

Fabrication of carbon fibers from electrospun poly(vinyl alcohol) nanofibers

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Abstract

Carbon fibers were fabricated from electrospun poly(vinyl alcohol) (PVA) nanofibers. Electrospun PVA nanofibers were treated with iodine vapor for different periods, subsequently carbonized at different temperatures, and the structural changes of the PVA nanofibers were analyzed. The nanofibers iodinated at 80 °C for 24 h led to a good carbon yield of 21% when carbonized at 1200 °C. The influence of metal nanoparticle on the fabrication of carbon fiber and its properties was also investigated by the addition of a metal salt, nickel(II) acetate tetrahydrate $[(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}]$, to the PVA spinning solution. Noticeably, after incorporation of nickel (Ni) nanoparticle continuous electrospinning was realized at lower polymer concentration than that of neat PVA. Moreover, smaller fiber diameter and a higher carbon yield (~34%) were obtained after carbonization. Transmission electron microscopy observation of the carbon fibers revealed that the addition of Ni-nanoparticles accelerated the formation of a graphitic structure at a lower carbonization temperature of 1200 °C.

Keywords

Carbon fiber, PVA nanofiber, electrospinning, iodine treatment, carbonization, Ni nanoparticle

Introduction

Research and development of nanofibers has gained much prominence in recent years due to the heightened awareness of their potential applications in many fields including textiles, chemical synthesis, medicine, engineering and defense.^{1,2} Among several methods for nanofiber production, electrospinning (ES) has been a pioneer technology for the production of ultra-thin membranes consisting of 1D nanostructured fibers from a rich variety of materials, including polymers, composites, and ceramics.³ Nowadays, research on the production methods and conditions of the ES technique have been reconsidered on account of its simplicity and versatility.^{4–8} Electrospun ultrathin fibers possess high porosity and a high surface area to volume ratio, which has contributed to the potential applications of electrospun fibers in carbon and graphitic nanofiber manufacturing.⁹

Carbon nanofibers derived from ES have further expanded the possible applications of nanofibers. For instance, high performance materials and high functional prepared from carbon nanofibers and nanotubes

have attracted significant attention, due to their outstanding characteristics of high modulus, high strength, high electrical and thermal conductivity, chemical and bio inertness and unique morphology over conventional fibrous nanomaterials.^{10,11}

Poly(vinyl alcohol) (PVA) is a semi-crystalline fiber with comparatively high carbon content (ca. 54.5%), and easily splits hydroxyl groups in the polymer chain make PVA favorable for use as a precursor for the production of carbonaceous materials. To date, poly(furfuryl alcohol),¹² poly(vinylidene chloride),¹³ polyimide,¹⁴ poly(acrylonitrile) (PAN),¹⁵ poly(vinylidene fluoride),¹⁶ poly(vinyl alcohol),^{17,18} and phenol resin¹⁹ have been used as starting polymer materials

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for this purpose. The earliest attempt, and subsequent work, utilized wet spun PVA fiber as a precursor for the fabrication of carbon fiber.^{20,21} Recently, electrospun PAN,^{1,22} pitch²³ etc. and different polymeric blends^{24–27} have been reported as precursors for the fabrication of carbon fiber. In this study, we report the fabrication of carbon fibers from electrospun PVA nanofibers. The decomposition of PVA at temperatures slightly higher than its melting point results in lower carbon yield; therefore, PVA precursors with high thermal stability are essential. Researchers reported that the dehydration of PVA from 100 to 290 °C under tension in a mixed gas atmosphere induces the thermal stability required for carbonization.^{17,21} Preoxidation or subsequent dehydration has also been employed as a PVA stabilization process.²⁰ In addition, iodine acts as a good stabilizer of PVA^{17,28} and promotes dehydrogenative polymerization during carbonization. Iodine treatment has also been successfully employed by our coworkers to produce carbon fiber from natural biopolymers such as silk fibroin.^{29–32} The carbon yield does not seem to be influenced by whether the polymer is thermoplastic or thermosetting, linear or cross-linked, but rather by whether it is capable of cyclization, ring fusion or chain coalescence at the onset of carbonization.^{33,34} Iodine treatment transforms the single bond in PVA hydrocarbon structure into a double bond polyene-like structure, which makes PVA molecules difficult to melt even at the relatively high temperature of carbonization.³⁴ In addition, the carbon microstructure formed is changed into stable graphite structure during carbonization.³⁵

Many researchers have incorporated functional components (e.g., nanoparticles, nanowires, or molecular species) into polymeric nanofibers, via ES interaction or liquid phase attachment or deposition/coating, to obtain a diversified range of composites and well defined functionalities. For example, chromium nitrate $[\text{Cr}(\text{NO}_3)_3]$ ³⁶ and palladium diacetate $[\text{Pd}(\text{OOCCH}_3)_2]$ ⁴ were added into the spinning solution to produce finer nanofibers from PVA and polylactic acid, respectively. Carbon nanotube reinforced polymeric composites were also prepared using ES.^{37,38} Iron salts have also been used for the growth of carbon nanotubes in carbon fiber from electrospun PAN fibers⁴ or improved graphitization of PVA films at lower temperature.¹⁷ Our coworkers have also reported that the addition of a small amount of Ni metal catalyst promotes the dehydration reaction of PVA during carbonization.³⁹

In this study, we attempted to prepare carbon fibers from electrospun PVA nanofibers followed by iodine treatment. We also explored the effect of metallic salt (Ni-acetate) addition into the PVA spinning solution. The spinning performance, carbon yield, diameter and

morphology of the resultant nanofibers were investigated.

Experimental details

Materials

PVA chips, atactic type, (Poval-HC, Kuraray Co. Ltd, Japan) with a degree of polymerization (DP) and saponification of ca. 1500 and 99.9%, respectively, were used. PVA requires additional purification processes to remove residual impurities such as sodium acetate, which promotes thermal decomposition during heat treatment. PVA was purified as follows: the PVA chips were washed with a sufficient amount of distilled water at 60 °C under agitation and the water was exchanged twice at 2 h intervals. The PVA was then stirred for 20 h in water followed by stirring in methanol for 24 h at room temperature. The washed PVA chips were filtered using a glass vacuum filter, and dried at 60 °C in a vacuum oven for 24 h. Special grade Ni(II) acetate tetrahydrate $[(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}]$ was purchased from Wako Pure Chemical Ind. Ltd., Japan and used as received.

Preparation of PVA nanofiber

Purified PVA was dissolved in distilled water at 90 °C for ca. 4 h. During electrospinning of PVA-HC, we tried with different concentrations of spinning solution ranging from 2 to 10 wt% and measured the viscosity of each solution and found the critical concentration was around 7 wt%. PVA-HC concentration below and over 7 wt% showed capillary instability that resulted in inconsistent electrospinning of nanofibers with more beads. Therefore, we preferred 7 wt% PVA concentration to obtain steady spinning and bead-free nanofibers.

