

Phenolic Resin-Based Carbon Thin Fibers Prepared by Electrospinning: Additive Effects of Poly(vinyl butyral) and Electrolytes

By Shinji IMAIZUMI,¹ Hidetoshi MATSUMOTO,^{1,2} Kenichi SUZUKI,¹ Mie MINAGAWA,¹ Masaru KIMURA,³ and Akihiko TANIOKA^{1,2,*}

Phenolic resin-based carbon nanofibers with a diameter of about 110 nm, the highest electrical conductivity of 5.29 S/cm and highest BET specific surface area of 792.7 m²/g were prepared by electrospinning, followed by successive carbonization. The addition of a high-molecular-weight polymer, poly(vinyl butyral) ($M_w = 340,000$), and electrolytes, pyridine and sodium carbonate, to the phenolic resin/MeOH solution can effectively form a thinner smooth fiber by electrospinning, and then the as-spun fabrics were successfully carbonized at 900 °C for 2 h. Thus the prepared carbonized fabrics are very flexible and showed a thinner diameter, a higher conductivity and a higher specific surface area as already described.

KEY WORDS: Electrospinning / Carbon Nanofiber / Phenolic Resin / Flexibility /

Recently, carbon nanofibers with a high conductivity, chemical stability, and mechanical strength have attracted much attention in many fields including electrodes, capacitors, emitters, catalyst supports, sorbents, filter media, and reinforcements.^{1,2} It has been pointed out that a smaller diameter gives rise to the higher electrical conductivity of the single carbon fiber and higher specific surface areas of carbon fabrics.³ In addition, a two- or three-dimensional carbon nanofiber network with a high conductivity is a promising material for flexible electronic and optical devices.⁴ Therefore, carbon nanofibers or nanofibrous fabrics with thinner diameters are required.

Electrospinning is a straightforward method based on an electrohydrodynamic process for forming continuous thin fibers.^{5–7} The advantages of electrospinning are (i) forming nano-microscaled fibers and (ii) the one-step forming of the two- or three-dimensional nanofiber network structure. On the other hand, the internal structures are irregular due to rapid solidification during electrospinning.⁸ Therefore, the reported mechanical properties of the carbonized fibers by electrospinning have not been very good. To overcome this disadvantage, we have reported the preparation of novolac phenolic resin-based carbon fabrics composed of microscaled fibers by electrospinning.⁹ The major advantage of the phenolic resin as the precursor of the carbon fibers is thermal stability leading to a dimensional stability after carbonization (curing of the as-spun fibers also improves the thermal stability). Another advantage is the high microporosity of the carbonized fibers (phenolic resin is well-known as a material for activated carbon). Therefore, the phenolic resin-based carbon fabrics were dimensionally stable, flexible, and highly porous. However, since the molecular weight of the phenolic resin is not

very high, the spinnability is low and the formation of a fiber thinner than a micron has been difficult to date.⁹

For electrospinning, the fiber diameter depends on the solution properties (*e.g.*, viscosity, conductivity, surface tension, permittivity, and boiling point) and/or operating conditions (*e.g.*, applied voltage, nozzle-to-target distance, and flow rate). Particularly, the viscosity and electric conductivity of the spinning solutions are crucial factors for controlling the fiber diameter.^{5,10–12} The high-molecular-weight polymers are effectively fabricated into thinner and homogenous fibers by electrospinning.¹³ The addition of electrolyte to the spinning solution also enhances the electrostatic repulsion force on the surface of the jet during electrospinning, and consequently, the diameter of the electrospun fibers decreases.^{6,7} In the present study, we attempted to prepare thin phenolic resin fibers through electrospinning by controlling both of the viscosity and conductivity of the polymer solution. We add a high-molecular-weight polymer, poly(vinyl butyral) ($M_w = 340,000$), and two kinds of weak electrolytes, pyridine and sodium carbonate, for controlling the solution properties of the spinning solution. The goal of this investigation is to prepare dimensionally-stable, flexible, porous, and thin carbon nanofiber fabrics from phenolic resin by electrospinning, followed by successive curing and carbonization.

