

Preparation of Carbon Fiber from Melt Spinnable PAN Co-polymer

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Carbon fiber is prepared from various carbonizable precursors of polyacrylonitrile (PAN), pitch, rayon. The carbon fibers have very strong mechanical properties because of the bond strength of carbon atoms.^{1–5} Their properties are lower density of 20% than iron, 70% than aluminum, 10 times higher strength than steel. Carbon fiber is mainly used as a reinforced composite and functionality materials. The composite material has been widely used over the industries, such as break disk of an aircraft, the nose cone of space shuttle, sporting goods, blades of wind mill etc. Though the excellent properties of the carbon fiber reinforced composite (CFRP) give strong potential to be applied to automobile, building materials, concrete structures, wind power generation blades, high-speed vehicles, marine structures, the applications are very limited due to the high price of the carbon fiber.^{6–10} Currently, the price of carbon fiber is \$30/kg and it is good to be half of the price for automobile application.⁸ PAN fiber is used to be manufactured by wet spinning, dry spinning or dry-jet wet. The production method is costive due to the use of large amounts of environmentally undesirable solvents and relatively low spinning speed in comparison with melt spinning. One of the choices of reducing the production cost is to use melt spinning technology in production of the precursor fiber.^{9–11}

Microwave is a form of electromagnetic energy in a lower frequency range of 300–300000 MHz which causes only molecular rotation rather than breaking molecular bonds. In general, heating by thermal conduction is slow, energy consuming process, and difficult in controlling of the reaction due to the non-selectivity of the energy level. In contrast, microwave energy can heat material at selective energy by frictions from the molecular rotation and/or ionic conduction.^{10–13} Microwave synthesis have been

reported, such as zeolitic imidazolate framework (ZIF), NaY zeolites, subphthalocyanine (SubPc), Poly(ϵ -caprolactone), etc.^{14–17} On the basis of the discussions, the microwave heating would be cost effective process. However, the fiber from melt spinning normally shows difficulties in stabilization for carbonization due to the fusible property in the process of heat treatment for carbonization. Therefore oxidizing agent such as O₂, N₂O, CO₂, H₂O, KMnO₄, HNO₃, KClO₃ is applied to the melt spun fibers to get infusible fibers.^{18–22} In this study, melt spinnable polyacrylonitrile (PAN) copolymers were synthesized by using microwave energy, and the precursor fibers was chemically modified with KMnO₄ to provide the condition for easier stabilization process.

Fig. 1 shows the yield of the copolymer after microwave irradiation at various times. The yield was around 30% from the monomer composition of 90/10(AN/MA) in the presence of 0.1wt% initiator (AIBN) in 200% DMSO solvent to applied monomer in 30 min. It was recognized that 30 min is enough reaction time to maximize the prod-

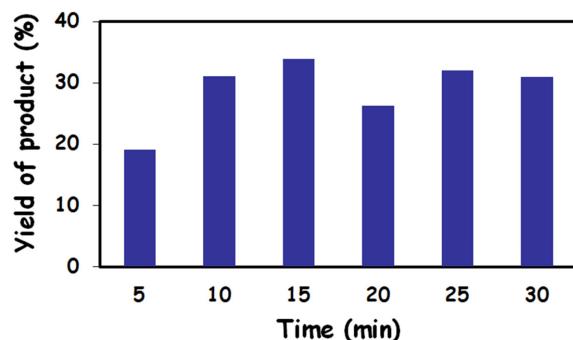


Fig. 1. Yields of AN90MA10(0.1)200% copolymer with various reaction time.