In the case of Ni incorporation, different PVA concentrations were again investigated, and continuous spinning with less beads was realized using a 6 wt% PVA solution containing Ni-acetate. Ni-acetate (4 wt% of the PVA solid content) was dissolved in the PVA solution; samples doped with Ni-acetate are denoted as PVA/Ni. Spinning of PVA nanofibers was carried out using a typical ES system as schematically shown in Figure 1. The system consists of mainly three major components: a high voltage direct current (DC) power supply, a metallic spinneret, and a grounded collector. A high voltage is applied between the spinneret and collector, consequently an electrically charged stream of polymer solution is generated, and the polymeric nanofibers are formed on the collector by vaporization of solvent. PVA nanofibers are collected as a web of fibers deposited on polyethylene mesh placed

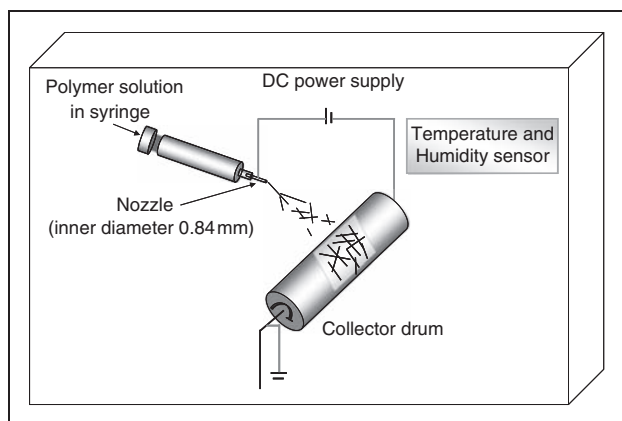


Figure 1. The schematic diagram of the experimental setup of electrospinning.

on the surface of the grounded collector. However, the method of electrospinning we used in this work is for experimental purpose. The bubble electrospinning technique can be used for mass scale production as reported elsewhere.^{40–42}

Iodine treatment

A PVA nanofiber mat was enclosed with a sufficient quantity of solid iodine in a glass bottle. The sealed vessel was placed in an 80 °C oven for different exposure periods during which iodine was vaporized. The color of the PVA sample became dark brown due to complex formation of the PVA with iodine. In the present paper, the iodinated PVA nanofiber will be denoted as I-PVA.

Carbonization

A ceramic tubular furnace (AMF-9P-III THV, Asahi Rika Seisakujo, Japan) was used for the carbonization process. I-PVA nanofiber was heated at 1 °C/min in the furnace under an Ar gas flow.

Measurements

Thermogravimetric analysis (TGA) was carried out with a Rigaku Thermoplus II TG 8120 under N₂ atmosphere from room temperature to 1000 °C at a heating rate of 10 °C/min.

Scanning electronic microscopy (SEM; Hitachi S-2380N) was conducted after the samples were sputtered with platinum. The diameter of the fibers was analyzed from SEM images using software (ImageJ; NIH, USA). The experimental results of fiber diameter represent the average of 100–150 individual measurements at different places.

Transmission electron microscopy (TEM; Jeol JEM-2010) was conducted using an accelerated voltage of 200 kV. Ground samples were dispersed in ethanol and the mixture placed on a copper mesh grid followed by carbon sputtering prior to measurement.

Wide angle X-ray diffraction (WAXD) measurements were performed by the reflection method using a Rigaku Rotorflex RU-200B X-ray generator equipped with a goniometer. The X-ray source was Ni-filtered Cu K_α radiation ($\lambda = 0.15418$ nm) generated at 40 kV and 150 mA. Crystallite size (D_p) was measured using Scherer's equation:

$$D_p = k\lambda/(\beta\cos\theta),$$

where β : full-width at half-maximum (FWHM), θ : half of Bragg's angle, λ : X-ray wavelength (0.154 nm) and k = shape factor (for spherical crystals with cubic symmetry, $k = 0.94$).⁴³

Raman spectra were recorded using a Kaiser Hololab 5000 spectrometer, equipped with a MK-II filter probe using an Nd:YAG laser ($\lambda = 532$ nm) generated at 50 mW.

Results and discussion

Electrospinning of PVA nanofibers

The morphology and diameter of electrospun fibers are dependent on the number of processing parameters, including the intrinsic properties of the solution (e.g. polymer type, viscosity, electrical conductivity, polarity, surface tension, and impurities) and the operational conditions (e.g., applied electric field and the distance between the spinneret and collector).^{3–8,40} In addition to these variables, the humidity and temperature also play an important role in determining the morphology and diameter of electrospun fibers.⁴⁴ In our current work, different spinning conditions were examined and based on the morphology, fiber diameter and diameter homogeneity, the optimum spinning condition was obtained at a PVA concentration of 7 wt%, solution extrusion rate of 0.5 mL/h, a 17 cm distance from the nozzle to the collector, an applied voltage 30 kV, a temperature of ca. 20 °C, and relative humidity of 14%. These conditions resulted in the production of nanofibers having a diameter range of 350–700 nm with good reproducibility.

Effect of iodine treatment on PVA nanofibers

PVA has relatively high carbon content among vinyl polymers and high molecular orientation in fiber form, but it melts below the carbonization temperature and is thermally decomposed into volatile low

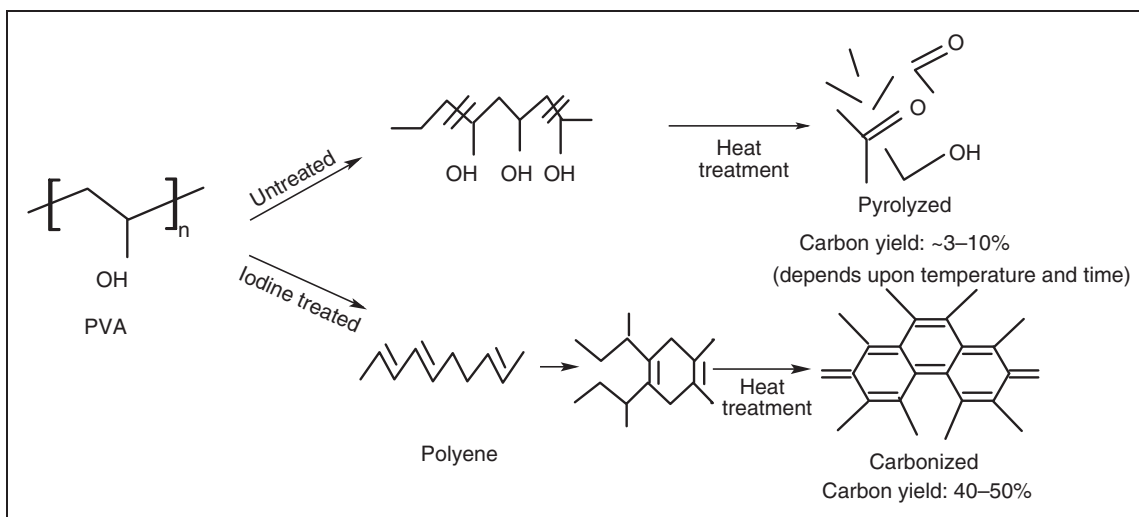


Figure 2. Possible behaviors of untreated and iodinated PVAs during heating.