EXPERIMENTAL

Materials

The phenolic resin (PhR, novolac resin, $M_w = 4,000–5,000$) was obtained from Gunei Chemical Industry, Japan. Poly(vinyl butyral) (PVB) with a molecular weight of 340,000 was

¹Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

²Laboratory for Innovation in Nanofibers Founded by New Energy and Industrial Technology Development Organization, NEDO, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

³Gun Ei Chemical Industry Co., Ltd., 700 Shukuorui-machi, Takasaki 370-0032, Japan

*To whom correspondence should be addressed (Tel: +81-3-5734-2426, Fax: +81-3-5734-2876, E-mail: tanioka.a.aa@m.titech.ac.jp).

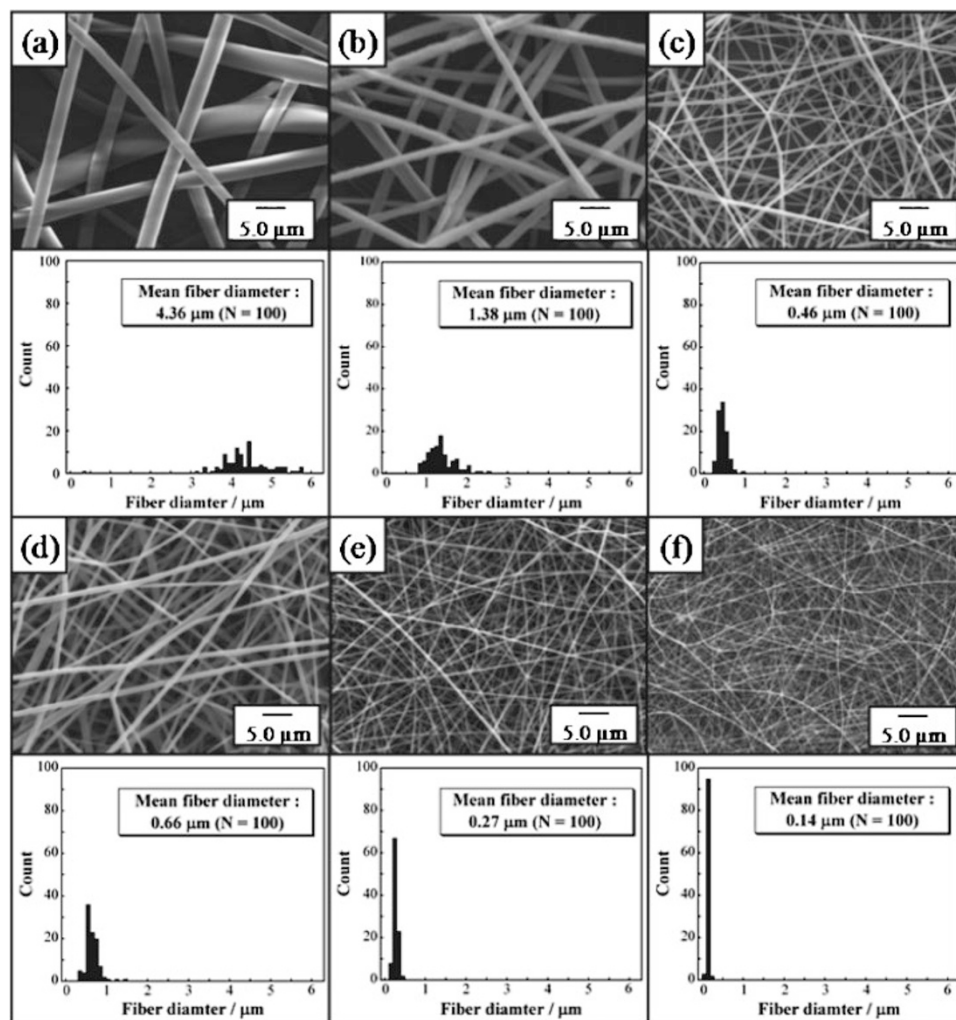


Figure 1. Surface SEM images and fiber diameter distribution of typical as-spun phenolic resin fibers from the following solutions: (a) PhR and PVB-110k with MeOH (P1 solution in Table I), (b) PhR and PVB-340k with MeOH (P12 solution), (c) PhR and PVB-340k with MeOH and Py (P21 solution), (d) PhR, PVB-340k, and Na_2CO_3 with MeOH (P23 solution), (e) PhR, PVB-340k, and Na_2CO_3 with MeOH and Py (P24 solution), and (f) PhR, PVB-340k, and Na_2CO_3 with MeOH and Py (P25 solution).

purchased from Wako, Japan. Methanol (MeOH), pyridine (Py), and sodium carbonate (Na_2CO_3) of extra-pure grade were obtained from Wako, Japan. These reagents were used without further purification. The PhR and PVB were dissolved in MeOH to form 10–45 wt % solutions.

Solutions Properties

The viscosities of all the solutions were measured by an oscillating-type viscosity meter (VM-100A, CBC Materials, Japan). The solution conductivities were measured using a conductivity meter (MM-60R, TOA, Japan) and a conductivity cell (CT-57101B, TOA, Japan). The surface tensions of the polymer solutions were determined by the pendant drop method using an analyzer (DropMaster 500, Kyowa Interface Science, Japan). All measurements were done at 25 °C.