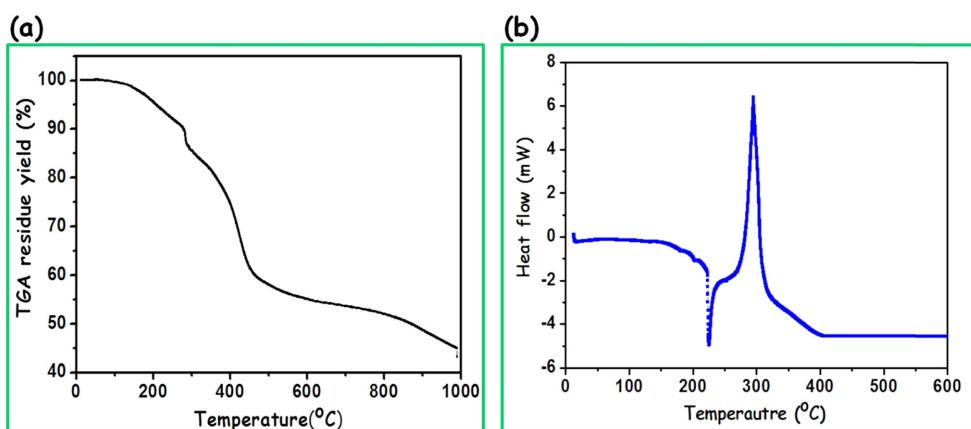


Fig. 2. Thermal properties of the AN90MA10(0.1)200% copolymer; (a) TGA and (b) DSC curve.

uct yield and get the melt spinnable PAN copolymers.

The thermal behaviors of AN90MA10(0.1)200% copolymer were analyzed by TGA and DSC under nitrogen atmosphere at a heating rate of 10 °C/min. TGA curve shows that the main mass loss from 280 to 450 °C, attributed to the pyrolysis of the fibers, is in agreement with the peak on the DSC curve of as-spun fibers. The loss slows down above 450 °C to give a yield of 52% at 800 °C. It appeared an endothermic melting peak at 220 °C and exothermic peak at 290 °C (*Fig. 2*).²³ Endothermic reaction is a melting point that copolymer is molten. In addition, exothermic reaction is temperature of dehydrogenation and cyclization reactions of the PAN. The actual maximum temperature was setup up to 190 °C in the melt spinning because AN90MA10(0.1)200% copolymer is molten at higher than the melting temperature.

The AN90MA10(0.1)200% copolymer were heated up to 190 °C at 5 °C/min in nitrogen atmosphere and hold for 30 min which is enough for fluidity. The spinning temperature for all runs was 190 °C, followed by stabilization and carbonization under nitrogen pressure. Pyrolysis is used for the conversion process from spun fibers into CFs. The chemistry of the stabilization process of PAN consists of cyclization, dehydrogenation, and crosslinking. As a result of the conversion of C≡N bonds to C=N bonds, a fully aromatic cyclized ladder type structure forms.^{24,25} Therefore, thermo-stabilization involves cyclization of the PAN component, enabling the spun fibers to be thermally stable (infusible) for the subsequent carbonization. A variety of physical changes take place during the thermo-stabilization process, which cause the initial changes in color of spun fibers from pale yellow to dark brown, as shown in *Fig. 3*.

The AN90MA10(0.1)200% copolymer synthesized by microwave energy is successfully melt spun. On the other

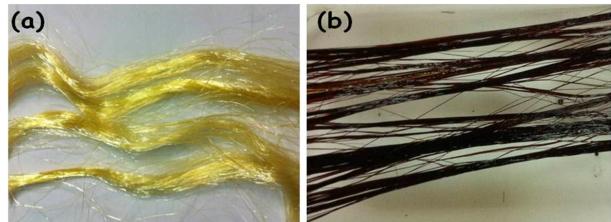


Fig. 3. Photographs of AN90MA10(0.1)200% copolymer based (a) melt-spun and (b) stabilized fiber.

hand, the fibers were stick together with brittle physical properties in the stabilizing process as shown in *Fig. 3(b)*. *Fig. 4* show the SEM images of the melt-spun, stabilized, and carbonized fibers obtained from PAN90MA10(0.1) 200% copolymer. The average diameter of the fibers was thick and decreases from 188 to 154 to 136 mm with increasing heat treatment by numerous evolution gasses during the pyrolysis, such as H₂O, NH₃, HCN, CO, CO₂, N₂, H₂, and CH₄.

