CARBON NANOFIBERS PREPARATION FROM PAN NANOFIBERS BY COTTON CANDY METHOD

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Abstract

The cotton candy method was used for preparing polyacrylonitrile (PAN) nanofibers. Molecular weight (MW) of PAN was $15 \times 10^4$ and $20 \times 10^4$ g/mol. The PAN was dissolved by N-Methyl-2-pyrrolidone (NMP). The concentration of PAN solution was varied at 3-10 wt%. The PAN solution was spun through the plunger at the speed of 100 and 1,000 rpm at air pressure of 0.2 MPa. The collecting distances were set at 20, 40, 60 and 80 cm. Morphology of the fibers was observed by scanning electron microscope. The PAN nanofibers were successfully formed at 10 wt% of PAN MW $15 \times 10^4$ g/mol and 5 wt% of PAN MW $20 \times 10^4$ g/mol. The fiber diameter decreased when increasing the collecting distances. The average fiber diameter was around 400-650 nm. The glass transition temperature and the oxidative degradation increased when increasing the concentration of PAN. Raman spectrometry of carbon nanofiber by PAN fibers from CoCaM showed high crystallinity and stretched strongly and alignment.

Introduction

Polyacrylonitrile (PAN) are generally made into micro- and nano-size fibers by wet or dry spinning, dry-wet jet spinning, pre-gelled gel spinning, electrospinning and the process called pressurized gyration [1-8]. The examples of PAN fibers are produced by solution or dry-jet wet spinning because the high polarity of nitrile groups makes the polymer infusible [3-4]. PAN is generally used as a precursor for carbon fiber production by oxidative stabilization continuing with carbonization process as well as for composites fibers and various applications [4-10].

Recently, electrospinning has been known for the fabrication of nanofibers. Various polymers have been successfully electrospun into ultrafine fibers in recent years mostly in solvent solution and some in melt form [10-14]. Thomson et al [12] reported about effects of parameters i.e. volumetric charge density, distance from nozzle to collector, initial jet radius, relaxation time and viscosity on nanofiber diameter from electrospinning model. The important knowing was the effect of jet radius for process control and prediction nanofibers production. Electrospinning is required high voltage and presented low productivity. An optimal method for making nanofiber with high productivity and low cost is required and developed.

The cotton candy method (CoCaM) is a novel method that can create a lot of nanofiber. CoCaM is a process of forming a fiber with only air injection [15-17]. Wongpajan et al [15] reported on the fabrication of poly(lactic acid) (PLA) nanofibers by CoCAM. From this study, the optimum condition of PLA nanofibers was at the nozzle temperature of 250 °C with controlled the air pressure of 0.2 MPa. The average diameter of PLA nanofibers was 500 nm by yielding the productivity of 140 g/h. Therefore it is possible to make a cost saving by CoCaM because it does not require heating and the electric field as well as provided fibers at high productivity.

In this study, the solution spinning of the cotton candy method (CoCaM) is proposed. This process is an innovative process for spinning nanofibers from polymer solutions using plunger force and air pressure flow for fiber forming. PAN was dissolved using N-Methyl-2-pyrrolidone (NMP), NMP is a colorless liquid and miscible with water. The effects of PAN molecular weight, solution concentration and processing parameters on PAN fiber morphology and fiber diameter were investigated. In addition, we focused on carbon nanofiber (CNF) in the carbon-based nanomaterial’s field. CNF is expected to various applications. However, the CNF have a high cost of production. Therefore we are trying to reduce a cost to make a preparation of precursor of the CNF by using PAN nanofibers from CoCaM.

Experimental

Materials and Sample Preparation

Polyacrylonitrile (PAN) with MW $15 \times 10^4$ g/mol was obtained from Sigma-Aldrich Corporation, USA. PAN
with MW $20 \times 10^4$ g/mol was supplied by Polysciences, Inc., USA. N-Methyl-2-pyrrolidone (NMP) was used as solvent, which was manufactured by Nacalai Tesque, Inc., Japan.