molecular weight molecules, which results in an unsustainable form of fiber and considerably low carbon yield.³⁴ Therefore, it is almost impossible to produce carbon fiber from PVA without pretreatment or additives. Some researchers have reported that the dehydration of PVA induced by iodine treatment enhances the thermal stability of PVA during carbonization.^{17,45,46} Presumably, iodine rearranges the PVA structure into water insoluble polyene-type structures that convert into cyclic polyaromatic structures during carbonization, which results in higher carbon yield. The dehydration of PVA by iodine treatment followed by carbonization can be considered to take place by the reaction scheme illustrated in Figure 2. As shown in Figure 3, the TGA curves of untreated PVA fiber and I-PVA (24h) were taken to study the degradation behavior of PVA polymer after iodination. Apart from the weight loss due to content water at the initial stage, the weight loss after iodination was significantly different. Untreated fiber has no weight loss up to 250°C and drastic weight loss was marked with a sharp declining of the curve at 300°C that ended at around 460°C, retaining only ≈2% of its weight. In contrast, the initial degradation of I-PVA fiber started at around 120°C and then further decomposition was completed at nearly 520°C, retaining ≈38% of its weight. In the TG curve of I-PVA, initial decomposition is likely to occur due to the evaporation of excess iodine together with desorbed water of PVA precursor, and the later decomposition phase of I-PVA is associated with the evaporation of iodine along with the oxidation of precursor fiber. Considering weight loss during heating, iodination has evidently improved the thermal stability of the precursor fiber. Possibly, cross-linking among PVA chains occurs during the

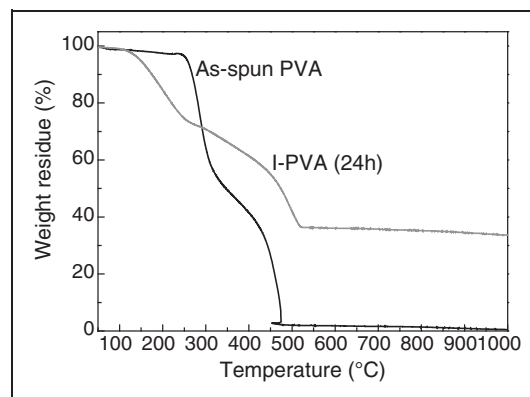


Figure 3. TGA thermograph of PVA as-spun nanofiber and I-PVA nanofiber subjected to 24h iodination.

thermostabilization process that can withstand a high temperature process as illustrated in Figure 2.

Morphological aspect. The morphological changes of nanofibers after iodine treatment were examined. Figure 4 shows the SEM images of PVA and I-PVA nanofibers prepared with different iodination periods of 3, 12, and 24 h with respective average diameter. The morphology of the iodinated nanofibers varies slightly compared to the original fiber (Figure 2a) with minuscule swelling of the PVA nanofiber due to absorption of iodine molecules. Even for an iodination time of 24 h, iodine has no significant effect on the nanofiber morphology. But the diameter of nanofibers exhibits a modest increase in diameter after 3 h iodination. However, further increase in the iodination period to

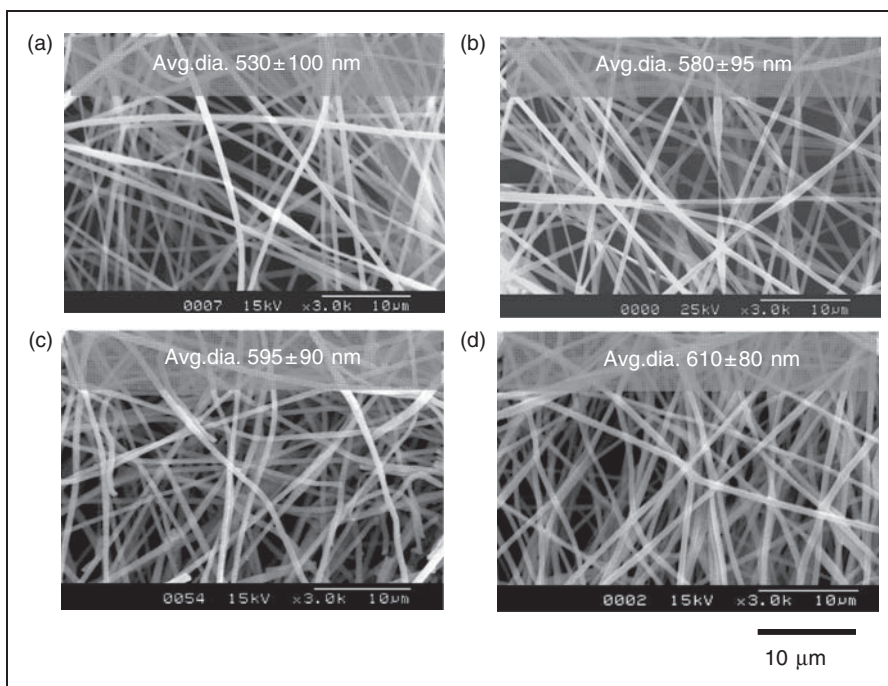


Figure 4. SEM images of PVA nanofibers subjected to different iodination periods of (a) 0 (no iodination), (b) 3, (c) 12, and (d) 24 h.

12 and 24 h results in little change to the nanofiber diameter. It appears that the PVA nanofibers initially absorb iodine over a 3 h iodination period and become saturated, and hence a significant change in diameter is not observed with further iodination.

Figure 5 shows SEM images of the carbonized samples obtained from differently iodinated PVA nanofibers with carbonization performed at 1200 °C. The reason for the carbonization temperature of 1200 °C is explained later. The neat PVA fiber melts completely during the carbonization process and becomes a solid film with cracks. The nanofibers iodinated for 3 h also show the melting phenomenon during the carbonization process. Such melting behavior may be attributed to the shorter iodination period of 3 h, which appears to result in insufficient thermal stability of the PVA nanofibers due to improper dehydration during heat treatment. In contrast, the nanofibers iodinated for much longer periods of 12 and 24 h retained their original fibrous structures without melting during carbonization. This reveals that the transformation of PVA into a stable cyclic aromatic structure by intermolecular crosslinking prior to carbonization is a prerequisite to retain the fiber structure. In this regard, longer iodination periods of 12 and 24 h, as evidenced by the Raman spectra in Figure 7, are found to be very favorable for the stabilization of PVA nanofibers prior to carbonization.

Figure 6 shows the diameter histograms of as-spun precursor nanofiber and the carbon fiber obtained from precursor nanofiber with a 24 h iodination period.

After carbonization, the average diameter becomes thinner than those of the iodinated PVA precursor fiber. The dehydration and subsequent carbonization of iodinated PVA nanofibers may lead to a finer structure by diameter contraction. Thus, the iodine treatment has appeared to be a decisive step for carbonization in the context of the fiber diameter.

Structural aspect. Raman spectroscopy is an effective way to investigate the structure of an iodinated material. Raman spectra of PVA nanofibers and I-PVA nanofibers with different iodination periods are shown in Figure 7. The spectrum of the as-spun PVA shows most pronounced scattering peaks at around 2912 cm^{-1} , which are assigned to the stretching vibrations of CH_2 and CH , and other peaks at ca. 1440 cm^{-1} assigned to the stretching vibrations of CH and OH in the PVA molecules.⁴⁷ For the fiber iodinated for 3 h, two major scattering peaks are observed at ca. 1120 and 1500 cm^{-1} , which are respectively assigned to the single and double bonds of the polyene structure.⁴⁸ This implied that PVA molecules were successfully dehydrated and changed into a polyene-like structure. The fibers iodinated for 12 and 24 h have almost the same Raman pattern. The scattering band appearing at ca. 1590 cm^{-1} indicates a polycyclic aromatic structure formed by intermolecular crosslinking of the polyenes.⁴⁹

An important aspect in carbon fiber production is the yield of residual carbon from a polymeric precursor, because lower yield generally results in higher

