

## Electrospinning of Direct Carbonizable Phenolic Resin-based Nanofibers

Yutaka Kawahara\*

Division of Environmental Engineering Science, Gunma University, 1-5-1, Tenjin-cho, Kiryu 376-8515, Japan

### Abstract

To produce the precursor fibers with nano-scale diameter for carbon nanofibers (CNFs), the electrospinning was attempted using water as the solvent of the spinning dope. For this purpose, directly carbonizable resolphenol formaldehyde resin not requiring its post cure treatment was used instead of conventional novolac type. The electrospinning could be made by hybridizing PVA and enhancing the electrospinnability. The as-electrospun fibers, however, were still so hydrophilic that the fibers were fused each other due to the moisture absorption. By hybridizing water-soluble feather keratin as a third component, whole fusion of electrospun fibers could be suppressed although some of the fibers were still partially fused. The electrospun fibers obtained will be applicable as a precursor for the production of non-woven CNF fabrics through direct carbonization.

**Keywords:** Electrospinning; Phenolic resin; Nanofibers; Direct carbonization

### Introduction

Carbon nanofibers (CNFs) as fillers have attracted considerable interest in recent years [1,2]. For the production of CNFs, novolacphenol formaldehyde resin is one of the most attractive candidates. The precursor fibers for CNFs can be produced through melt-spinning of novolacphenol formaldehyde resin at 100-110°C using a conventional melt-spinning apparatus followed by the post cure treatment with formaldehyde. The post cure treatment, however, is the lengthy process, e.g. the precursor fibers should be soaked in an acid solution containing hydrochloric acid and formaldehyde and heated to 110°C at 0.2°C/min and held for 16 h to cure the resin [3]. Therefore, in the present study, directly carbonizable resolphenol formaldehyde resin not requiring its post cure treatment was used instead of novolac type. Moreover, the electrospinning [4] was attempted to obtain nano-scale fibers directly using water as the solvent of resolphenol formaldehyde resin at room temperature. The electrospinning using water as the solvent is highly attractive from the viewpoints of safety as well as productivity. An explosion-proof structure is not necessary to the electrospinning apparatus. Accordingly, thinner CNFs will be produced from the direct carbonization [5] of as-electrospun resolphenol formaldehyde resin-based nanofibers.

In this paper, the electrospinning conditions for the production of resolphenol formaldehyde resin-based fibers was reported.

### Materials and Methods

#### Materials

Water-soluble resolphenolic resin (resol type IG-1002, nonvolatile: 50%) was supplied by DIC Co. (Tokyo, Japan). Water-soluble feather keratin powder (KERATIDE<sup>®</sup>, Mw: 1.5-2.0 kDa) was supplied by Toyo Feather Industry Co., Ltd. (Kanagawa, Japan). Polyvinyl alcohol (PVA, Mw: 66,000-79,200, saponification value: 96 mol%) was purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and used as received. Other chemicals used in this study were all laboratory-grade from Wako Pure Chemical Industries, Ltd.

#### Electrospinning

The total nonvolatile concentration of the spinning dope was kept constant at 10 wt% changing the composition of the materials (Table 1).

Electrospinning was conducted at room temperature in ambient air with the setup shown in Figure 1. The solution was loaded into a glass

Test No.	1	2	3	4
Concentration of dope, wt%	10	10	10	10
Mass ratio, %				
Water-soluble phenolic resins	80	60	50	0
Water-soluble keratin	0	30	40	70
PVA	20	10	10	30
Spinning conditions				
Applied voltage between the tip of nozzle and collector, kV	10.0	13.5	12.0	13.5
Flow rate of the polymer solution, microliter/min	5.0	1.5	1.5	5.0
Rotation speed of collector, rpm	90	90	60	90

Table 1: Electrospinning conditions.

syringe equipped with a stainless steel needle, which was connected to a high-voltage supply. The solution was continuously supplied using a syringe pump at a certain rate through the needle. The distance between the tip of the needle and the collector was approximately 13.5 cm.

Li et al. [6] demonstrated that electrospun fibers could be aligned parallel over long length scales during the spinning process by using a collector consisting of two conductive strips separated by a void gap of variable widths up to several centimeters. Thus, a collector consisting of several fins similar to a pinwheel was designed. The electrospun fibers spanning across two arbitrary fins were collected and used for further measurements.