Furthermore, the composition of AN/MA was varied by adding another component itaconic acid(IA) and increased the initiator concentration to 2 wt%, then resulted an increase of the PAN co-polymer yield of higher than 80% from the composition AN83/IA1/MA16(2)50%, as shown in *Fig. 5*. The IA addition gives advantages of reduction of onset temperature of stabilization and lowering heat of reaction avoiding the introduction of hot spots.^{26,27} The yield increase would be resulted from enhanced reactivity by more frequent collision at higher monomer concentration and reduced activation energy at higher initiator concentration.

As shown in *Fig. 6*, the diameter of AN83IA1MA16(2) 50% copolymer based melt-spun fiber was reduced average diameter to 90–100 μm with uniform and homoge-

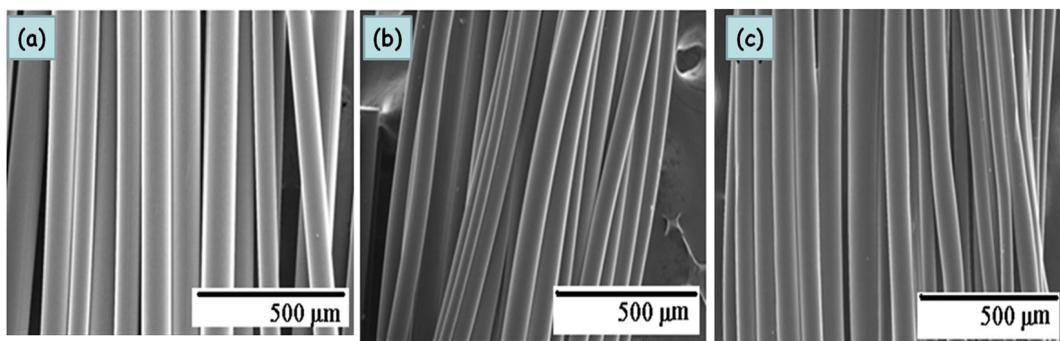


Fig. 4. SEM images of AN90MA10(0.1)200% copolymer based (a) melt-spun, (b) stabilized, and (c) carbonized fibers.

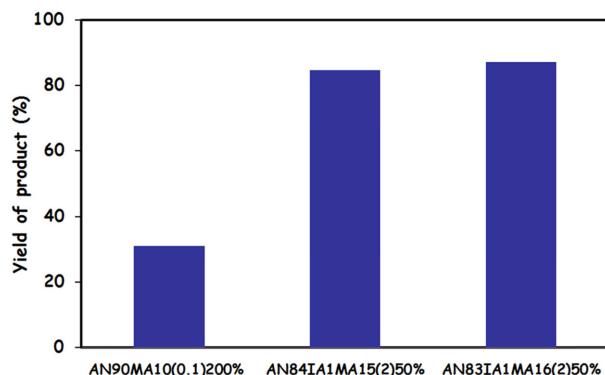


Fig. 5. The production yield of various copolymer.

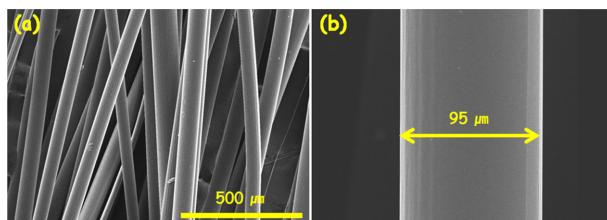


Fig. 6. SEM images of AN83IA1MA16(2)50% copolymer based melt-spun fiber at (a) low and (b) high magnification.