Electrospinning

The electrospinning device is the same as that used in our previous study.⁹ The electrospinning device consists of a

syringe-type infusion pump (MCIP-III, Minato Concept, Japan), a high voltage regulated DC power supply (HDV-20K 7.5 STD, Pulse Electronic Engineering, Japan), and a grounded substrate (aluminum sheet, 100 × 100 mm² area). The polymer solutions were contained in a syringe with a stainless steel nozzle (0.5 mm internal diameter). The applied voltage was 15 kV, the distance between the tip of the nozzle and the collector was 150 mm, and the flow rate of the solution was 0.01 mL/min. The electrospinning was carried out at 25 ± 1 °C and at less than 35% relative humidity.

Curing and Carbonization

The as-spun phenolic resin fabrics were cured by adding formaldehyde and then carbonized at 900 °C in a ceramic furnace for 2 h under a continuous nitrogen purge.⁹

Characterization of Fabrics

The surface morphologies of the phenolic resin fabrics before and after carbonization were observed using a scanning

Table I. Compositions and physical properties of spinning solutions

Sample number	Phenolic resin (wt %)	PVB (wt %)	MeOH (wt %)	Pyridine (wt %)	Na ₂ CO ₃ (wt %)	Viscosity (mPa sec)	Surface Tension (mN/m)	Conductivity (mS/m)	Fiber diameter (μm)
P1 ^a	43.6	1.4 ^b	55			49.8	24.1	0.55	4.36
P2	43.6	1.4	55			103.0	—	0.31	4.98
P3	44.1	0.9	55			69.1	26.7	0.26	4.14
P4	44.5	0.5	55			40.4	24.7	0.25	2.99
P5	38.8	1.2	60			55.4	28.0	0.24	4.10
P6	39.2	0.8	60			36.3	30.3	0.22	2.47
P7	39.6	0.4	60			21.1	32.3	0.22	1.91
P8	33.5	1.1	65			30.8	33.0	0.23	2.39
P9	34.3	0.7	65			17.9	34.5	0.27	1.59
P10	34.6	0.4	65			11.4	—	0.07	1.33
P11	29.1	0.9	70			12.5	39.6	0.56	1.88
P12	29.4	0.6	70			9.33	42.1	0.28	1.38
P13	29.7	0.3	70			6.08	42.5	0.30	0.93