#### Thermogravimetric analysis (TG)

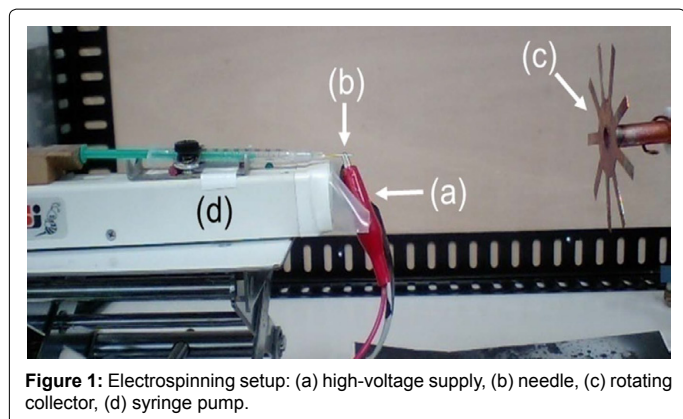
TG was performed using an analyzer (WS-002, Bruker AXS K.K., Yokohama, Japan) on a 10 mg sample prepared from No.3 dope in Table 1. The sample preparation procedure was as follows: a certain amount of the dope was dried at 60°C for 60 min. The obtained film was milled, and 10 mg was sampled. The TG measurement was made at a heating rate of 20°C/min, up to 800°C, under N<sub>2</sub> gas flow at 50 mL/min.

\*Corresponding author: Yutaka Kawahara, Professor, Division of Environmental Engineering Science, Gunma University, 1-5-1, Tenjin-cho, Kiryu 376-8515, Japan, Tel: +81 277 30 1491; E-mail: [kawahara@gunma-u.ac.jp](mailto:kawahara@gunma-u.ac.jp)

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**Figure 1:** Electrospinning setup: (a) high-voltage supply, (b) needle, (c) rotating collector, (d) syringe pump.

## Results and Discussion

When the electrospinning was made using an aqueous solution containing only the water-soluble resolphenol formaldehyde resin (w-ph), the electrospinning resulted in just spraying. To enhance the electrospinnability of the dope, PVA was hybridized. It was found that the spinning dope hybridizing PVA to the amount of 20%, i.e. the mass ratio of PVA vs. w-ph of 1:4 on a nonvolatile base was enough to secure the stable spinning. The spinning conditions were summarized in Table 1, No.1. The rotation speed of the collector reached 90 rpm, and the as-electrospun fibers could span across arbitrary outermost peripheral parts of the fin-collector.

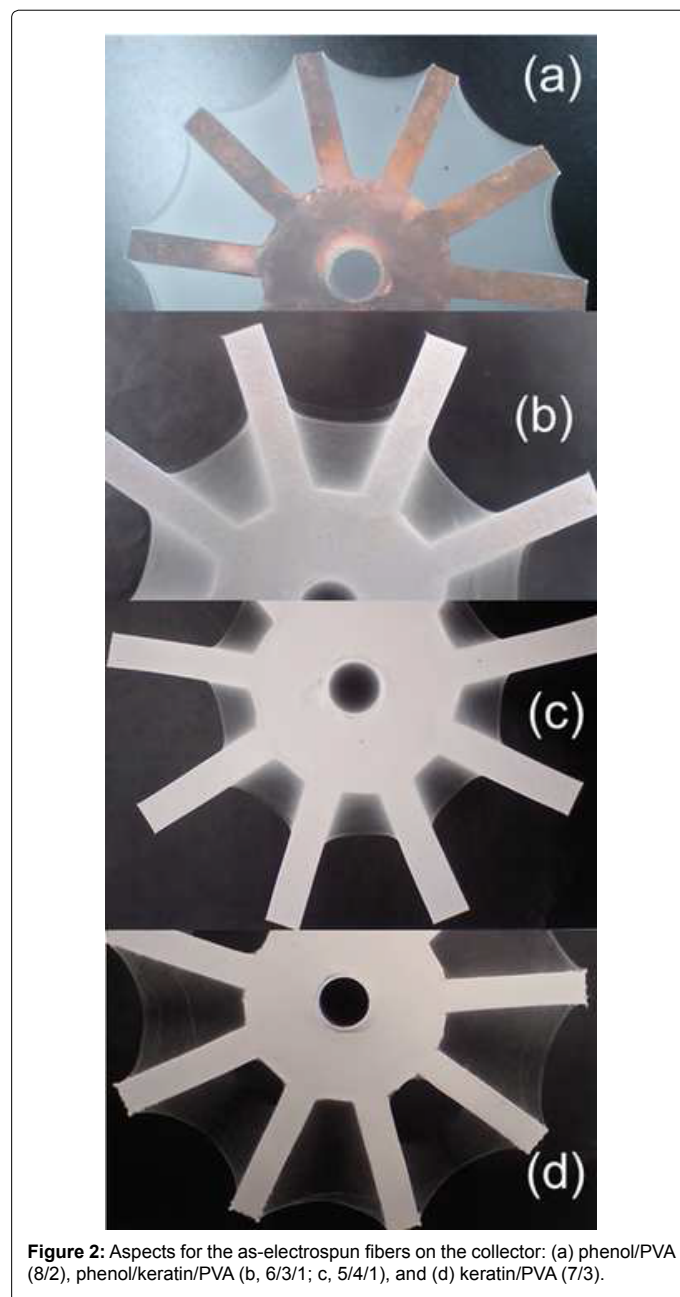
With the geometrical configuration of the collector used in this study, when the fibers were collected across two arbitrary fins, they experienced a strong stretching force due to Coulomb interactions between the positive charges on the fibers and the negative imaginary charges on the grounded fins, i.e. electrodes [6]. Thus, the electrospun fibers tended to be aligned in parallel across the gap between the two fins.