PAN was dissolved in NMP. The solution concentrations were 3, 5 and 10 wt%. The Solution Plunger Spinning Technique (SPST) of the cotton candy method was used in this research. Figure 1 illustrates the schematic of the solution plunger apparatus. A nozzle has three holes for feeding solution, which are located above an air outlet. The solution was feeding in a hopper, after that it was blown and stretched by air. The stretched PAN solution was collected on a mesh and deposited as PAN fibers. The plunger speed was set at 100 rpm and 1000 rpm with air pressure of 0.2 MPa. The collecting distances were varied from 20, 40, 60 and 80 cm. After dried at room temperature, a thin layer of PAN fibers was carefully taken off from the collector and dried at 60 °C at least 12 h before observing morphology.

Figure 1. Illustration of the solution plunger process.

Carbonization of carbon nanofiber was carried out in two steps. The first step is flame-proofing. The nano PAN fibers were heated at room temperature to 270 °C with heating rate of 5 °C /min, held for an hour under compressed air atmosphere.

In the second step, carbonizing was carried out. The flame-proofed fibers were heated until 1400 °C with heating rate 7 °C/min then held at 1400 °C for 10 minutes in nitrogen atmosphere.

Characterization

Morphology of fiber was observed using scanning electron microscope (SEM, JSM 5200 JEOL, Japan). The diameters of the fibers were measured using ImageJ software.

Thermal properties of fibers were analyzed by differential scanning calorimetry (MDSC2920, TA Instruments, USA). The fibers of about 5 mg were placed and sealed in an aluminum pan. The fibers were heat at room temperature to 400 °C at heating rate of 10 °C/min under nitrogen atmosphere.

Raman spectroscopy was performed using a Jasco NRS-2100, with laser excitation line at 532 nm. Spectra were collected 5s exposure time, 5 accumulations, and a laser power of 100mW.

Results and discussion

Effect of Molecular weight and concentration on PAN Fibers Morphology

PAN solution was sprayed from the nozzle, which forced by constant plunger speed and air pressure. Figure 2 presents SEM photographs of PAN fibers forming of 3 wt% to 10 wt% at MW $15 \times 10^4$ g/mol. It can be seen layer of PAN film at 3wt% and 5 wt%. On the other hand, the PAN fibers was clearly seen at 10wt% concentration of MW $15 \times 10^4$ g/mol.

Figure 2. SEM photographs of PAN fibers with MW $15 \times 10^4$.

Figure 3. presents SEM photographs of PAN fiber with MW $20 \times 10^4$ g/mol. The PAN fibers were formed at all concentration, especially at 5wt% and 10 wt%. At 3wt% the shape of the PAN product has some of small fiber that is shown in Figure 3 (a). On the other hand, fine PAN fibers are clearly presented at 5wt% and 10wt% of MW $20 \times 10^4$ g/mol as depicted in Figure 3 (b) and (c), respectively. Hence, the morphology changed from the film to the uniform fiber shape when increased concentration and MW of PAN. Nevertheless, at 10wt%,
the viscosity of the PAN was high, which had to increase the plunger speed to 1,000 rpm.

![SEM photographs of PAN fibers with MW 20×10⁴.](image)

**Effect of Collecting Distance on PAN Fibers Morphology**

The effect of distances between the nozzle and the collector on fiber morphology at 10wt% of MW 15×10⁴ g/mol is shown in Figure 4. Fiber diameters are summarized in Figure 5. Figure 4 presents SEM photographs of PAN fibers at 10wt% of MW 15×10⁴ g/mol with various collecting distances. The PAN fibers seemed to be finer when increasing the collecting distance. However, amounts of the fibers decreased at higher collecting distance, which was due to low volume of PAN solution at longer position from the nozzle. It can be noted that the fibers were agglomerated and combined together.

![Effect of collecting distance on morphology of PAN fibers with MW 15×10⁴.](image)

Figure 5 (a) and (b) illustrate fiber distribution and fiber diameters at various collecting distances of MW 15×10⁴. The distributions of fibers were narrow. The average diameters were around 495 nm to 510 nm. At this PAN concentration, the fiber diameters are nearly at all collecting distance as depicted in Figure 5.

