

Effect of Viscosity on the Morphology of Electrospun Polyacrylonitrile Fibers as a Linear Actuator and Artificial Muscles

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ABSTRACT

Polyacrylonitrile (PAN) nanofibers, which are pH-sensitive and exhibit soft actuation as a linear actuator and artificial muscles, were prepared by electrospinning to investigate the effect of viscosity on the morphology of PAN fibers. Experimental results revealed that higher viscosity is critical for the formation of unbeaded nanofibers because surface tension is almost constant throughout the experiment. Uniform, smooth, and continuous fibers with diameters of about 700 nm were achieved for the 10 wt% PAN fibers at a flow rate of 0.5 mL/h and an electric field of 0.875 kV/cm.

Key words : Polyacrylonitrile (PAN), Electrospinning, Viscosity, Nanofiber, Artificial muscle

1. Introduction

As the understanding of the biological systems steadily increased, researchers came to realize that the natural world has the ubiquitous design of muscles to power diverse organisms from whales to microorganism, like bacteria. This realization prompted a shift in the traditional design paradigm based on motors-gears-bearing-links to a novel biomimetic scheme based on muscle-tendon-joint-bone connection.¹⁾ Polymer gels have been known to exhibit an interesting structure consisting of a tangled network of polymer chains immersed in a liquid medium, which is analogous to the muscle proteins observed in living creatures.^{2,3)} Polymers are classified into two groups: Nonelectrically deformable polymers^{2,3)} and Electroactive Polymers (EAPs).^{4,9)} The former is actuated by nonelectric stimuli, such as pH, light, temperature, etc. The latter is deformed by an electric field or the diffusion of ions.^{4,9)} Electronic polymers, such as electrostrictive, electrostatic, piezoelectric, and ferroelectric, require high activation electric fields (>150 V/mm) for the potential use in robotic applications.^{2,5)} In contrast, ionic EAPs, such as gels, polymer-metal composites, conductive polymer, and carbon nanotubes, require a low driving voltage (1~5 V).^{5,7)} However, ionic EAPs should be operated in a liquid state.

Polyelectrolyte gels are a special class of polymer systems consisting of a cross-linked polymer network with ionizable groups in a liquid phase. Polyelectrolyte gels are divided into two types: anionic and cationic polymer gels. Anionic

polymer gels have acid groups (-COOH), like the salts of polyacrylic acid, polystyrenesulfonic acid, and polyvinylphosphonic acid. These acid groups form -COOH- ions when the pH of the surrounding medium rises above its pKa (the negative logarithm of the acid dissociation constant representing the tendency of a compound to lose H⁺ ions). Anionic polymer gels swell and collapse at high and low pH values, respectively. On the other hand, cationic polymer gels have amonio groups, like polydimethyl-diallylammonium chloride, polyvinylpyridine hydrochloride, and polylysine hydrochloride. These amine groups form -NH₃⁺ when pH of the surrounding medium decreases below pKa. These gels swell and collapse at low and high pHs, respectively.

Unlike polyacrylic acid gels, stronger polyacrylonitrile (PAN) fibers exhibited a dimensional change of 70% within a few seconds when the system was moved from an acid to base as compared to polyacrylic acid gels, which took days or weeks. PAN is a homopolymer of acrylonitrile. Polyacrylonitrile is a vinyl polymer and a derivative of the acrylate family of polymers. PAN is made by free radical vinyl polymerization of the acrylonitrile monomer. The fiber is fire-proof after oxidation, and it is then called oxidized PAN or Oxypan. This process is considered to be a thermostabilization process where the PAN fibers are converted into infusible fibers due to which they stay intact during the carbonization process at very high temperatures to produce carbon fibers. Carbonization of the oxidized fibers is done at 3000°C in inert atmosphere that converts the fibers into 100% carbon. PAN fibers have more potential in the development of the linear actuator and artificial muscles.^{2,3)} In order to activate the PAN fibers as artificial muscles, two steps must be applied: preoxidation at 200 - 220°C and

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saponification (boiling them in 1 N LiOH for 30 min). Prior to the activation of the PAN fibers, the morphology of the as-spun PAN fibers was optimized in the present study by varying PAN concentrations.

2. Experimental Procedure

PAN powder (Aldrich Chemical Co., Inc., Japan) and dimethylformamide (DMF, Fisher Scientific) were used as a precursor. PAN powder was added to DMF solvent in a composition range of 4 to 10 wt%. The mixture was stirred with a magnetic stirrer until the lumps of the powder was broken up and well dispersed. Then, the mixture was stirred at temperatures between 40~50°C for 20 min. The white disperse mixture turned into transparent light yellow solution after heating. The PAN/DMF solution was heated for the least possible time to avoid the vaporization of the solvent, which alters the concentration of the solution. The precursor PAN/DMF solution was then filtered by using a sintered glass filter (16~40 μm) to remove possible impurities in the solution.

