SUPERPARAMAGNETIC CORE/SHEATH COMPOSITE NANOFIBERS VIA COAXIAL ELECTROSPINNING

B.W. Ahn*, M.H. Hahn, T.J. Kang
Department of Materials Science and Engineering, Seoul National University, Seoul, Korea
* Corresponding author(felix0512@gmail.com)

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1 Introduction

One-dimensional magnetic nanostructures have recently attracted much attention because of their intriguing properties that are not realized by their bulk or particle form[1]. These nanostructures are also potentially useful for the application to ultrahigh-density data storage, as well as the sensor and bulletproof vest[2-4]. The magnetic particles in magnetic nanofibers of blending types can't fully align along the external magnetic field because magnetic particles are arrested in solid polymer matrix. To improve the mobility of magnetic particles, we used magneto-rheological fluid (MRF) having the good mobility and dispersibility. Superparamagnetic core/sheath composite nanofibers were obtained with MRF and poly-ethylene terephthalate (PET) solution via a coaxial electrospinning technique. Coaxial electrospinning is suitable for fabricating core/sheath nanofibers encapsulating MRF materials within a polymer sheath. The magnetite nanoparticles in MRF were dispersed within core part of the nanofibers. This study aimed to fabricate core/sheath magnetic composite nanofibers using coaxial electrospinning and characterize several properties. In this study, we report the successful fabrication of core/sheath structured magnetic nanofibers by coaxial electrospinning. Optimum conditions (flow rate, applied voltage and distance) to fabricate core/sheath structured magnetic nanofibers with uniform dispersion of magnetic nanoparticles in the core part were explored. The magnetic and mechanical features of the magnetic nanofibers were characterized.

2. Experimentals

2.1 Materials

Ferrofluid (EFH-1) was purchased from Ferrotec, USA. Poly-ethylene terephthalate (PET, M_w 19,200) bright chip was purchased from TORAY SAEHAN, Korea.

The magneto-rheological fluid (MRF) was fabricated by blending the mineral oil and ferrofluid. PET solution of 12 wt% was manufactured by dissolving PET into TFA.

2.2 Coaxial electrospinning

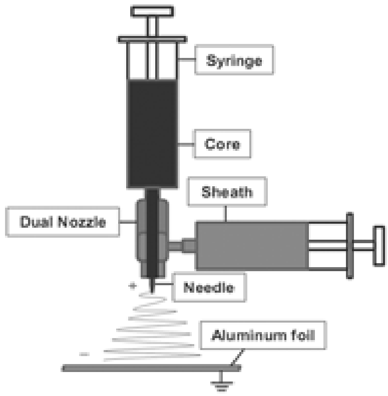

Fig.1. A schematic of the coaxial electrospinning

The coaxial electrospinning apparatus is shown in Figure 1. Coaxial electrospinning was performed with varying core and sheath flow rates to determine appropriate values. The basic components of the setup are composed of two syringe pumps, a high power voltage supply and a coaxial spinneret. The sheath and core flow rate varied to seek out optimum conditions. The applied voltages ranged from 15 to 18 kV. Distance between spinneret and collector was kept at 15 cm. The collect was an aluminum foil placed above a flat metal plate.

2.3 Characterization

The morphology was observed by using High Resolution-Transmission Electron Microscopy (HR-TEM, JEOL JEM-3010) and Field Emission-Scanning Electron Microscope (FE-SEM, JEOL JSM-6700F). The mechanical properties were analyzed by using Atomic Force Microscope (AFM, Park SYSTEMS XE-100). Lastly, magnetic behavior was measured using Superconducting Quantum Interference Device magnetometer (SQUID, Quantum Design MPMS XL5).

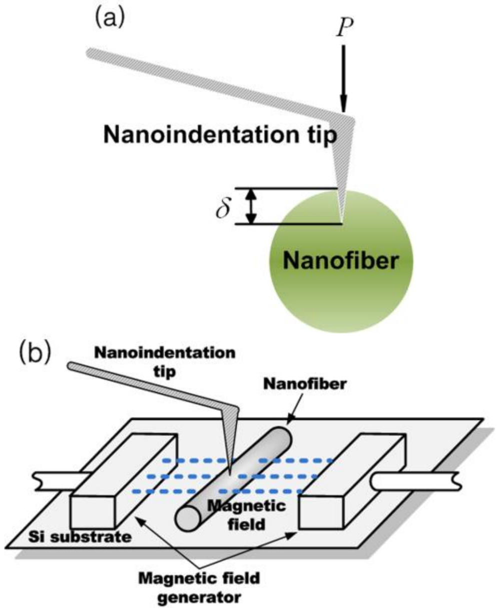

Fig.2. Schematic diagrams of (a) nanoindentation test and (b) nanoindentation test with a magnetic field generator.

