

Study on the Relationship Between Evolved Gases in Carbonization of Stabilized Polyacrylonitrile Fibers with 12,000 Filaments and Their Mechanical Properties

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ABSTRACT

In this study, we proposed a carbonization mechanism of stabilized polyacrylonitrile (PAN) fibers with 12,000 strands (12 k) as a function of heating rates through the *in-situ* thermogravimetric analysis and mass spectroscopy during carbonization process. In order to simulate an actual manufacturing process of carbon fibers (CFs), stabilized fibers were carbonized at up to 1200 °C through heating rates of 20, 25, and 30 °C/min. We investigated the relationship between the rates and the structural and mechanical properties of the CFs analyzed by X-ray diffractometer and Raman spectroscopy. The high heating rate leads to higher decomposed temperature and carbonization yields of the stabilized fibers compared to the other rates. Therefore, it is believed that the structural and mechanical properties of the CFs could be improved by suitable removing uncyclized atoms under 500 °C and inducing intermolecular bonding between the stabilized PAN polymers above 1000 °C.

KEYWORDS: Polyacrylonitrile (PAN), Carbon Fiber, Mass Spectroscopy, Carbonization, Mechanical Properties.

1. INTRODUCTION

Carbon fibers (CFs) contain more than 90% of carbon atoms as a 1-dimensional fiber shape, which have higher specific tensile strength than steel fibers.^{1,2} In addition, low coefficient of thermal expansion, good wear resistance, and high thermal conductivity make them attractive reinforcements in composites as applying various industries such as sports goods, automobile, aerospace, and constructions.^{3–11} There are three well-known precursors for manufacturing CFs; rayon, pitch, and polyacrylonitrile (PAN). More than 90% of commercial CFs is PAN based

CFs because they show high tensile strength compared to CFs from other precursors.^{12,13}

PAN-based CFs are prepared by fiber spinning, stabilization, and carbonization. A dope with around 20% PAN in solvent is wet or dry-jet spun followed by stretching to increase the molecular orientation along the longitudinal direction, leading to higher tensile strength. PAN fibers are stabilized at 200–300 °C under air atmosphere, and chemical reactions such as cyclization, oxidation, and dehydrogenation take place, leading to conversion from linear to ladder structure. The stabilized fibers are infusible in carbonization, which is heat treatment up to 1500 °C under an inert gas.^{14,15} Various studies to analyze the evolved gases from the polymers using Mass spectroscopy have been reported.^{16–18} In carbonization, Fitzer et al., reported a rate of gas production of PAN fibers along temperature

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Received: 14 April 2017

Accepted: 22 June 2017

up to 1000 °C, and various gases such as NH₃, HCN, H₂O, CH₄, CO, and CO₂ are evolved and removed.¹⁹ It is well known that these result in closed micro pores in CFs, which affect the tensile properties.²⁰ Therefore, systematic studies to correlate gas evolution with the tensile properties of CFs are of importance to optimize the carbonization process. However, previous studies reported the evolved gases during carbonization up to 1000 °C even though commercial CFs were manufactured at above 1000 °C.^{19,21} In addition, CFs for mass spectroscopy were mismatched with the CFs for mechanical analysis. In this study, types and amount of gases in the carbonization of stabilized fibers were investigated by *in-situ* mass spectroscopy in a tailor made reactor, where fibers with a middle tow size (12,000 strands) can be loaded. The effect of heating rate on the gas evolution was observed and the tensile properties of the resulting CFs were measured.

2. EXPERIMENTAL DETAILS

CFs were prepared using commercialized PAN polymeric fibers with 12,000 (12 k) filaments (LanZhou Bluestar Fiber Co. Ltd., China). The polymeric fibers were stabilized in an air atmosphere at a heating rate of 5 °C/min to the 230 °C. Holding time at 200, 210, and 220 °C is 10 min, and the fibers held at 230 °C for 4 hr. The stabilized fibers were carbonized using a thermogravimetric analyzer (TGA) in Ar atmosphere at various heating rates, which were 20, 25, and 30 °C/min to mimic an actual process for carbonization, to 1200 °C. As shown in Figure 1, the mass to charge ratio (m/z) of the evolved gases during carbonization were detected using mass spectroscopy (HPR-20 QIC, HIDEN, United Kingdom). In order to precisely analyze, we used a secondary electron multiplier (under 10⁻⁷ torr) and a Faraday (above 10⁻⁷ torr) detector as a function of gas pressure.