The electrospinning apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22 gage B-D metal needle, a grounded collector and a high voltage supply (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with current and voltage digital meters.^{10,11} The solution was placed in a 5 mL B-D luer-lok syringe attached to the syringe pump and was fed into the metal needle at a flow rate of 0.5 mL/h. A piece of flat aluminum foil was placed 14 cm below tip of the needle to collect the nanofibers at a DC voltage of 16 kV. The as-spun nanofibers were dried for 5 h in air.

The surface tension of the solution was measured by using a Nima tensiometer (DST9005, dynamic tensiometer). The kinematic viscosity was measured with a 200 gage Cannon-Fenske viscometer, while the density was measured by pycnometer. The dynamic viscosity was calculated from kinematic viscosity and density data.¹¹ The diameter and the morphology of the fibers were evaluated using a scanning electron microscope (SEM, Hitachi S-3000H, Japan). All specimens were coated with Au/Pd to ensure higher conductivity. For SEM observation, PAN fibers were collected by placing silicon wafers on the aluminum foil during electrospinning.

3. Results and Discussion

The properties of different concentrations of polymer solutions are given in Table 1 and Fig. 1. It is observed that the

Table 1. Properties of the PAN/DMF Solution

PAN concentration (wt%)	Surface tension (mN/m)	Density of solution (g/mL)	Kinematic viscosity (mm ² /sec)	Dynamic viscosity (cP)
4	32.8±1	0.9537	48.7	46.4
6	33.6±1	0.9717	171.4	166.5
8	32.8±1	0.9766	557.8	544.7
10	33.8±1	0.9794	1548.6	1516.7

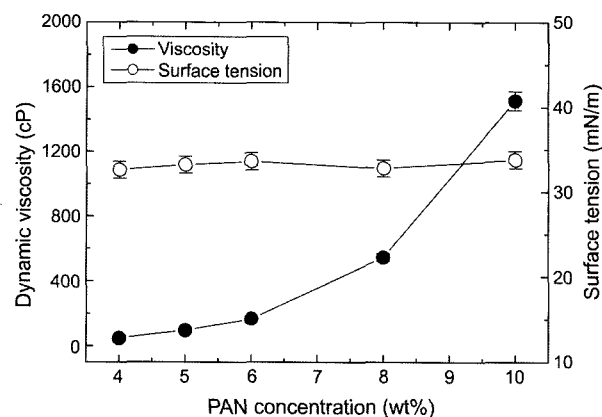


Fig. 1. The variation of solution viscosity and surface tension as a function of PAN concentration. Note that flow rate and electric field were 0.5 mL/h and 0.875 kV/cm, respectively.

change in surface tension is negligible with the change in concentration, which is in good agreement with previous studies.^{10,11} The value of the surface tension is approximately half the value of that of the water (72 mN/m at 25°C). Obviously, the low value of surface tension may lead to the formation of fiber instead of polymer droplets. Lee *et al.*¹¹ reported that although the precursor solution had a similar surface tension, the morphology of electrospun fibers was changed from droplets, beads-on-string, to fibers with increasing viscosity, implying that the viscosity of the solution is likely to be a key factor for the formation of nanofibers.^{10,11} On the other hand, flow rate and electric field were previously determined to be insignificant to fiber formation in comparison to the viscosity.^{2,10}

Spherical or spindle-type beads were observed for the electrospun fibers at viscosities ranging from 46 to 1000 cP (PAN concentrations from 4 to 9 wt%), as depicted in Figs. 1 and 2. It is reported that the viscosity and surface tension of the precursor solution affect the formation of beads. Higher viscosity and net charge density favor the fibers without beads and the thin fibers. However, surface tension causes the formation of beads, indicating that reduced surface tension is preferable for the formation of fibers without beads.¹² Therefore, it is conceivable that relatively high viscosity and low surface tension may be effective for the fabrication of uniform fibers. As viscosity rose, the size of the beads decreased significantly, probably due to the elongational flow of the jet into oriented and entangled networks,¹² as shown in Fig. 2(d)-(e). Uniform, smooth, and continuous fibers were found in the compositions with PAN concentration of 10 wt% or higher due to the increase in viscosity because the viscosity increased approximately exponentially by raising the PAN concentration. It is found that the value of viscosity is crucial to the fiber morphology because the variation of surface tension is negligible throughout the experiment. Also, the diameter of PAN nanofibers rose as the viscosity was raised. Unbeaded, smooth, and continuous PAN nanofibers with diameters of