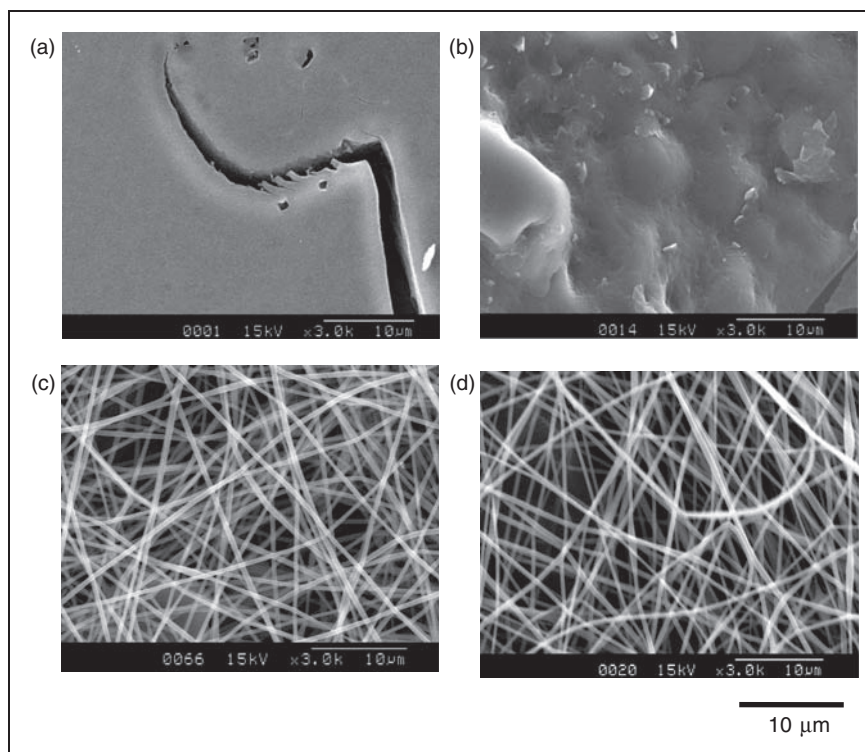


Figure 5. SEM images of carbonized PVA nanofibers subjected to different iodination periods of (a) 0, (b) 3, (c) 12, and (d) 24 h and then carbonized at 1200°C.

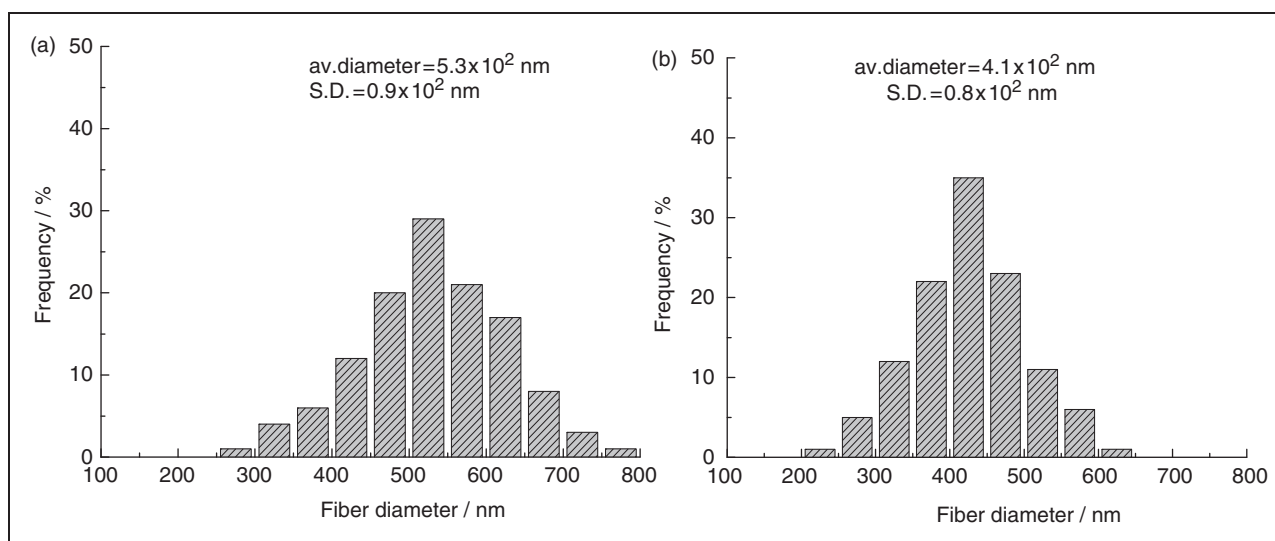


Figure 6. Diameter distributions of (a) as-spun PVA and (b) carbonized PVA nanofibers subjected to 24 h iodination and carbonized at 1200°C.

production costs. The carbon yield obtained for different iodination periods is presented in Table 1. As speculated, the carbon yield was significantly improved from 2 to 16% with 3 h iodine treatment. An increase in the iodination period to 12 h further increases the carbon yield to 21%. The reason for the higher yield

of carbon fibers from an iodinated PVA sample can be attributed to the increased intramolecular cross-linking of the polyene molecules followed by the formation of polycyclic structures resulting from iodination.⁵⁰ This may inhibit the generation of volatile components during heating and lead to higher

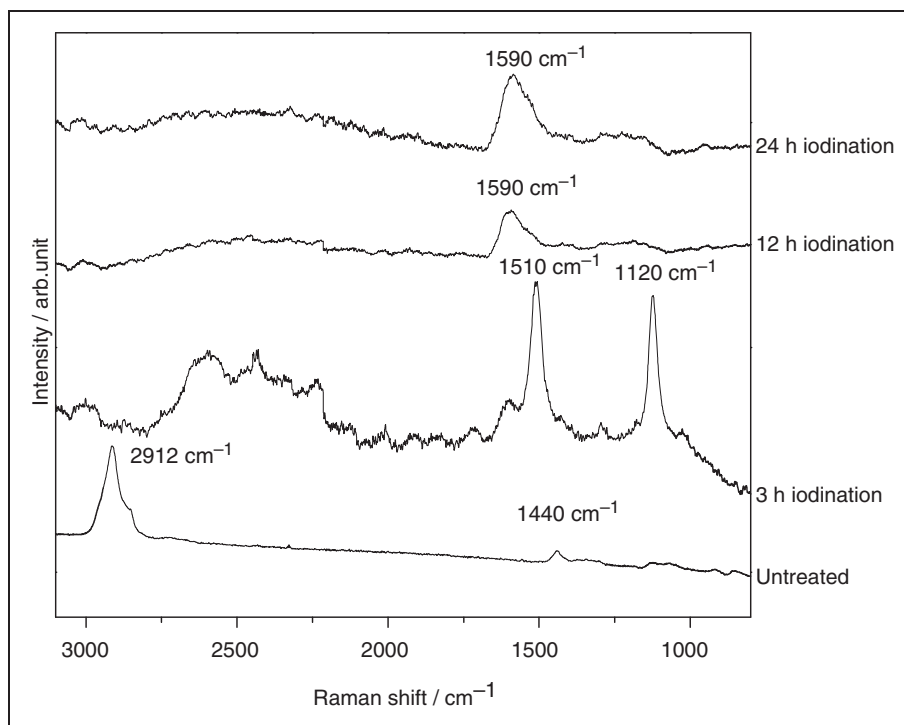


Figure 7. Raman spectra of I-PVA nanofibers subjected to different iodination periods.