![Effect of collecting distance on (a) fiber distribution and (b) fiber diameter of PAN fibers with MW 15×10⁴.](image)

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Figure 4 and Figure 7 present fiber morphology and fiber diameter of PAN 5 wt% of MW 20×10⁴ g/mol. From Figure 6, it can be seen that the PAN fibers were fine and straight at all collecting distances. The number of fibers decreased when increasing the distance from the nozzle to the collector. The fiber distribution was broad. The average diameter was about 550 nm to 650 nm as depicted in Figure 7 (a). At higher PAN molecular weight, the fiber diameter decreased with increasing the collecting distance as shown in Figure 7 (b). From the results, the collecting distance of 40 cm was selected for reproducibility for higher productivity of PAN fibers, which was less of remaining solution and good yields of PAN fibers.

![Effect of collecting distance on (a) fiber distribution and (b) fiber diameter of PAN fibers with MW 15×10⁴.](image)
Figure 6. Effect of collecting distance on morphology of PAN fibers with MW $20 \times 10^4$.

Figure 7. Effect of collecting distance on (a) fiber distribution and (b) fiber diameter of PAN fibers with MW $20 \times 10^4$.

## Thermal Properties of PAN fibers

Figure 8 illustrates DSC thermogram of PAN fibers with 10 wt% of MW $15 \times 10^4$ and 3-5 wt% of MW $20 \times 10^4$ g/mol. Thermal properties are summarized in Table 1. In Figure 8, it can be seen the endothermic slope of glass transition temperatures ($T_g$) and the exothermic peak of oxidative transition temperature of the PAN fibers. $T_g$ of the PAN fibers was around 91 °C to 153 °C. The oxidative transition temperature was about 290 °C to 320 °C. Both glass transition temperature and the oxidative transition temperature were varied according to PAN concentration and molecular weight. The values were increased with increasing the concentration. The oxidative degradation temperature will be applied for thermal stabilization of the PAN fibers precursor before carbonization to carbon nanofiber production.

![DSC thermogram of PAN fibers](image)

**Figure 8.** DSC thermogram of PAN fibers.

**Table 1.** Thermal properties of PAN fibers.

<table>
<thead>
<tr>
<th>MW (g/mol)</th>
<th>Content (wt%)</th>
<th>$T_{g1}$ (°C)</th>
<th>$T_{g2}$ (°C)</th>
<th>Oxidative transition (°C)</th>
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<tr>
<td>$15 \times 10^4$</td>
<td>10</td>
<td>129.4</td>
<td>-</td>
<td>315.8</td>
</tr>
<tr>
<td>$20 \times 10^4$</td>
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<td>109.9</td>
<td>132.2</td>
<td>290.7</td>
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<tr>
<td></td>
<td>5</td>
<td>91.8</td>
<td>153.4</td>
<td>320.0</td>
</tr>
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</table>

## Carbonization of Carbon Nanofibers

The Raman spectra of carbon nanofibers are shown in Figure 9. D band has a very shape peak at 1342 cm$^{-1}$ and FWHM of D peak is 66.95. G band has a small peak at 1573 cm$^{-1}$ and FWHM of G peak is 23.87. These peaks separate completely. The ratio of the D and G peak intensities ($I_D/I_G$) is 2.59. This value indicates high crystallinity of carbon nanofiber. It is guessed that nanofiber fabricated from PAN nanofibers by CoCaM is stretched strongly and polymer chain is aligned.
**Figure 9. Raman spectra**

**Conclusions**

PAN solution spin from the nozzle was varied at different solution concentrations, molecular weights and collecting distances. Fine PAN fibers were yielded at concentration of 10wt% at MW $15 \times 10^4$ g/mol and 5 wt% at MW $20 \times 10^4$ g/mol. At higher molecular weight, fiber diameters decreased when increasing the collecting distances. The reproducibility of PAN fibers would be selected at the collecting distance of 40 cm. The average PAN fibers was around 400-650 nm. The oxidative transition temperature was about 290–320 °C for using as thermal stabilization temperature of the PAN fibers precursor. The solution spinning technique from the cotton candy method presented the convenience to operate and produce PAN nanofibers. Raman spectrometry of carbon nanofiber showed high crystallinity and good alignment by using PAN nanofibers from CoCaM.

**References**