Morphologies and Tensile Strength of Metallized Hybrid Nanofibers

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ABSTRACT

We report that the metal-deposited single nanofibers can be successfully prepared by a combined technique of electrospinning and metallization. The tensile strength of the metal-deposited single nanofibers was investigated by recently developed tensile test machine. The tensile strength of 50 nm Cu-deposited (ca. 480 MPa) single nanofibers was clearly higher than that of pure polymer (ca. 110 MPa) single nanofibers, which is attributed to the formation of metallic hard-coating layers onto the surface of single nanofibers. In addition, we investigate the annealing behavior of Cu/Ni deposited nanofibers to find out optimum conditions enabling to prepare the metal alloy nanofibers.

Keywords: metallized nanofibers, electrospinning, metallization, tensile strength, single nanofibers

1 INTRODUCTION

When the diameters of polymer fiber materials are shrunk from micrometers to nanometers, there are several amazing characteristics such as very large surface area to volume ratio, flexibility in surface functionalities, and superior mechanical performances. These outstanding properties make the polymer nanofibers to be optimal candidates for many important applications, such as electronics, medicine, sensor, and controlled release technology, etc [1-4]. However, despite of the potential mentioned above, the application of nanofibers has been limited due to its poor mechanical properties. Therefore, the development of a novel method is required to improve the mechanical properties of the nonwoven nanofiber webs as well as single nanofibers.

Recently, we have succeeded in preparation of the metal (Cu)-deposited hybrid nanofiber webs by using a combined technique of electrospinning and metallization. It was found that metal-deposited hybrid nanofiber webs exhibited higher mechanical properties and enhanced surface resistivity depending on the thickness of the deposited metal layers [5]. This result has triggered to investigate in detail the morphologies and mechanical properties of the metal-deposited hybrid single nanofibers. However, until now a few studies for evaluating the mechanical properties of single nanofibers have been reported [6-8]. Recently, we have also reported the mechanical properties of single nanofibers by using developed tensile test machine [8], and demonstrated that the test machine is well operated for measurement of mechanical properties of nano/micro-sized fibers. In this study, we attempt to prepare the Cu or Cu/Ni deposited hybrid nanofibers using electrospun nanofibers as a template, and explore the annealing conditions, such as annealing temperatures and times, to find out optimum annealing process for the alloy nanofibers. The tensile strength and morphologies of the Cu-deposited and Cu/Ni metallized nanofibers will be reported.

2 EXPERIMENTAL

2.1 Materials

The polystyrene (PS, degree of polymerization ~ 2000) and polyacrylonitrile (PAN, Mw ~ 150k g/mol) were purchased from Wako and Aldrich, respectively. The polyurethane (PU, ca. 14 wt%) stock solution, which is currently used for mass production electrospinning, was kindly provided by TECHNOS Co., Ltd., Japan [8]. The PU nanofiber webs (500 $\pm$ 50nm in diameter) used for metallizing were kindly supplied by Finetex EnE, Inc. Korea. High purity copper (99.99%, wire-cut) and Nickel (99.9% up, grains 2-5mm) were purchased from Kojundo Chemical Laboratory Co., Ltd., Japan. All chemicals were of analytical grade and used without further purification.

2.2 Electrospinning

To investigate the tensile strength of single nanofibers, we prepared the pure polymer (PS, PAN, and PU) single nanofibers and Cu-deposited single PU nanofibers by using a combined technique of electrospinning and metallization, respectively [5, 8-12]. In order to produce electrospun nanofibers, a high-voltage power supply (Har-100*12, Matsusada, Co., Japan) was used as the source of the electric field. The PS was dissolved in DMF, and the concentration of PS solution was ca. 35 wt%. The PAN solutions of 15 wt% dissolved in DMF were used for electrospinning. Each polymer (PS, PAN, and PU) solution was supplied through a plastic syringe attached to a capillary tip with an inner diameter of 0.6 mm. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution, and a negative electrode (cathode) was attached to a metallic collector. The voltage was controlled at the range of 8-10 kV. The distance between the capillary tip and the collector was fixed to be 15 cm. All solutions were electrospun onto a rotating metallic collector at room temperature under identical conditions. The diameters of the obtained PS, PAN, and PU nanofibers were found to be ca. 700, ca. 400 nm, and ca. 500, respectively.