The density of the prepared CFs was measured using a density gradient column (Ray-Ran TEST EQUIPMENT Ltd., United Kingdom). Averaged values with 4 time measurements of each CF were reported. Tensile strength and

modulus of a single filament for 30 filaments prepared under same conditions were obtained using a FAVIMAT⁺ (Textecno, Germany). A cross-section and diameter of the CFs were observed by scanning electron microscope (SEM) under 8,000× magnification. Crystalline properties of the CFs were analyzed using Raman spectroscopy (Horiba, LabRAM HR, France) and X-ray diffractometer (Rigaku, Smart Lab, Japan).

3. RESULTS AND DISCUSSION

3.1. *In-Situ* TGA-Mass Spectroscopy Analysis for Evolved Gases During High Temperature Carbonization

Figure 2 shows the weight losses of the stabilized PAN fibers during the carbonization process as a function of heating rates. As the rates increase, starting temperature to reduce the weight and carbonization yields also increase. The yield of the fibers carbonized at a rate of 30 °C/min exhibits approximately 57.3%, which is the best char yields among the other carbonization conditions. Therefore, it is believed that a rapid heating and short-term carbonization in an actual process could affect an increase of the yield.

In order to the investigate critical factors for the different yields as a function of the rates, we analyzed evolved gases derived from the decomposition of the stabilized PAN fibers using *in-situ* mass spectroscopy as shown in Figure 3. There are seven kinds of gases such as H₂O, CO, CO₂, NH₃, CH₄, HCN, and N₂. All gases were evolved at high temperature as the rate increased similar to the TGA results. A water vapor ($m/z = 18$), which was produced through a reaction of oxygen and hydrogen bonded to the PAN backbone, is the largest amount among the gases. The vapor evolved at around 200 °C might be produced from hydroxyl groups, which was generated in the stabilization process.²² Secondary ionization peaks related to the vapor, which have 80% intensity versus the first ionization peak ($m/z = 18$), were observed in $m/z = 17$ molecules at a similar temperature.²³ Oxygen functional groups produced during stabilization process reacted with

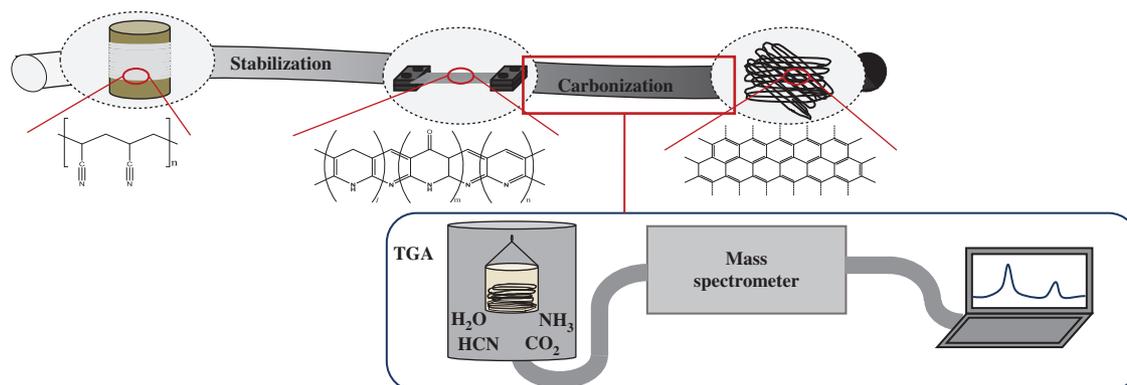


Fig. 1. A scheme of the *in-situ* TGA-mass spectroscopy.

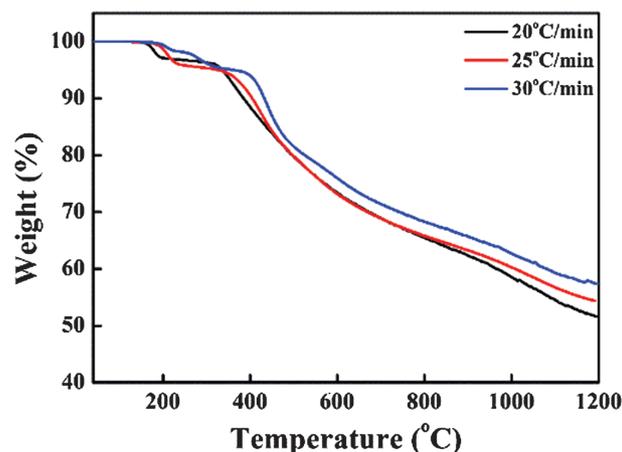


Fig. 2. Weight losses of stabilized PAN fiber during carbonization as a function of heating rates from 20 to 30 °C/min.