The mechanical properties of core/sheath magnetic composite nanofibers were measured using nanoindentation. The samples for this test were collected on the Si wafer by coaxial electrospinning. The moduli are calculated using the Hertz theory from the load-indentation depth data[5]. The elastic modulus of one nanofiber was measured by nanoindentation method (Fig..2). A nanoindentation tip (pyramidal shape, Park system, Korea) and magnetic field generator (-0.03 ~ +0.03 T, Park system, Korea) were installed to atomic force microscope (AFM, XE-100, Park system, Korea). We observed the change in elastic modulus of one nanofiber when the external magnetic field was applied. The elastic modulus of nanofibers was calculated according to the following equations. The relative elastic modulus E_r is given by

$$E_r = \sqrt{\frac{9P^2}{16R_e\delta^3}}$$

where, P is the applied force, δ is the indentation depth, and R_e is the equivalent radius for a indenter in contact. R_e is given by

$$R_e = \sqrt{\frac{R_t^2 R_f}{R_t + R_f}}$$

where, R_t is the indenter tip radius (25 nm) and R_f is the radius of the nanofiber. R_f was determined by analysis of the height profile using AFM. Every measurement was done with the nanofibers which diameter was about 600±50 nm. The elastic modulus of nanofiber E_f is given by

$$E_f \approx E_r(1-\nu_f^2)$$

where, ν_f is the Poisson's ratio of the nanofiber (0.33).

3. Results and discussion

3.1 Morphology

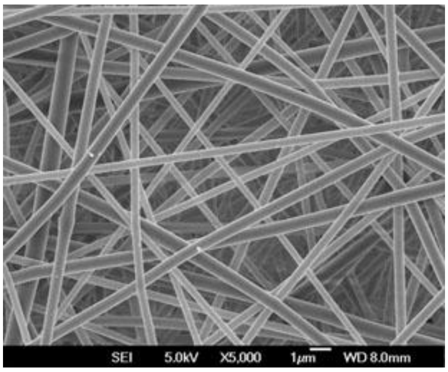

Fig.3. A SEM image of MRF/PET nanofiber.

SEM images of MRF/PET nanofibers were shown in Figure 3. The mean diameter of these nanofibers was 500~600 nm (Figure 4). For fabricating continuous core/sheath magnetic composite nanofibers, various parameters should be controlled such as applied voltage, solution viscosity, concentration, and flow rate etc. Among them, the immiscibility of two liquids is the key factor in manufacturing the core/sheath magnetic composite nanofibers. We prepared core/sheath magnetic nanofiber successfully with control of several parameters (Fig. 5). The mass ratio of mineral oil and ferrofluid was 1.5 :1. The flow rate of core and sheath fluid were 7 and 5 $\mu\ell$/min, respectively.

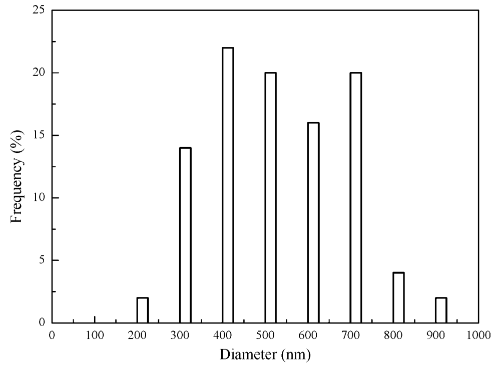

Fig.4. Diameter distribution of MRF/PET nanofibers.

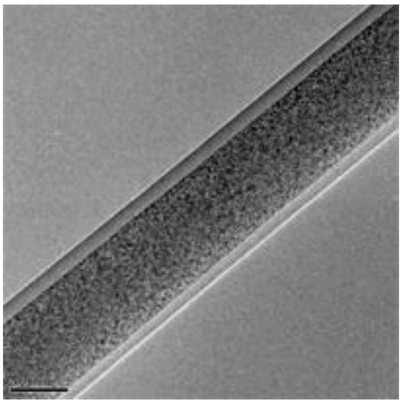

Fig.5. A TEM image of MRF/PET nanofiber.