Table 1. Carbon yield of carbonized PVA nanofibers subjected to different iodination periods and carbonized at 1200°C

| Iodination period (h) | 0 | 3 | 12 | 24 |
|-------------------------------|-----------|------------|------------|------------|
| Carbon yield (wt%) \pm S.D. | 2 \pm 2 | 16 \pm 3 | 21 \pm 2 | 21 \pm 2 |

carbon yield. The carbon yield remains constant, even after an increase of the iodination period up to 24 h, which may be due to saturation of the PVA molecules with iodine, as observed for the Raman spectra of the 12 h and 24 h iodinated nanofibers shown in Figure 7. Therefore, iodine treatment is proven to be an effective means to enhance the carbonization efficiency of PVA nanofibers.

WAXD measurements were performed to examine the structure of the carbonized PVA nanofibers. Figure 8 shows that the precursor PVA nanofiber exhibits a typical semi-crystalline structure with a peak in the range of $2\theta = 17\text{--}21^\circ$. Upon iodination, the crystal structure of the fibers completely disappears. The carbon fibers prepared with different iodination periods show two broad peaks at around $2\theta = 18\text{--}28^\circ$ and $43\text{--}45^\circ$, which correspond to the (002) and (10) diffractions of disordered micrographite stacking, respectively.^{51,52} An electron diffraction pattern of carbonized fiber with 24 h iodination and carbonized at 1200°C has been investigated to determine the molecular orientation of

derived fiber (not shown in this paper) which indicates the carbonized fiber is isotropic and possesses randomly oriented crystals. Thus, it can be said that iodine treatment has an influence on the PVA molecules to produce a disordered graphite-like structure.

Bin et al. reported that a PVA composite film attained the maximum uptake of iodine at 24 h doping and then the uptake decreased with further increase of the iodination time.¹⁷ Similarly, our co-workers also recently found that an iodination period of 24 h was optimum for stabilization of PVA for carbonization.³⁹ Therefore, in the present work, an iodination period of 24 h was also considered to be optimum to obtain intact carbon nanofibers, in terms of structural morphology and carbon yield.

Effect of carbonization temperature on fiber structure

Morphological aspect. The morphologies of 24 h iodinated carbon fibers carbonized at different iodination temperatures of 800, 1000 and 1200°C were examined using SEM and the results are shown in Figure 9. Irrespective of the carbonization temperature, the fibrous appearance of the PVA nanofiber webs remains intact and is similar to the PVA nanofiber precursor. No significant difference in appearance was observed with variation of the carbonization temperature.

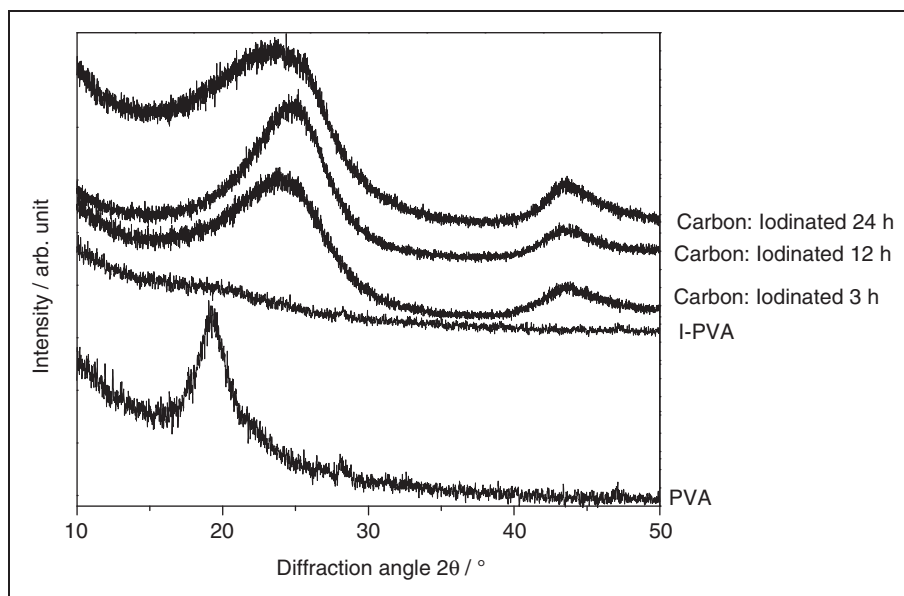


Figure 8. WAXD profiles of PVA, I-PVA (24 h) and carbonized PVA nanofibers subjected to different iodination periods and carbonized at 1200°C.

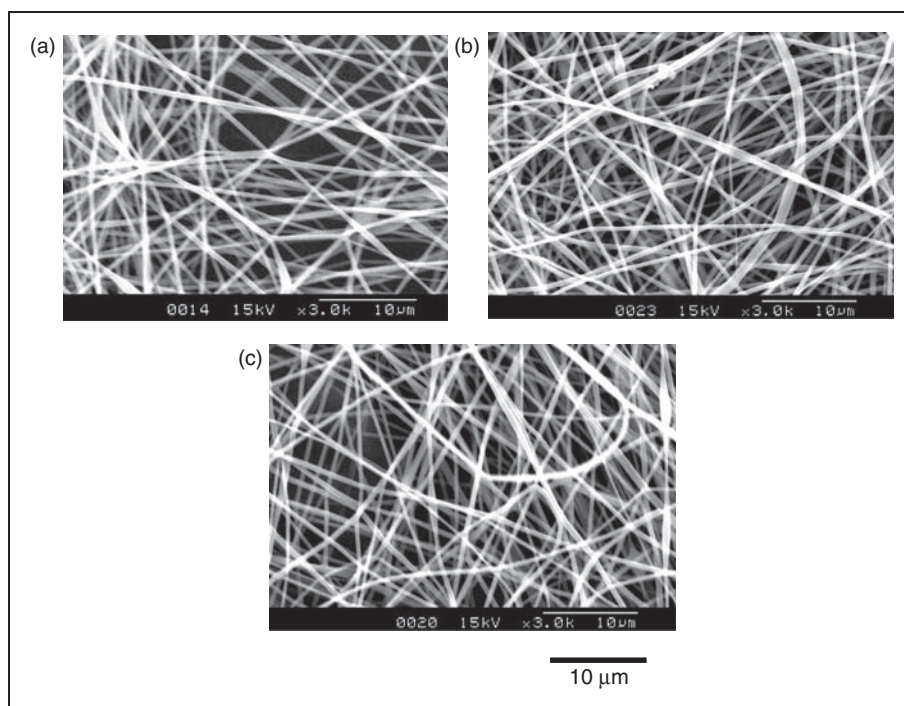


Figure 9. SEM images of carbonized PVA nanofibers subjected to 24 h iodination and carbonized at (a) 800°C, (b) 1000°C, and (c) 1200°C.