The as-electrospun fibers, however, were still so hydrophilic that the fibers were fused each other due to the moisture absorption and were converted into a sheet of film (Figure 2a). To suppress the fusion of the electrospun fibers, water-soluble feather keratin (w-fk) was hybridized as a third component. W-fk tends to self-assemble as the solvent water vaporizes [7]. Moreover, L-proline contained in w-fk will promote the carbonization of resolphenol formaldehyde resin through co-carbonization reactions [8], which is attractive when the as-electrospun fibers are converted into CNFs through carbonization. It was found that the spinning dope hybridizing w-fk to the amount of 30%, i.e. w-ph/w-fk/PVA=6/3/1, was enough to secure the spinning (Figure 2b). The spinning conditions were summarized in Table 1, No. 2. However, in this case, the electrospun fibers could span across less than half-length of the fins at the same rotation speed used for w-ph/PVA spinning, which means that the electrospinnability was lowered by adding w-fk. When the w-fk fraction in the dope was increased to 40%, the coating area of the fins by the electrospun fibers further decreased even though the rotation speed of the collector was lowered to 60 rpm (Table 1, No. 3 and Figure 2c). When the w-fk fraction in the dope exceeded 40%, spanning across the fins became difficult.

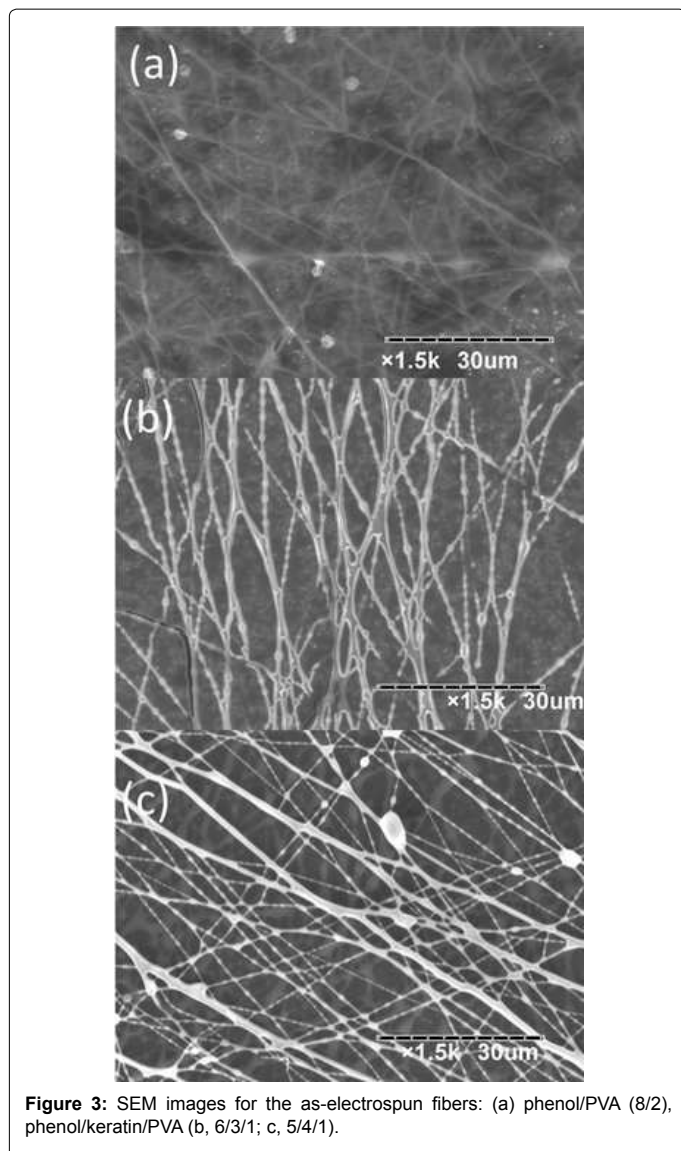
Electrospinnability is greatly influenced by Berry number of the spinning dope [9-11]. Berry number ( $Be$ ) is defined as the product of the polymer concentration ( $c$ ) and the solution intrinsic viscosity ( $[\eta]$ ), i.e.  $Be=c[\eta]$ . The average molecular weight of w-fk was no more than 2 kDa, which may reduce the viscosity of the dope and lower the electrospinnability. However, in the case of PVA and w-fk spinning system, electrospinning could be made even though the w-fk fraction