carbon atoms in the PAN at 230 °C, leading to weak and strong production of CO ($m/z = 12$) and CO₂ ($m/z = 44$) as shown in Figures 3(b) and (c), respectively. Ammonia ($m/z = 17$) derived from the termination of the chain reaction between the stabilized PAN polymer chains was produced at around 370–420 °C.²⁴ Methane ($m/z = 16$) was

mainly generated at around 400 °C due to the dehydrogenation reaction during the carbonization process. Hydrogen cyanide ($m/z = 27$) was generated at relatively low (250–400 °C) and high temperature (~950 °C). Similar to hydrogen cyanide, nitrogen ($m/z = 28$) was also generated at low and high temperature. Interestingly, nitrogen was mainly evolved at the range from 900 to 1200 °C.

We proposed three reaction steps, when stabilized PAN fibers were changed into the carbon fiber, on the basis of weight losses and mass spectra. The first is the decomposition of uncyclized molecules. Stabilized PAN fibers always have uncyclized molecules due to the steric hindrance and heterogeneity between the PAN chains.²⁵ The uncyclized molecules with no stable bonding could be easily decomposed at relatively low temperature (200–300 °C) even though carbonization was performed in an inert atmosphere. It is observed that a weight loss derived from decomposition of uncyclized molecules could be approximately 10% in this study.

The second step is the generation of gases due to intra-molecular bonding in the PAN chains. The reaction induced the generation of NH₃, CH₄, HCN and N₂ molecules at similar temperature for the decomposition of uncyclized molecules. Three molecules in the former