Structural aspect. Raman spectra of these carbonized fibers were measured and are shown in Figure 10. The peak profiles of the as-spun PVA precursor nanofibers and I-PVA nanofibers were previously discussed (Figure 7). For carbonized fibers obtained at different temperatures, two new peaks appeared at ca. 1340 and 1590 cm^{-1} , which correspond to the D (characteristics

of a disordered sp^2 phase) and G bands (characteristic of the in-plane stretching vibration mode E_{2g} of well crystallized graphite), respectively.⁵³ The peak positions remain the same with an increase of the carbonization temperature; however, when closely examined, the intensity of the G band appears sharpest for the 1200°C carbonized sample. This indicates that the

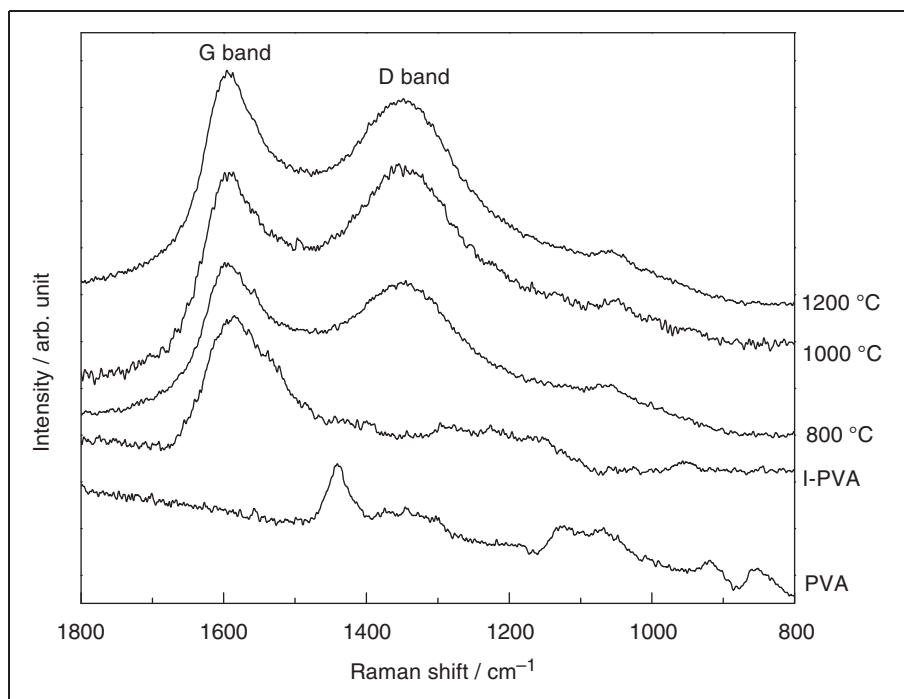


Figure 10. Raman spectra of PVA and carbonized PVA nanofibers subjected to 24 h iodination and different carbonization temperatures.

graphite structure is better developed at a carbonization temperature of 1200 °C, compared to the carbon fibers carbonized at 800 and 1000 °C.

Figure 11 shows WAXD profiles of the carbon fibers derived from different carbonization temperatures. Similar to Figure 9, each pattern has two peaks in the range of $2\theta = 18\text{--}28^\circ$ and $43\text{--}45^\circ$, which indicates the respective diffractions of the (002) and (10) graphite planes. The shape of the first peak becomes sharper and moves towards lower angles for the fibers obtained at a carbonization temperature of 1200 °C. This may imply an improvement in ordered graphitic crystal growth for this fiber. However, the carbon yield for each carbonization condition was measured and was around 21%. Considering the overall morphology and structural analysis, the carbonization temperature of 1200 °C was found optimum in this study.

Effect of Ni particle addition to the spinning solution on carbonized PVA nanofibers

The addition of metal ions influences the thermal decomposition and carbonization behavior of vinyl polymers.^{36,54,55} We recently reported a significant enhancement of carbon yield (ca. 48%) and acceleration of graphite formation after the addition of Ni-acetate to PVA fiber.³⁹ The nucleation and growth processes of graphene layers in carbon nanotubes are also influenced by Ni nanoparticles.⁵⁶ Therefore, we

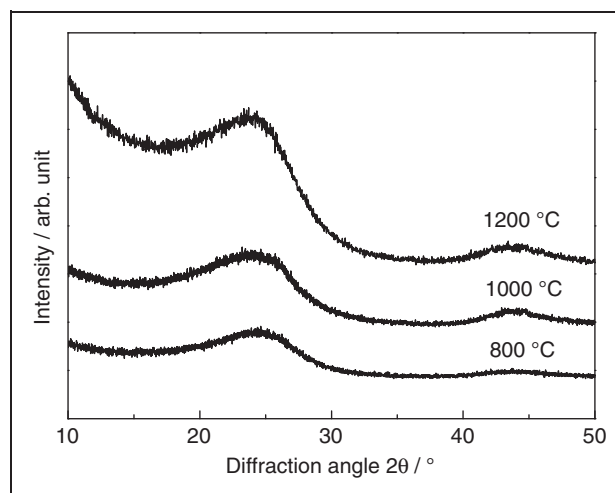


Figure 11. WAXD profiles of carbonized PVA nanofibers subjected to 24 h iodination at different carbonization temperatures.

have investigated the influence of Ni ion addition on PVA nanofibers to achieve carbon nanofibers with good yield and morphology.

The addition of metal particles to a spinning solution usually changes its properties, such as conductivity and viscosity. Therefore, the electrical conductivity of the spinning solution was measured after the incorporation of Ni-acetate. The electrical conductivity of neat

PVA solution was 2.5 mS/m, whereas that of the spinning solution with Ni-acetate was 186.7 mS/m. The addition of an electrolyte increases the elasticity of the spinning solution, which tends to yield fibers with smaller diameters.¹¹ In contrast, highly conductive solutions exhibit less spinnability¹² and also lead to more bead formation during ES.^{3,5} In the present study, 7 wt% PVA solution with Ni-acetate (4 wt% of the PVA solid content) gave unstable spinning performance when using the same process parameters as those for neat PVA electrospinning. In order to

obtain stable spinning with less bead formation, different PVA concentrations were investigated, and a 6 wt% PVA solution containing Ni-acetate was found to be appropriate.

Morphological aspect. Figure 12 shows SEM images of different PVA/Ni nanofibers. The as-spun PVA/Ni nanofibers are visibly smooth with no entanglement and have an average diameter of 4.8×10^2 nm. After 24 h iodination, the PVA/Ni nanofibers became swollen and obvious. The PVA/Ni nanofibers carbonized at

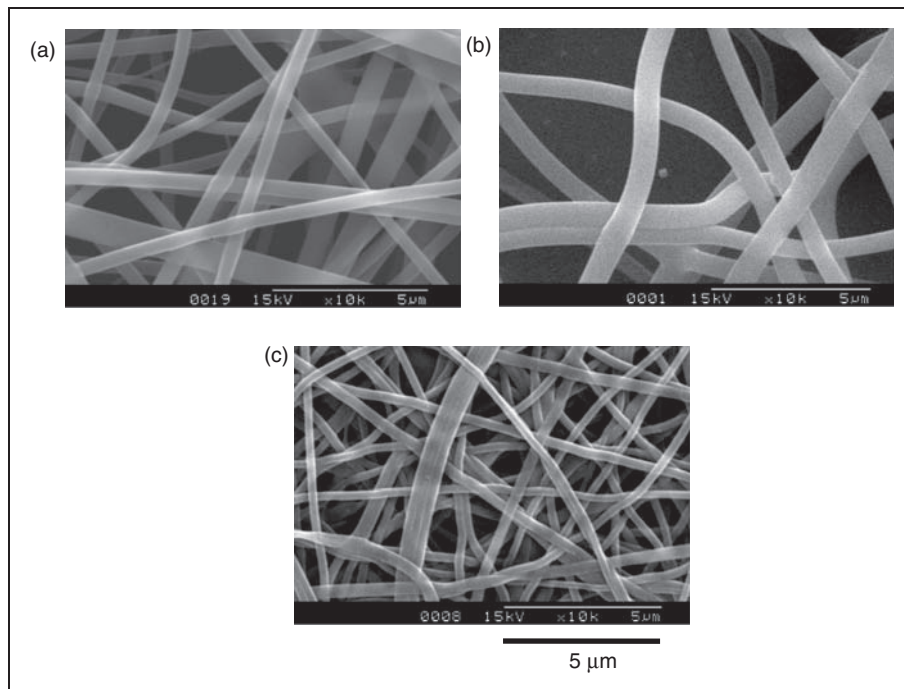


Figure 12. SEM images of (a) as-spun PVA/Ni, (b) 24 h iodinated PVA/Ni, and (c) PVA/Ni nanofibers carbonized at 1200°C.