2.3 Metallization

A system UEP-6000 (ULVAC, Inc. Japan) was used to deposit a metallic layer onto the organic nanofibers. A high-purity target copper (99.99%) and nickel (99.9% up) were mounted on the vapor plate, and each nanofiber web was fixed on the rotating holder with a side facing the target. The distance between the target and the substrates was fixed 400 mm, and the vacuum pressure and the power was set at 2.0 x 10^{-3} Pa and 10 kV, 270 mA, respectively. The deposition rate of the metallic layer was controlled to be about 1.0 Å/sec (copper deposition) and 0.2 Å/sec (nickel deposition), respectively. All depositions were performed on both sides of nanofibers, and the Cu/Ni (9:1, in thickness) layers were prepared with the thickness of 90 nm Cu and 10 nm Ni.

2.4 Annealing Process

After the Cu/Ni metal depositions, in order to produce the alloy nanofibers, the obtained Cu/Ni metal-deposited nanofibers were placed into the alundum crucible, and annealed in the electric furnace under N_2 atmosphere. Annealing process was conducted at various annealing temperatures and times to find out the optimum conditions for metal alloy nanofibers. The annealing temperature and time were varied at the ranges of 400 ~ 900 ^oC and 3 ~ 24 hr under N_2 atmosphere, respectively. The heating rate was 5 ^oC/min.

2.5 Characterization

For determining the tensile strength of single nanofibers, we specially developed the test machine (FITRON NFR-1000, RHESCA Co., Japan, Fig. 1). The detailed descriptions (such as sampling, conditions, etc.) for measuring the tensile strength of the pure single nanofibers and metal-deposited hybrid nanofibers were well written in our previously reported paper [8,13]. The morphologies of Cu/Ni metallized nanofibers were characterized by field emission scanning electron microscopy (FE-SEM) (Hitachi model S-5000).

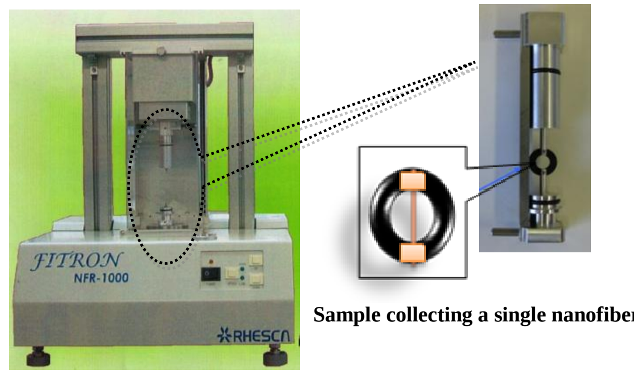

Figure 1: Specially developed tensile test machine for the measurement of single nanofibers.

3 RESULTS AND DISCUSSION

3.1 Tensile strength of Pure and Metal-Deposited Single Nanofibers

Fig. 2 shows typical stress-strain curves of pure PS and PAN single nanofibers at room temperature. These curves show a peculiar characteristic of the plastics and elastomers, which is obviously different from the metals. Moreover, compared to PU single nanofibers (~ 170 MPa, in Table 1), both PS and PAN single nanofibers exhibited higher modulus, suggesting that the PS and PAN are more brittle. The tensile strength of PAN single nanofiber (ca. 3.6 GPa) was certainly higher than that of PS single nanofiber (ca. 0.8 GPa), whereas the Young`s modulus of PS single nanofiber (ca. 47.7 GPa) was slightly higher than that of PAN single nanofiber (ca. 18.5 GPa). That is, the mechanical properties of single nanofibers were quite different depending on the physicochemical properties of pure polymers used (PS, PAN, and PU).

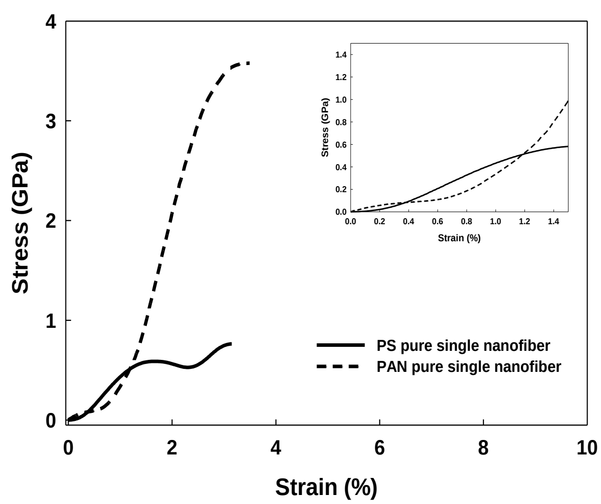

Figure 2: Stress-strain curves of pure PS (solid line) and pure PAN (dotted line) single nanofibers (load: 10mN, loading speed: 10 μm/s).