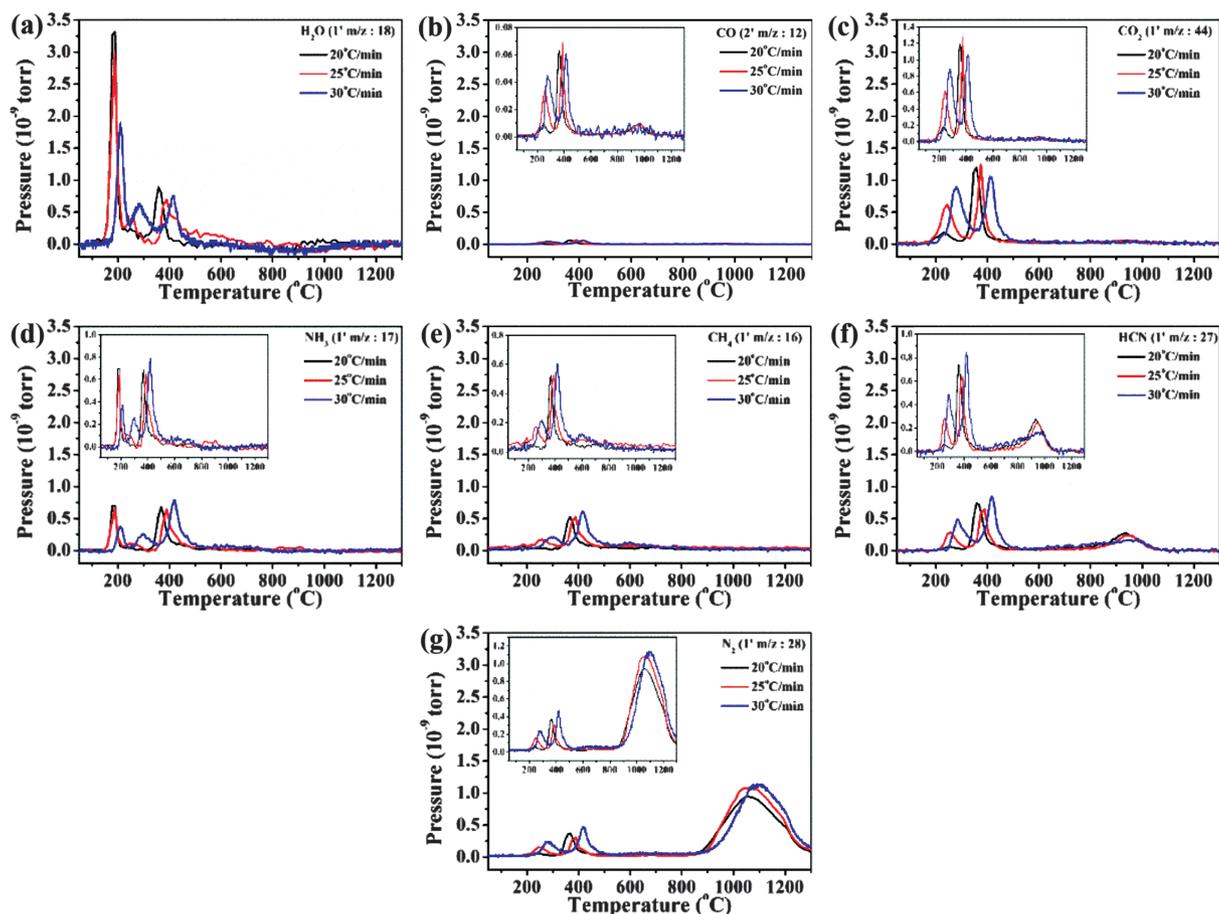


Fig. 3. Mass spectra of the evolved gases during carbonization: (a) H₂O, (b) CO, (c) CO₂, (d) NH₃, (e) CH₄, (f) HCN and (g) N₂.

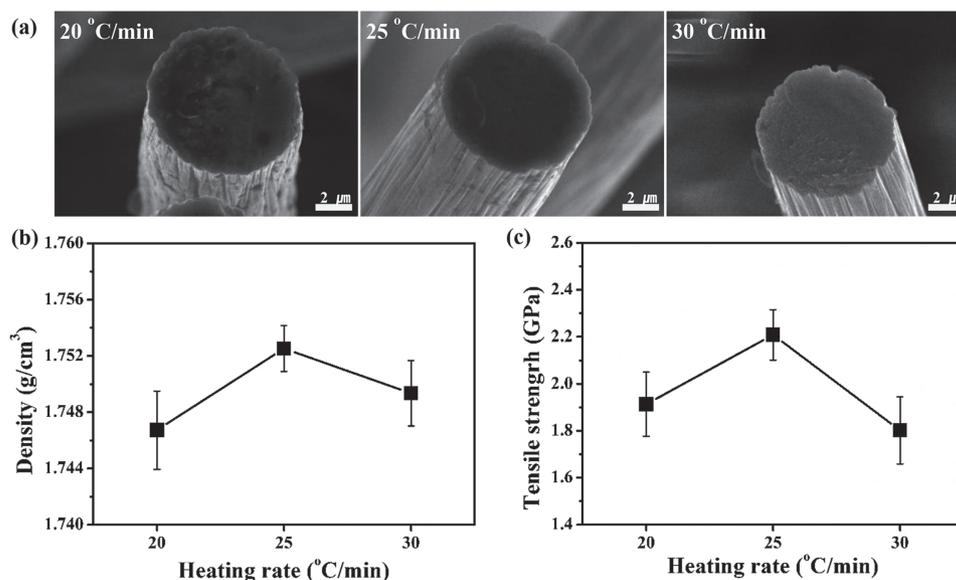


Fig. 4. Morphology and physical properties of carbonized fibers at various heating rates: (a) SEM images, (b) density and (c) tensile strength.

arose from the dehydrogenation reaction of cross-linking between heterocyclic rings.²⁶ The generation of N_2 at relatively low temperature was related to the intra-bonding formation between $C=N$ and neighbored $C=N$.²⁴ Therefore, this step induced intra-molecular bonding of PAN chains, leading to an increase of the densification of the carbonized intermediates.

In the final step, the inter-molecular bonding results in generating gases. Goodhew et al. reported that HCN and N_2 gases were evolved when PAN fibers were carbonized at high temperature due to the inter-molecular bonding between PAN chains.²⁷ On the basis of the mass spectra, it is easily confirmed that the generated amount of N_2 was five times higher than that of HCN. In addition, evolution of N_2 molecules was maximized at the temperature range from 1000 to 1100 °C, while HCN was mainly generated at 950 °C. Therefore, it is believed that inter-molecular bonding could be induced by an elimination of nitrogen atoms in the PAN through the formation of N_2 gas at a

high temperature above 1000 °C, leading to the realization of mechanical and chemical properties of CFs.²⁸

3.2. Tensile Strength and Structural Analysis for CFs Prepared Using *In-Situ* TGA-Mass Spectroscopy System

The diameter, density, and tensile strength of CFs prepared as a function of heating rates were measured in order to confirm the mechanical properties of the CFs. The CFs irrespective of the heating rates show circular shape with a diameter of approximately 8 μm as shown in Figure 4(a). Interestingly, the density of the CFs increased from 1.746 to 1.752 g/cm³ with a heating rate of 20 and 30 °C/min, respectively. It is known that T700-grade CFs, which have outstanding mechanical properties compared to T300-grade CFs, manufactured by Toray company shows 1.80 g/cm³, while T300-grade CFs is 1.76 g/cm³.^{29,30} The relatively high density of the CFs with high heating rate results in an increment of 400 MPa for tensile strength.