3.2 Magnetic properties

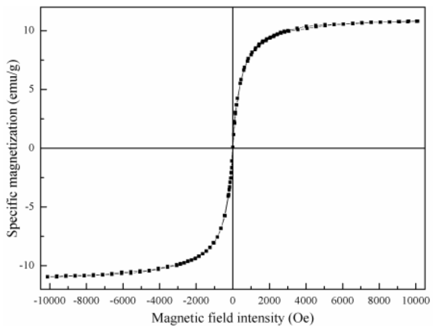

Fig.6. A magnetic curve of MRF/PET nanofibers.

Magnetic curves of MRF/PET nanofibers at room temperature are shown in Figure 6. The hysteresis loops of each nanofiber were that of a typical superparamagnetic material with small coercivity (12.32 Oe) and negligible remnant magnetization at zero field (0.42 emu/g). It is known that superparamagnetism is often observed for magnetic nanoparticles with sizes less than 10 nm. It also suggested that bulk Fe_3O_4 shows ferromagnetism because lager size domain of the bulk form induce alignment of magnetic dipole moments to be parallel for minimizing thermodynamic internal energy[6,7]. However, it is well known that even ferromagnetic materials show superparamagnetic behavior at room temperature when the particles size becomes dozens nanometers[7]. Therefore, the superparamagnetic behavior of each magnetic nanofiber may be related to the small particle size (5~10 nm). This critical diameter typically depends on the material properties. The saturation magnetizations, M_s, were 17.10 and 10.80 emu/g. It was considerably smaller than M_s of bulk iron (330 emu/g). This is general phenomenon of magnetic nanomaterials[6]. Figure 7 shows susceptibility of MRF/PET nanoweb as a function of magnetic field intensity.

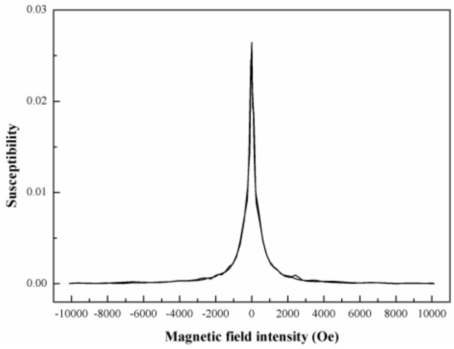

Fig.7. Susceptibility of MRF/PET nanofibers.

3.3 Nanoindentation

Figure 8 showed that loading and unloading curves for single core/sheath magnetic composite nanofiber with and without the magnetic field applied. When the external field applied, the loading and unloading curves shifted upward, indicating a significant increase in modulus of the sample. The improvement of modulus is thought to be related with the strong dipole-dipole interaction between magnetic nanoparticles occurred by alignment of magnetic nanoparticles with help of the great fluidity of the MRF. Table 1 presented mechanical properties calculated from Figure 8.

With the application of to the magnetic field, a distinct increase in modulus and hardness is observed. This indicates that the dipole-dipole interaction and exchange coupling effect of magnetic nanoparticles are the reason for the sharp increase in stiffness of the nanofiber.

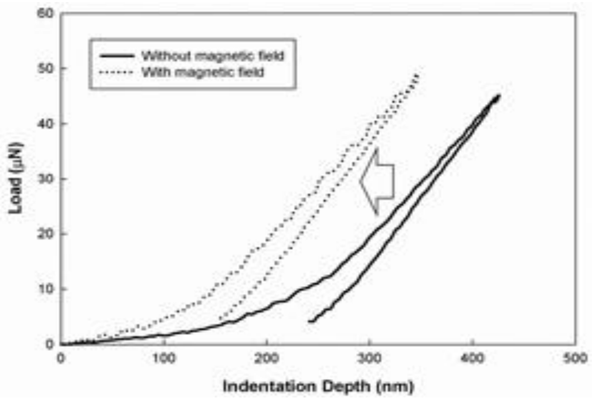

Fig.8. Load vs. displacement indentation curves of a single MRF/PET nanofiber when magnetic field was applied or not.

Table 1. Elastic moduli of MRF/PET nanofibers

	Elastic Modulus (GPa)	Diameter (nm)
Without Magnetic field	0.17	550 ± 50
With Magnetic field	0.28	550 ± 50

4. Conclusions

Also, the magnetic composite nanofibers having core/sheath structure were fabricated directly from coaxial electrospinning. Magnetic nanoparticles were uniformly distributed in the core part. Through the successful fabrication of the core/sheath magnetic composite nanofibers, the magnetic properties as well as mechanical properties with applied magnetic field were distinctly increased due to the dipole-dipole interaction between magnetic nanoparticles in MRF. The core/sheath magnetic composite nanofibers are expected to the many application fields such as the sensor or intelligent bulletproof vest because the core/sheath magnetic composite nanofibers are immediate response in external field.

Acknowledgement

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