In addition, the tensile strength of pure PU, 30 nm and 50 nm Cu-deposited single PU nanofibers at room temperature were also carried out, and summarized in Table 1. As seen in Table 1, the tensile strength of the Cu-deposited PU single nanofibers were increased with increasing the thickness of deposited copper layer. Compared to pure PU nanofibers (ca. 170 MPa), Young`s modulus for the Cu-deposited PU nanofibers with the copper layers of 30 nm and 50 nm were increased to ca. 610 MPa and ca. 750 MPa, respectively, due to the formation of metallic hard-coating layers onto the surface of PU nanofibers [8]. As seen in Fig. 3a, it was observed that the PU nanofibers had an amorphous structure, whereas the Cu 50 nm-deposited hybrid PU nanofibers clearly showed typical crystalline peaks (Fig. 3b), suggesting the successful deposition of metals on the surface of the nanofiber template. The three peaks are observed at $2\theta=43.58^o$, 50.08^o, and 73.58^o, corresponding to the (111), (200), and (220) reflections [5], respectively. Through these facts, it is expected that the Cu-deposition onto the PU nanofibers would be a useful method to control the tensile strength of single PU nanofiber.

Table 1: Mechanical properties of pure PU single nanofiber and Cu-deposited PU nanofibers with different thickness of the layers

Thickness of copper layer	Tensile Strength (GPa)	Young`s Modulus (GPa)	Elongation at Break (%)
Pure PU	0.11	0.17	65.2
30nm	0.54	0.61	82.0
50nm	0.48	0.75	68.4

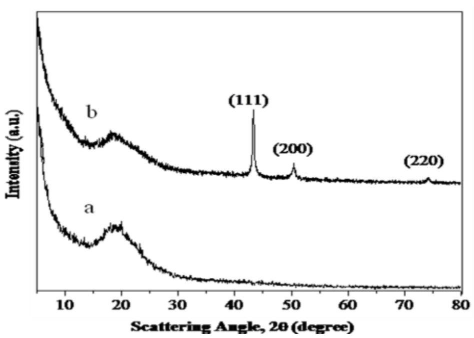

Figure 3: XRD patterns of pure PU nanofibers (a), 50 nm Cu-deposited PU nanofibers (b).

3.2 Morphologies of the Metallized Nanofibers

3.2.1. Effect of Aging Time

In general, the surface morphology of electrospun nanofibers is smooth and uniform, whereas the surface of metal-deposited nanofibers becomes rough, suggesting the successful deposition of metallic layers onto the surface of nanofiber template [5]. Fig. 6 shows FE-SEM images of the Cu/Ni deposited PU nanofibers annealed at 600 ^oC for different aging time under N_2 atmosphere. The atomic composition of the Cu/Ni double-layer was controlled to be Cu : Ni = 9 : 1 in thickness of each layer. Firstly, it should be noted that even after removal of the nanofiber template by annealing process, the fibrous morphologies were satisfactorily conserved. As seen in FE-SEM images at higher magnification (Fig. 6, insets), the irregular shaped and different sized nanoparticles were observed, presumably indicative of the Cu (as a base fiber) and Ni (as a surface area) nanoparticles. Moreover, it seems that the different shaped nanoparticles were converged gradually as increasing the aging time, probably indicating that the Ni nanoparticles in the surface layer migrate into Cu base fiber [14]. In addition, it was also observed that the Cu/Ni metallized nanofiber webs became denser as increasing the aging time although the diameter of metallized fibers was not changed.

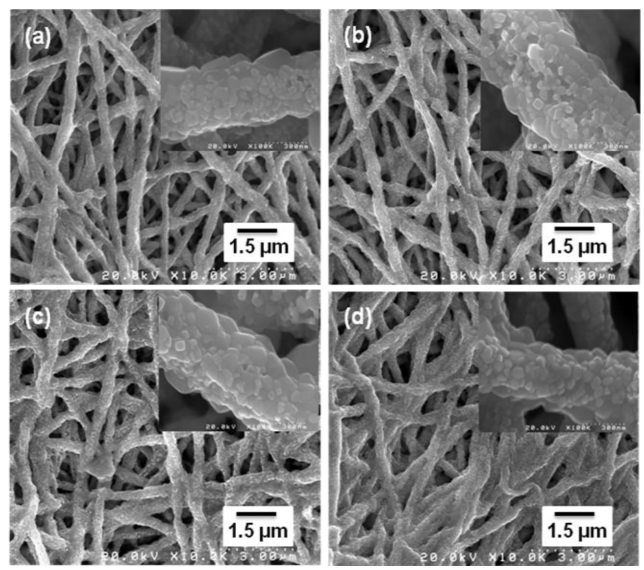

Figure 4: FE-SEM images of Cu/Ni (9:1, in thickness) double-layer coated PU nanofibers after annealing. The annealing process was carried out at 600 ^oC for 3 hr (a), 6 hr (b), 12 hr (c) and 24 hr (d), respectively.