P14	29.4	0.6	63	7		11.9	24.1	17.11	1.05
P15	29.4	0.6	56	14		15.1	24.5	16.70	1.01
P16	29.4	0.6	49	21		17.5	25.3	18.40	0.97
P17	29.4	0.6	14	56		36.6	32.8	5.24	1.44
P18	24.5	0.5	67.5	7.5		6.35	24.9	16.20	0.68
P19	24.5	0.5	60.0	15.0		7.99	25.3	14.25	0.57
P20	24.5	0.5	52.5	22.5		9.16	25.6	18.51	0.54
P21	24.5	0.5	45	30		10.4	26.5	18.40	0.46

P22	23.997	0.6	70		0.003	9.92	35.2	2.64	0.68
P23	23.97	0.6	70		0.03	8.92	39.6	9.35	0.66

P24	12.73	2.25	51	34	0.02	18.0	51.7	6.40	0.27
P25	7.9	2	54	36	0.1	9.67	50.9	40.10	0.14

^aP1 was prepared in our previous study.⁹ ^bPVB-110k.

electron microscope (SEM, SM-200, Topcon, Japan) operated at 10 kV. All SEM samples were sputter-coated with Au. The adsorption isotherms and the Brunauer-Emmett-Teller (BET) specific surface areas¹⁴ of the carbonized fabrics were determined using an adsorption apparatus (ASAP 2010, Micromeritics, USA). Carbon dioxide was selected as the probe molecule. The electrical conductivities along the surface direction of the fabrics (10 × 20 mm²) were measured by a four-point probe method using a low resistivity meter (Loresta-EP MCP-T360, Mitsubishi Chemical, Japan).

RESULTS AND DISCUSSION

Preparation of Thin Phenolic Fiber by Electrospinning

Our previous paper showed that the addition of PVB (PVB-110k, $M_w = 110,000$) to the PhR/MeOH solution improved the electrospinnability (Figure 1a, and ref 9). To prepare thinner fibers by electrospinning, we added to the high-molecular-weight polymer (PVB-340k, $M_w = 340,000$) an organic electrolyte (Py) and an inorganic electrolyte (Na₂CO₃). The following four series of solutions were prepared: (i) PhR and PVB-340k with MeOH, (ii) PhR and PVB-340k with MeOH and Py, (iii) PhR, PVB-340k, and Na₂CO₃ with MeOH, and (iv) PhR, PVB-340k, and Na₂CO₃ with MeOH and Py. The composition and properties of the spinning solutions are listed in Table I. Figure 1 shows the SEM images and fiber diameter distributions of the typical as-spun phenolic resin fibers from the various series of solutions.

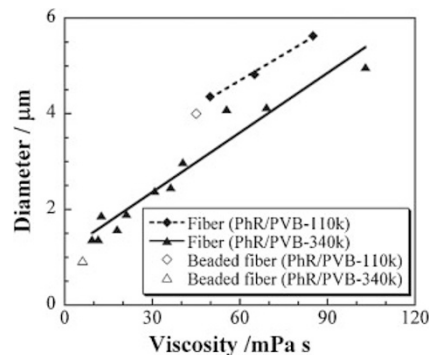


Figure 2. The effect of solution viscosity on the diameters of the as-spun fibers.

Additive Effect of High-Molecular-Weight Polymer

Figure 2 shows the effect of the solution viscosity on the diameter of the as-spun fibers. The more viscous solution tends to form a thicker fiber. The addition of high-molecular-weight PVB-340k improved the electrospinnability from the lower-viscosity solution (the thresholds between beaded fiber and smooth one for PVB-340k and PVB-110k are 10 mPa s and 45 mPa s, respectively) and we grew a thinner fiber (Figure 1b). The diameter of the thinnest smooth fiber in this series (P2-P13 in Table I) was 1.33 μm from the P10 solution (Figure 1b), but the fiber diameter distribution is comparatively large. We used the fiber from P12 solution with a diameter of 1.38 μm and narrow diameter distribution for the next carbonization.