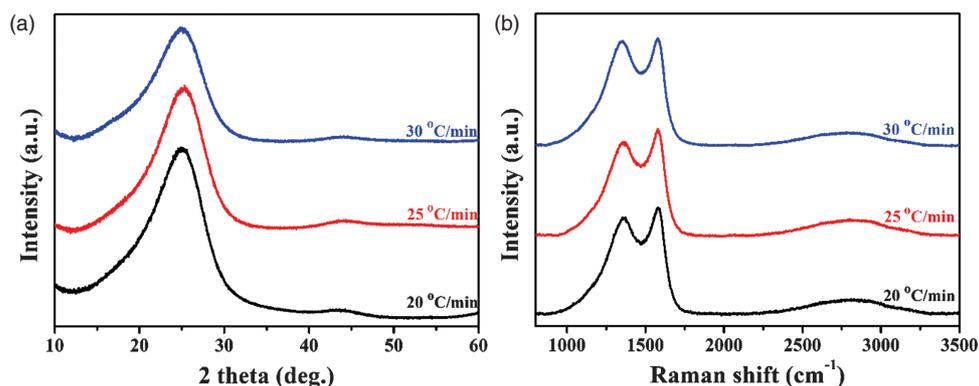


Fig. 5. (a) 1D XRD and (b) Raman spectra of carbon fibers as a function of heating rates.

Table I. Crystalline properties of carbon fibers.

Heating rate (°C/min)	20	25	30
L_c (nm)	1.073	1.304	1.221
d_{002} (nm)	0.357	0.351	0.356
L_a (nm)	3.401	3.894	3.677

$$d_{002} \text{ (nm)} = \frac{\lambda}{2 \sin \theta} \quad (1)$$

$$L_c \text{ (nm)} = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

$$L_a \text{ (nm)} = 4.4 \times \left(\frac{I_D}{I_G} \right)^{-1} \quad (3)$$

It is believed that high char yields suppressed the formation of pore and void in the CFs, leading to high densification.

The structural properties of CFs were analyzed by XRD and Raman spectroscopy as shown in Figure 5. The inter-layer spacing (d_{002}), crystallite height (L_c), and crystallite diameter (L_a) of the CFs as a function of the heating rates were calculated using the spectra and Eqs. (1)~(3) and summarized in Table I.^{31–34} The inter-layer spacing of the CFs is almost 0.35 nm irrespective of the rates because the final carbonization temperature is the same at 1200 °C. However, L_c and L_a of the CFs prepared under 20 °C/min heating rate were the lowest values compared to the other CFs. The amount of evolved N₂ gas at above 1000 °C was the lowest when the fibers were carbonized at a heating rate of 20 °C/min. This indicates that inter-molecular reactions occur relatively less than other conditions, leading to suppress the growth of crystalline. In the case of 30 °C/min, inter- and intra-molecular bonding reaction and an elimination of amorphous carbon simultaneously took place due to the rapid heating rates, leading to low-density differences because of bonding formation between crystalline and amorphous carbon. Therefore, CFs prepared under a heating rate of 25 °C/min, which induced the reactions of inter-molecular bonding and crystalline growth, showed outstanding mechanical and structural properties. It is believed that the carbonization rate and time are important factors to seriously affect the properties of CFs, even though the simulated system have some differences in an actual carbonization process in terms of tension, reactor size, and heating rates. In addition, the degree of elimination for the evolved gases also affects the properties of the CFs.

4. CONCLUSION

In this study, we investigated relationship between gases evolved at high temperature (~1200 °C) and the properties of CFs as a function of heating rates using middle tow PAN fibers (12 k) and tailor-made *in-situ* TGA-mass

spectroscopy system. The PAN fibers produced various kinds of gases due to the elimination of uncyclized atoms, intra-molecular bonding, and inter-molecular bonding during carbonization process. As the heating rate increased, the evolved temperature of the gases and the char yields also increased. In addition, a lower heating rate relatively suppress the inter-molecular reaction, while a higher rate induces simultaneous reactions for inter- and intra-molecular bonding and an elimination of amorphous carbon, leading to a decline of the mechanical properties of the CFs. Therefore, it could be concluded that carbonization rate and time to induce the reaction of inter-molecular bonding and crystalline growth are important factors to realize CFs with outstanding mechanical properties.

Acknowledgments: The authors acknowledge the financial supports of this work from the Korea Institute of Science and Technology, and the Industrial Core Technology Development Program and the Carbon Valley R&D Project (R0000689) funded by the Ministry of Trade, Industry and Energy, Republic of Korea.

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