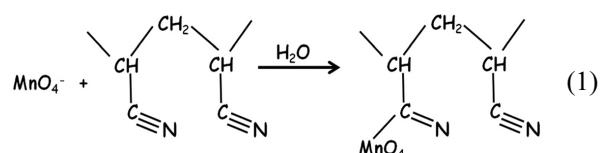
neous surface, compare with the AN90MA10(0.1)200% copolymer. The spinnability can be evaluated by the fiber diameter from spinning. Therefore, the spinnability was improved by increases in concentrations of MA and initiator, represented by the increase in the wind up speed to 60 mm min⁻¹.

However, AN83IA1MA16(2)50% copolymer based melt-spun fibers were also partially molten and fragile through the stabilization process. The precursor fibers were oxidized in aqueous KMnO₄ solution before stabilization to avoid the melt down of the spun at the stabilizing process. The wide-scan XPS spectra in Fig. 7a imply that the surface of unmodified and KMnO₄-modified AN83IA1MA16(2)50% copolymer based melt-spun fibers contain only the expected

three elements (e.g., C, O, N). The deconvolution of the O1s XPS spectra (Fig. 7b) revealed three Gaussian curves centered at 530.2, 532.1 and 533.5 eV, which can be assigned to COO-/O=CO and C-OH/O=C and O=C-OH/R-O-R, respectively.²⁸

Quantitative peak analyses were also carried out to determine the concentrations of the surface elements by XPS. It was found that the KMnO₄-modified melt-spun fiber has higher content in a spun fiber, as shown in Table 1. The carbon content of a modified melt-spun fiber have no great difference as compared to those in a unmodified melt-spun fiber, whereas the oxygen content increased from 10.42% in pristine to 24.08% in KMO₄ modified fiber. The higher oxygen content was involved in the functional groups of C=O, HO-C=O, etc. In particular, the C=O and COOH intensities increased significantly after the modification, compare with the C-OH group, as summarized in Table 1. It suggests that the oxygen functional groups increased on the melt-spun fiber surface by the KMnO₄ modification, then, the activated C-O and -OH groups by the KMnO₄ modification would be oxidized further to form ketone (C=O) and carboxylic acid groups (COOH).

We suppose that the dissociated K⁺ and MnO₄⁻ ion in water can diffuse into the fibers. The interaction between K⁺ and a fiber is mainly in the nature of physical absorbance, while the MnO₄⁻ has a strong trend to attack the macromolecule of a PAN fiber through the interaction between MnO₄⁻ and a fiber, as following eq. (1).²⁹ Therefore, the oxygen content increased in the modified spun fibers (Table 1), which might promote the cyclization and thermal oxidation rate as an active site.³⁰