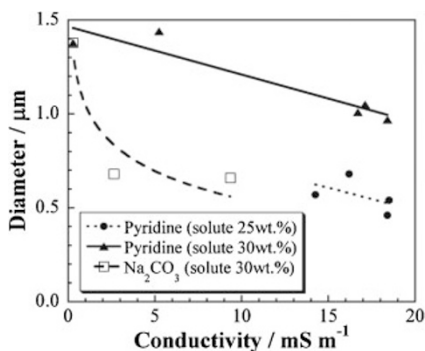


Figure 3. The effect of solution conductivity on the diameters of the as-spun fibers.

Additive Effect of Electrolytes

In general, the addition of electrolytes to the spinning solution increases the solution conductivity and enhances the formation of the field-induced electric charges causing electrostatic repulsion on the surface jet. This effect allows the forming of thinner fibers by electrospinning.¹¹

We first used Py as the organic electrolyte (P14-P21 in Table I). The advantage of the organic electrolyte, such as Py, is that it is evaporated during spinning and does not remain in the as-spun fiber. The addition of Py was effective for forming thin fibers (Figure 3). The thinnest fiber diameter in this series (P14-P21 in Table I) was 0.46 μm from the P21 solution (Figure 1c). Figure 3 shows that fiber diameter linearly decreases with an increase in solution conductivity due to the addition of Py.

We next examined the additive effect of an inorganic salt (P22 and P23 in Table I). We selected Na_2CO_3 as the electrolyte. The solution conductivity increased with an increase in the amount of Na_2CO_3 (Table I). Figure 3 shows that the fiber diameter logarithmically decreased with an increase in the solution conductivity due to the addition of Na_2CO_3 . The thinnest fiber diameter in this series (P22 and P23 in Table I) was 0.66 μm from the P23 solution (Figure 1d).

To prepare much thinner fibers by electrospinning, we added electrolytes of both Py and Na_2CO_3 to the polymer solutions (P24 and P25 in Table I). The addition of both electrolytes achieved the desired synergetic effects, and we definitely prepared the as-spun fibers with diameters of 0.27 μm and 0.14 μm from the P24 and P25 solutions, respectively (Table I, Figure 1e and 1f).

Carbonization and Characteristics of Carbon Nanofiber Fabrics

The as-spun phenolic resin fabrics were cured by adding formaldehyde along with the acid catalyst to improve the dimensional stability before carbonization. We selected three kinds of as-spun fabrics with the average fiber diameters of 4.36, 1.38, and 0.14 μm for the carbonization. Na_2CO_3 was removed during neutralization of the as-cured fabric using ammonium hydroxide. The PVB was completely decomposed during the carbonization.

Figure 4 shows the surface SEM images and a photo image of the carbonized fabrics. The carbonization yield was around 50%. Free standing (size: 10 \times 10 cm^2 ; thickness: see Table II)