was increased to 70% (Figure 2d). The spinning conditions were summarized in Table 1, No.4. The decrease in electrospinnability for the w-ph/w-fk/PVA system was probably due to the occurrence of molecular interaction. Aspects of the as-electrospun fibers are shown in Figure 3. It is seen that the as-electrospun fibers were still partially fused (Figure 3b and 3c). The addition of w-fk could not prevent the fibers from fusing each other. However, non-woven CNF fabrics may be producible after carbonization. On the other hand, PVA nanofibers with the diameter less than ca. 300 nm can be crystallized by the water vapor annealing at room temperature [12], which will be useful to handle the non-woven fabrics.

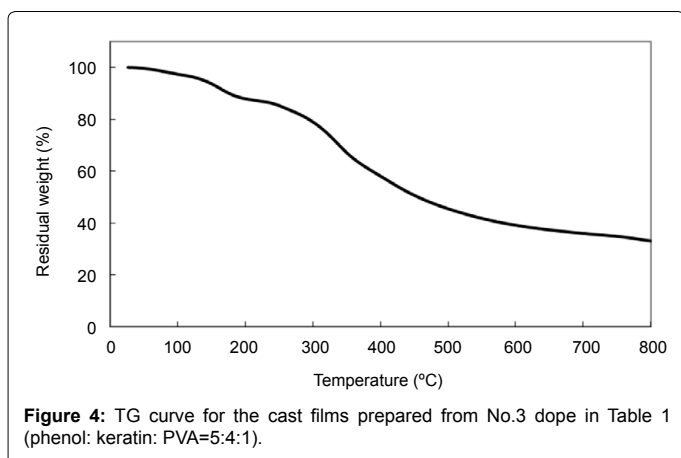
The TG curve for the cast films prepared from No.3 dope in Table 1 is shown in Figure 4. The yield of charcoal at 800°C was 33.1%. The yield of charcoal was defined as the relative mass of charcoal against the



**Figure 2:** Aspects for the as-electrospun fibers on the collector: (a) phenol/PVA (8/2), phenol/keratin/PVA (b, 6/3/1; c, 5/4/1), and (d) keratin/PVA (7/3).



**Figure 3:** SEM images for the as-electrospun fibers: (a) phenol/PVA (8/2), phenol/keratin/PVA (b, 6/3/1; c, 5/4/1).



**Figure 4:** TG curve for the cast films prepared from No.3 dope in Table 1 (phenol: keratin: PVA=5:4:1).

mass of the starting sample. The yield of PVA-based charcoal at 800°C was no more than 5% [13]. Therefore, considering the composition of the cast film, the carbon yield exceeding 30% seems to be brought about

by the co-carbonization effect between the w-ph and w-fk [8].

## Conclusion

To produce the precursor fibers with nano-scale diameter for CNFs, the electrospinning was attempted using water as the solvent of the spinning dope. For this purpose, directly carbonizable resolphenol formaldehyde resin not requiring its post cure treatment was used instead of conventional novolac type. The electrospinning could be made by hybridizing PVA and enhancing the electrospinnability. The as-electrospun fibers, however, were still so hydrophilic that the fibers were fused each other due to the moisture absorption. By hybridizing water-soluble feather keratin as a third component, whole fusion of electrospun fibers could be suppressed although some of the fibers were still partially fused. The electrospun fibers obtained will be applicable as a precursor for the production of non-woven CNF fabrics through direct carbonization.

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