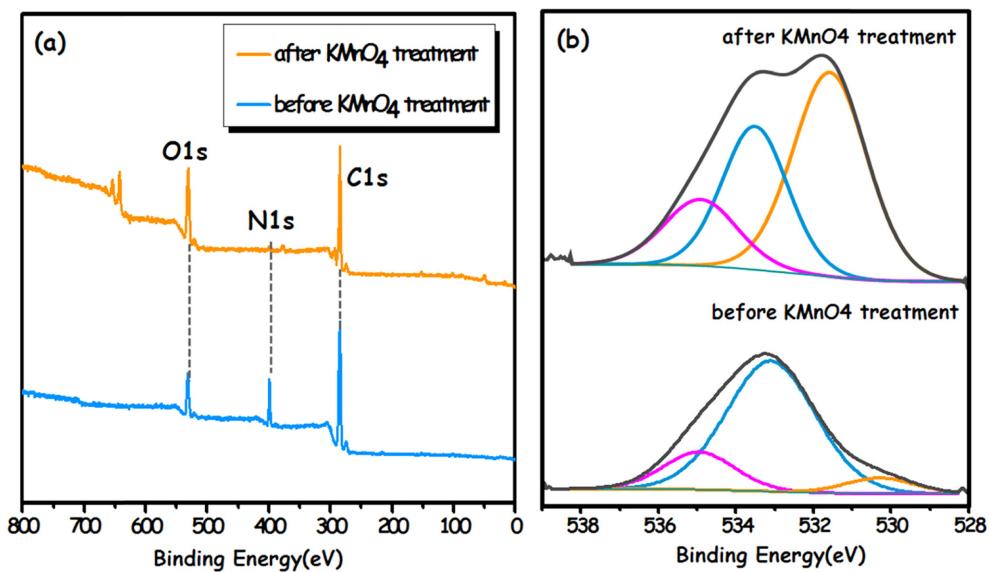


Fig. 7. XPS spectra of (a) a wide-scan XPS spectrum, (b) the deconvolution of O1s of unmodified and KMnO₄-modified AN83IA1MA16(2)50% copolymer based melt-spun fibers.

Table 1. Chemical composition and oxygen-containing functional groups for unmodified and KMnO₄-modified AN83IA1MA16(2)50% copolymer based melt-spun fibers

Sample	Chemical composition			Functional groups ^a		
	carbon	oxygen	O1s/C1s	-C=O	R-OH	-COOH
Pristine	77.81	10.42	0.13	0.77	8.04	1.89
KMnO ₄ modified	74.29	24.08	0.32	13.03	8.11	4.22

^aAnalyzed from O1s core-level scan spectra

For this reason, in the case of the modified melt-spun fiber, the stabilization process under oxidative conditions can be omitted in the conversion process from precursor fibers into CFs under inert condition.³¹ The carbonyl and carboxyl functionalities of the chemical oxidized spun fiber lead to ester and anhydride linkages through dehydration reactions, condensation, crosslinking, and elimination reactions in the heat treatment process. Therefore, it did not show melting behavior any longer through the heat treatment in the carbonization process in N₂ atmosphere, as shown in Fig. 8a–b. The average fiber diameter is also reduced to 30 mm when carbonized at 800 °C. The SEM images (Fig. 8b) show the deposition of uniform particles on carbon fibers surface after 800 °C pyrolysis. They represent that the particles are spherical shape and uniformly dispersed on the surface of the carbon fiber. The elemental mapping of EDX shows the presences of K, Mn, C, and O atoms in the fiber (Fig. 8c). In the future, the carbonized fibers can be developed for activated carbon fibers with controlled pore size depending not only on the activity but also the size of the particle of the metals with catalyst functions. The mechanism of the activation

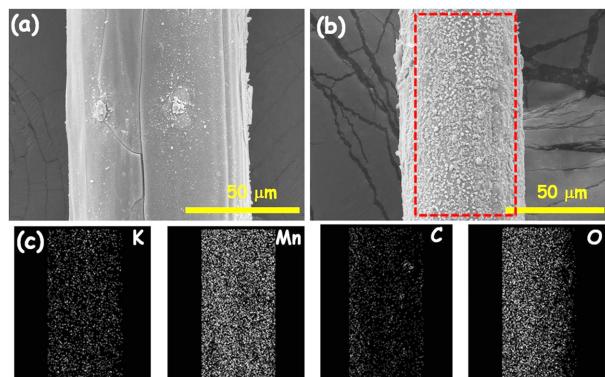


Fig. 8. SEM images of (a) stabilized, (b) carbonized fiber, (c) the elemental mapping of carbonized fiber developed from modified spun fiber.

of the carbon fiber stabilized by KMnO₄ needs to be studied further.

In conclusion, low cost production of the carbon fibers would be approached by adoption of economic process, such as melt spinning of the precursor and microwave energy application for the polymerization. The PAN copolymer synthesized by microwave energy showed good

melt spinnability. The spun into fiber was stabilized in the air and then carbonized under an N₂ gas atmosphere. Moreover, the fusible problem in the stabilization process was solved by the chemical oxidation with the KMnO₄ solution, because the element K and Mn would be acted as catalysts in oxidation of the carbon fibers. The results of this study also proposes the potential of the low cost production of the activated carbon fibers with controlled pore size.