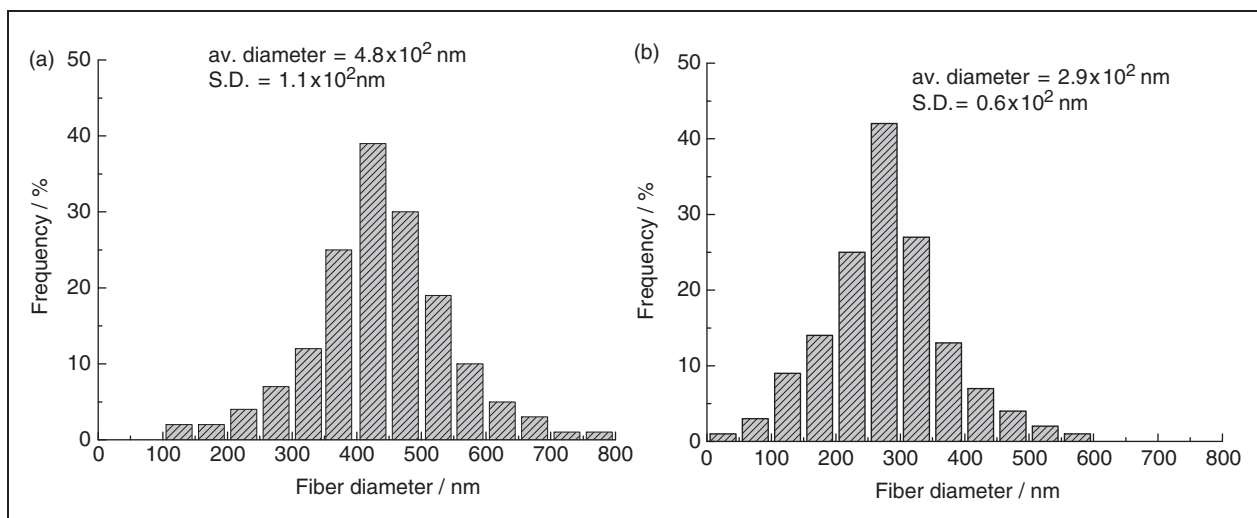


Figure 13. Diameter distribution of (a) as-spun PVA/Ni, and (b) carbonized PVA/Ni nanofibers.

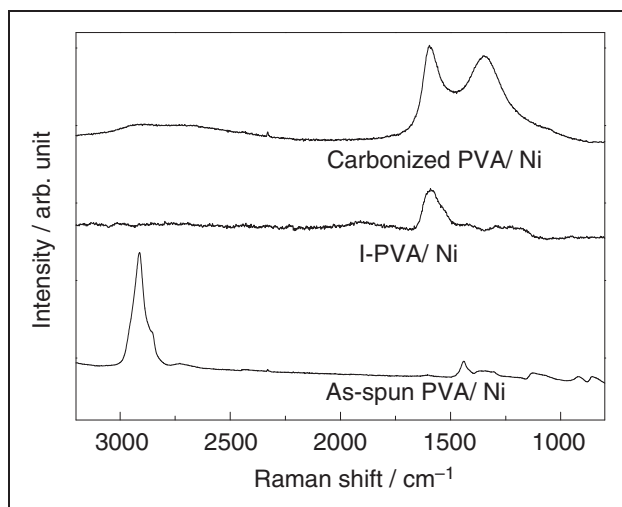


Figure 14. Raman spectra of as-spun PVA/Ni, iodinated PVA/Ni and carbonized PVA/Ni nanofibers.

1200 °C appear to be intact. Figure 13 shows a histogram of the fiber diameter for as-spun PVA/Ni nanofibers and carbonized PVA/Ni nanofibers. The diameter distribution pattern of carbonized PVA/Ni nanofibers also resembles a normal distribution pattern with an average fiber diameter of 2.9×10^2 nm that is much finer than the that of precursor one.

Structural aspect. Figure 14 shows Raman spectra of the as-spun PVA/Ni nanofibers, iodinated PVA/Ni nanofibers (24 h) and carbon fibers carbonized at 1200 °C. Addition of Ni-acetate to the spinning solution does not result in such a distinctive structural change of the Raman spectrum. Iodinated PVA/Ni shows a relative sharp peak at ca. 1590 cm^{-1} , which indicates the formation of polycyclic aromatic structures by intermolecular crosslinking of polyenes in the PVA nanofibers. After carbonization of PVA/Ni nanofibers the presence of a sharp G band at ca. 1590 cm^{-1} and the D band at ca. 1350 cm^{-1} confirms the formation of the carbon structure.

Figure 15 shows WAXD profiles of carbon fibers derived from PVA/Ni nanofibers carbonized at 1200 °C and neat PVA nanofibers carbonized at 1500 °C. Pure PVA nanofibers carbonized at 1500 °C have a broad (002) peak and a small (10) peak of the graphene layer, which confirms their disordered graphite structure. The peaks of the PVA/Ni derived carbon fiber at ca. $2\theta = 26^\circ$ and ca. $2\theta = 43^\circ$, assigned to the (002) and (10) diffractions, respectively, became significantly sharper, which signifies the formation of a very highly ordered graphite-like structure. In contrast, the carbon fibers derived from neat PVA nanofibers at the same carbonization temperature of 1200 °C (in Figure 11) showed a disordered graphite structure. Therefore, the

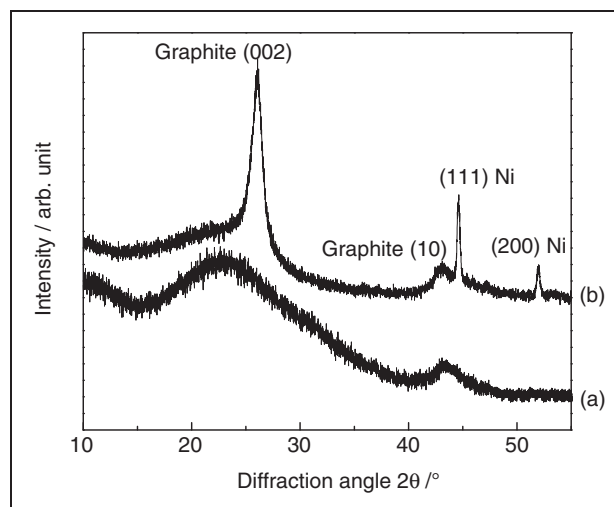


Figure 15. WAXD profiles of carbon fibers from (a) neat PVA nanofibers carbonized at 1500 °C, and (b) PVA/Ni nanofibers carbonized at 1200 °C.

presence of Ni metal particles induced the formation of a graphite-like structure at a lower carbonization temperature of 1200 °C. However, the sharp peaks at $2\theta = 44.6^\circ$ and $2\theta = 52^\circ$ in PVA/Ni derived carbon fiber indicated the (111) and (200) reflection of Ni metal respectively, no other peaks of Ni-oxide or Ni-iodide crystallite were observed.⁵⁷ In addition, the reduction growth of Ni-nanoparticle (Ni^0) was resulted from interaction of Ni^{2+} and reducing agent C, where C might contribute from either the ligand (CH_3COO^-) or the PVA polymer which was not investigated in this study. The crystallite size (D_p) of Ni-nanoparticle was measured from the WAXD data using Scherrer formula, where diffraction curves were fitted by Gaussian function. The D_p were found to be 29.62 nm for Ni (111) and 26.4 nm for Ni (200) which are comparable with the Ni nanoparticle sizes observed in the following TEM image (average size 30–40 nm).