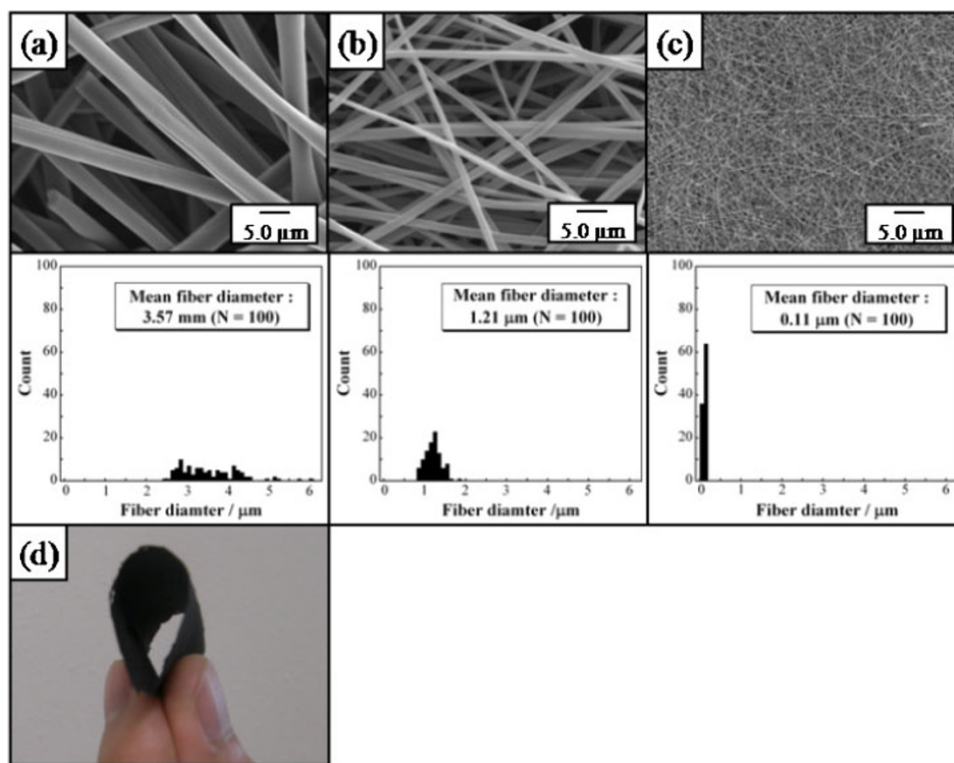


Figure 4. Surface SEM images and fiber diameter distribution of carbon fiber fabrics for (a) C1, (b) C2 and (c) C3, in Table II, and (d) a photograph of C2.

Table II. Physicochemical properties of carbon fiber fabrics

Sample	Average fiber diameter (μm)		Thickness (mm)	Electrical conductivity (Scm ⁻¹)	BET specific surface area (m ² g ⁻¹)
	as-spun	carbonized			
C1 ^a	4.36	3.50	0.348	0.72	495.0
C2	1.38	1.23	0.080	1.75	607.8
C3	0.14	0.11	0.015	5.29	792.7

^aC1 was prepared in our previous study.⁹

and flexible (see Figure 4d) carbon fiber fabrics were obtained. Figure 4 demonstrates that the carbonization decreased the fiber diameter. The thinnest diameter of the prepared carbonized fiber was 110 nm (Figure 4c). Table II shows the physicochemical properties of the carbonized fiber fabrics. The electrical conductivities increased with a decrease in the fiber diameter of the carbon fabrics; the conductivity of the fabrics with the diameter of 3.50 μm was 0.72 Scm⁻¹, whereas that of the fabrics with the diameter of 110 nm increased to 5.29 Scm⁻¹. This would be due to an increase in the fiber-fiber connections in the fabrics based on a decrease in the fiber diameter (see Figure 4). The BET specific surface area of the carbon fabrics was in the range of 495.0–792.7 m² g⁻¹, and increased with a decrease in the fiber diameter. This is caused by the high porosity of the phenolic-resin-based carbon material⁹ and the increase in the surface area with a decrease in the fiber diameter.

CONCLUSION

In the present study, we prepared thin phenolic resin fibers through electrospinning by controlling both the viscosity and conductivity of the spinning solution. We accomplished a good formation of the thin phenolic-resin fiber with a diameter of 140 nm through electrospinning by the combined use of a high-molecular-weight polymer (PVB-340k) and two kinds of electrolytes (Py and Na₂CO₃). After curing and carbonization of the as-spun fabrics, flexible carbon fiber fabrics with a diameter of 110 nm were obtained. In addition, the carbonized fabrics with a thinner diameter showed a higher conductivity, a higher specific surface area, and flexibility. The prepared carbon fabrics with a diameter of 110 nm had the highest electrical conductivity of 5.29 Scm⁻¹, and BET specific surface area of 792.7 m² g⁻¹. The prepared thin carbon fibrous fabrics with a high conductivity and high porosity are promising

materials for flexible electronic devices, such as a field emitter,¹⁵ photochemical cell,^{16,17} and batteries.¹⁸

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