EXPERIMENTAL

Materials and Characterizations

The monomers, acrylonitrile (AN), methyl acrylate (MA), itaconic acid (IA), initiator AIBN (2,2'-azo-bis-isobutyronitrile) were obtained from Aldrich Co. The dimethyl-sulfoxide (DMSO) purchased from Yakuri Pure Chemical was used as solvent in this reaction. AN and MA were washed with aqueous NaCl (to remove inhibitor), washed twice with distilled water, and distilled at reduced pressure before use. Samples for differential scanning calorimeter (DSC) experiments were heated to 500 °C under nitrogen atmosphere at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA 50 (Shimadzu, Inc.). The samples were heated to 800 °C in nitrogen in an electric furnace at a rate of 10 °C/min. Viscosity measurements were performed at 25 °C using a BROOKFIELD viscometer (LVDVII+). Surface layer morphologies were analyzed using a scanning electron microscope (SEM) with Energy-dispersive X-ray (EDX) spectroscopy model Hitachi, S-4700. As-spun and stabilized fibers were sputter-coated with a platinum layer before being subjected to a SEM analysis. The surface functionalities of the copolymer were examined by Fourier transforms infrared spectroscopy (FT-IR, Nicolet 200 instrument). All the samples were analyzed using the KBr pellet technique and scanned in the range from 4000 to 400 cm⁻¹. The yield of the copolymer was determined by the weight % of copolymer on the basis of the total amount of monomer used. Microwave irradiation of the samples was studied by microwave oven (KR-A202B).

Synthesis of PAN Copolymer

Monomer AN, MA, IA put together in a given weight fraction in DMSO solvent in cover tight Teflon bottle, and then the sample was polymerized under microwave irradiation of 100 Watt (KR-A202B, Dae Woo, Korea) for various times. After cooling down to room temperature, the polymers washed with methanol until no remaining of

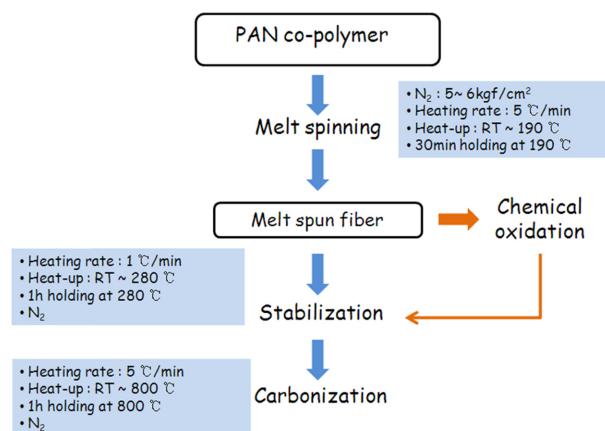


Fig. 9. Schematic of preparation process of carbon fiber.

solvent and unreacted monomers and finally dried it under vacuum at 70 °C for 24h. The copolymer produced from the monomer composition of 90/10(AN/MA) in the presence of 0.1 wt% initiator (AIBN) in DMSO solvent (ratio of total monomer and solvent is 1:2) was identified as AN90MA10(0.1)200%.

Carbon Fiber Preparation

The PAN copolymer was spun into fiber through the using a melt spinning apparatus at melting temperature (DAQSTATION DX1000, YOKOGAWA, Tokyo, Japan). PAN copolymer were heated up to 190 °C (5 °C/min) in nitrogen atmosphere and hold for 30 min. Fibers were initially spun through a round single-hole spinneret having 0.5 mm diameter, and then collected on a aluminum drum located down 52 cm from the spinneret at with average speed at 50 mmin⁻¹. In addition, the melt spun PAN copolymer fibers were dipped in 3 wt% KMnO₄ aqueous solution for 4 hours, which is followed by washing with distilled water and dried at room temperature. It was additionally heated up to 280 °C in a tubular furnace under nitrogen atmosphere and carbonized at 800 °C in nitrogen atmosphere. The overall process of carbon fibers from PAN copolymer is presented in Fig. 9.

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