Figure 16 describes the possible structural models of our carbon fibers derived from neat PVA and PVA/Ni.⁵² It shows that the carbon fiber with Ni particle has more ordered structure and longer graphene layer than the neat one, which is further supported by the TEM images of carbon fibers derived from PVA/Ni nanofibers shown in Figure 17. In TEM images other than Ni nanoparticles, the curvy layer-like structure confirms the presence of a graphene layer.⁴⁶ So the carbon fibers are believed to show an ordered structure in a very short range and show disordered structure in the long range. The interlayer spacing in a graphite sheet is known to be approximately 0.33 nm,³³ and in this case, the spacing was ascertained to be ca. 0.35 nm. These results reveal the formation of a turbostratic graphite-like structure in the

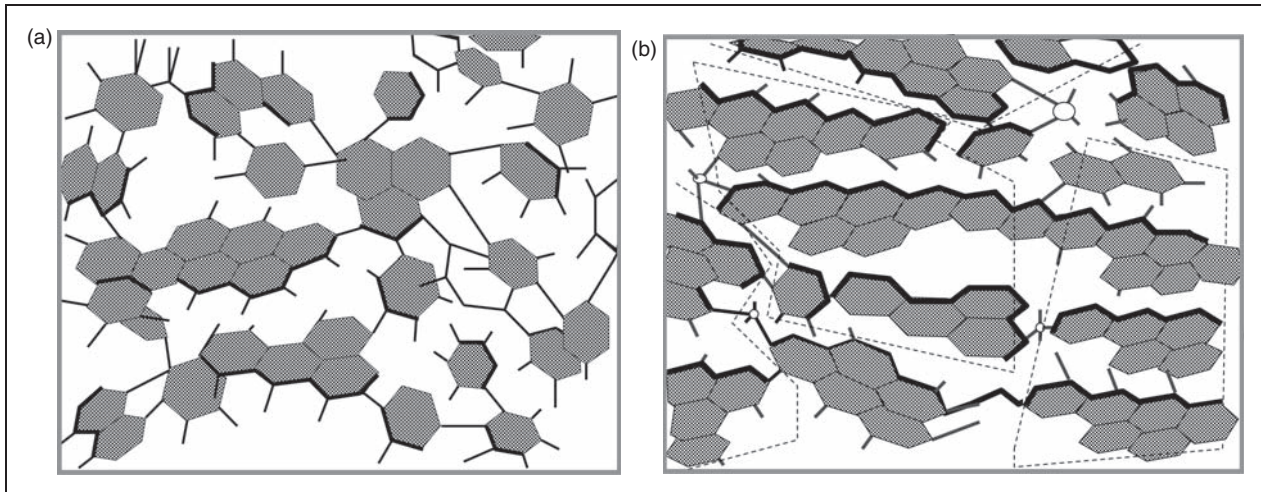


Figure 16. Possible structural models of carbon fibers derived from (a) neat PVA, (b) PVA/Ni (adapted from⁵²). The dotted lines in Figure 16(b) indicate the ordered stacking of carbon structure.

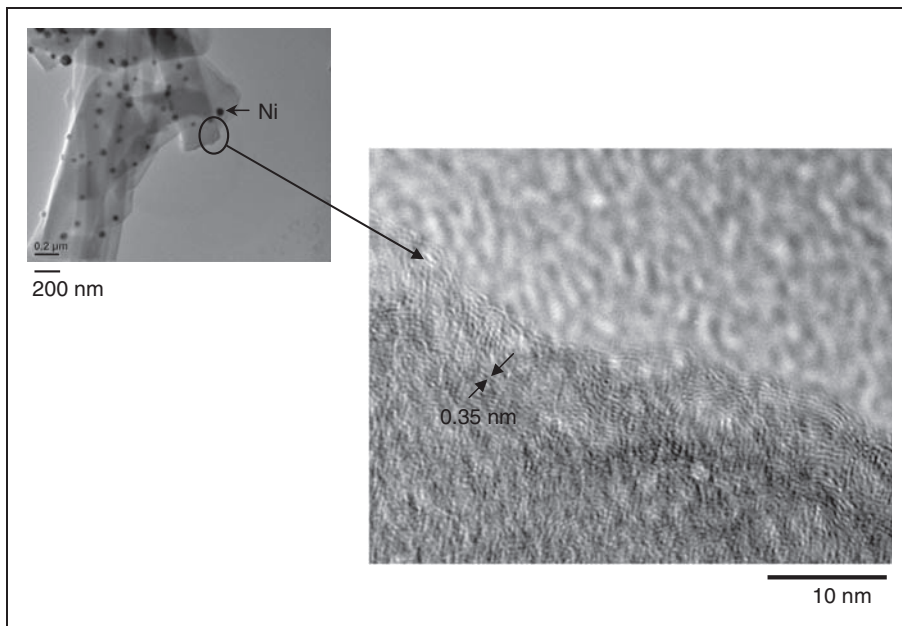


Figure 17. TEM images of PVA/Ni nanofibers carbonized at 1200°C.

PVA/Ni nanofibers carbonized at a low carbonization temperature of 1200 °C.

In addition, the carbon yield was noticeably increased from 21 to 34% after Ni addition. It is feasible that Ni stabilizes intramolecular volatile components during heating, which leads to higher carbon yield. Thus, it can be said that Ni improves the carbonization efficiency of the PVA polymeric precursor as a source of carbon material. Furthermore, the derived carbon fiber expectantly possessed splendid magnetic property due to the presence of Ni nanoparticles.⁵⁷

Conclusions

A simple and effective method was developed to fabricate carbon fibers from precursor PVA nanofibers prepared by ES followed by iodine treatment. Iodine causes structural changes of the PVA nanofibers and imparts thermal stability to endure the carbonization process, which results in improved carbon yield. In this study, 24 h iodination time and carbonization at 1200 °C for 24 h were found to be favorable to obtain good carbon fibers in terms of the structural parameters and carbon yield.

Furthermore, Ni metal nanoparticles were successfully incorporated into the PVA nanofibers using a spinning solution doped with Ni-acetate, which increases the conductivity of the spinning solution. Constant spinning was possible with incorporated Ni when using a lower polymer concentration than that used for pure PVA nanofibers. Moreover, the carbon fiber derived from a PVA/Ni nanofiber precursor resulted in smaller fiber diameter and higher carbon yield. The results also revealed that Ni significantly accelerates the formation of the ordered graphite structure, even at a lower carbonization temperature of 1200 °C.

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