-failure.

20 to 280 °C and subsequent holding for 120 min, resulting from O_2 uptake. Fourier transform-infrared spectroscopy revealed formation of oxygen-containing functional groups after non-isothermal heating. These became stronger with decreasing intensities of peaks related to original fibers such as aliphatic C-H bending, aliphatic C-H stretch, and aromatic C-H stretch. Mass spectrometry showed that O_2 uptake started at around 150 °C along with H_2O, but CO and CO_2 started being produced at 160 °C. A subsequent temperature holding at 280 °C led to an O_2 pressure back to half of initial level. The longer stabilization resulted in higher tensile strength of pitch fibers with a higher strain-to-failure, indicating intermolecular cross-linking reactions had lead to a network formation of pitch molecules. The stabilized fibers were carbonized at 1500 °C in a furnace under nitrogen atmosphere. Maximum tensile strength of ~900 MPa was obtained from CF stabilized for 60 min at 280 °C, and further stabilization caused a decrease in strength, suggesting that optimal stabilization time existed in a given stabilization condition.

Acknowledgments. This work was supported by a grant from the Korea Institute of Science and Technology Institutional program and the Carbon Valley project funded by the Ministry of Knowledge Economy, Republic of Korea.

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