The similar annealing phenomena were also observed at the annealing temperature of 400 ^oC. Fig. 6 shows FE-SEM images of the Cu/Ni deposited PU nanofibers annealed at 400 ^oC for different aging time under N_2 atmosphere. That is, the surface roughness of the Cu/Ni metallized nanofibers annealed at 400 ^oC became coarse and rough as increasing the aging time, which is the similar aging phenomena to the case of the annealed at 600 ^oC. This is not fully understood, but it could be considered that as the fiber diameter slightly decreased the segregation between Cu and Ni particles occurred.

3.2.1. Effect of Aging Temperature

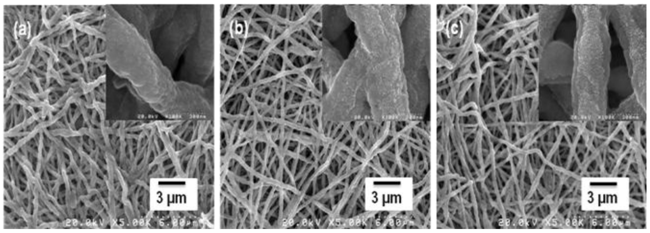

Figure 5: FE-SEM images of Cu/Ni (9:1, in thickness) double-layer coated PU nanofibers after annealing. The annealing process was carried out at 400 ^{o}C for 6 hr (a), 12 hr (b) and 24 hr (c), respectively.

Fig. 6 shows FE-SEM images of Cu/Ni deposited annealed at different annealing temperatures for 10 hr. As seen in Fig. 6a, before annealing the surface of metal-deposited hybrid nanofibers exhibited a rough surface morphology, which is ascribed to the formation of the metallic granular nanoparticles (ca. 23 nm), whereas the surface roughness of the pure nanofibers was smooth. Moreover, after annealing at 700 ^{o}C for 10 hr, the metallic granular nanoparticles grew to larger irregular shaped metal particles, which may be attributed to the massive copper migration and aggregation during annealing at higher temperature. The migration and aggregation of metal nanoparticles are probably driven mostly by the instability of metal atoms due to their high surface free energy, and therefore would produce thermodynamically stable particles with bigger sizes [14]. In addition, these micrographs show that sintering was observed in particles annealed at 900 ^{o}C. These results can be explained with the results by the variation in crystallite size due to annealing, as confirmed by FE-SEM analysis.

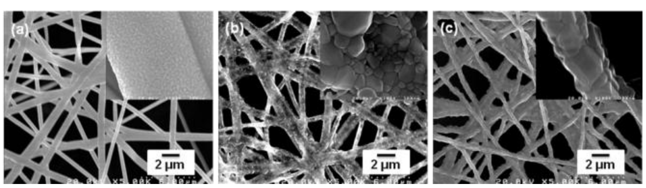

Figure 6: FE-SEM images of Cu/Ni (2:1, in thickness) deposited nanofibers before (a) and after annealing at 700 ^{o}C (b) and 900 ^{o}C (c) for 10 hr, respectively.

4 CONCLUSIONS

The tensile strength of metal-deposited single nanofibers were successfully evaluated by using specially developed the test machine. The tensile strength of 50 nm Cu-deposited (ca. 480 MPa) single PU nanofibers was clearly higher than that of pure PU polymer (ca. 110 MPa) single nanofibers, which is attributed to the formation of metallic hard-coating layers onto the surface of single nanofibers. As a result, it was concluded that the Cu-deposited layer onto the polymeric single nanofibers generally led to increase the tensile strength and young`s modulus of the single nanofibers. In addition, we investigated the annealing behavior of Cu/Ni deposited nanofibers to find out optimum conditions enabling to prepare the metal alloy nanofibers. By controlling the annealing conditions, such as temperatures and times, a great various results were obtained. Future work is in progress to investigate the crystal structure and formation mechanism of Cu/Ni alloy.

5 ACKNOWLWDGEMENTS

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