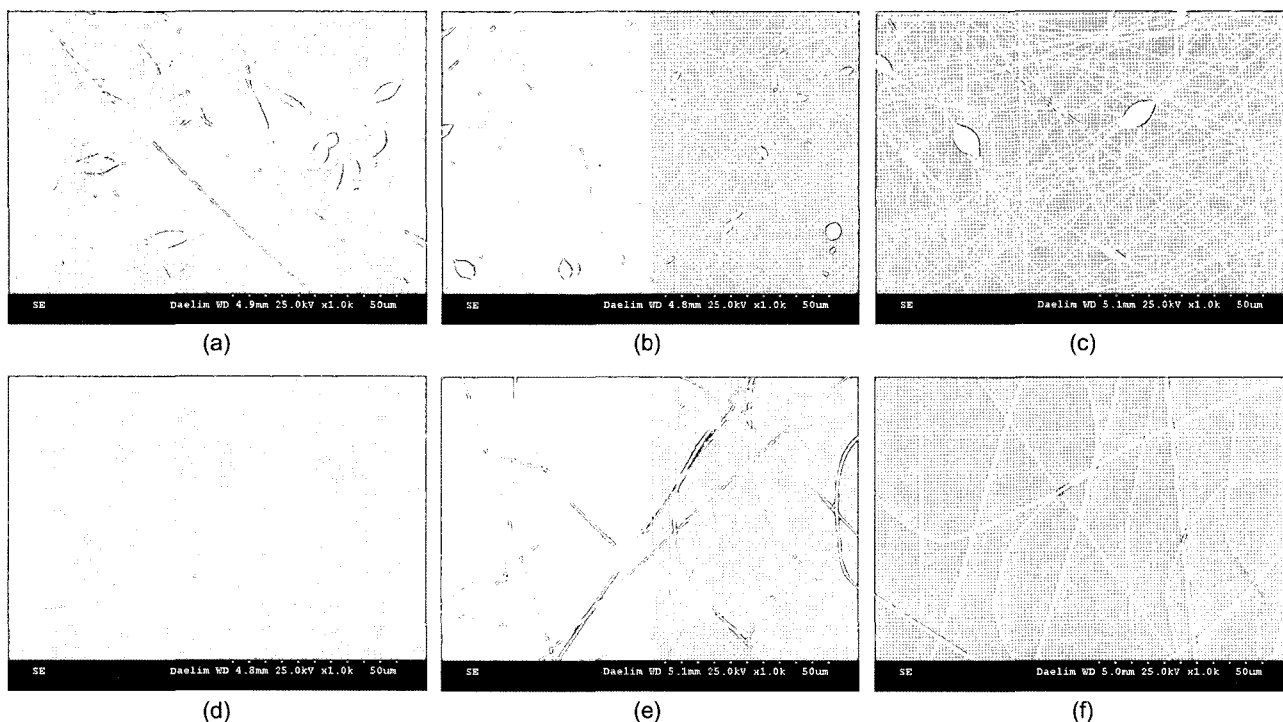


Fig. 2. SEM images of electrospun PAN nanofibers containing various PAN concentrations; (a) 4%, (b) 6%, (c) 7%, (d) 8%, (e) 9%, and (f) 10%. Note that flow rate and electric field were 0.5 mL/h and 0.875 kV/cm, respectively.

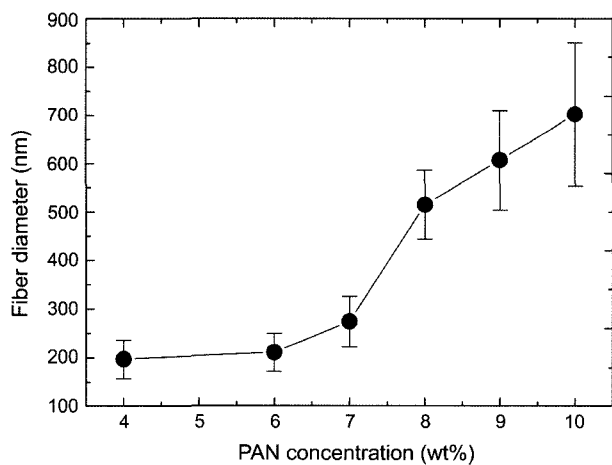


Fig. 3. Variation of PAN fiber diameter as a function of PAN concentrations. Note that flow rate and electric field were 0.5 mL/h and 0.875 kV/cm, respectively.

~700 nm were obtained for the 10 wt% PAN fibers. Studies for activated PAN polymer gels as artificial muscles are in progress and will be presented later.

4. Concluding Remarks

PAN nanofibers were prepared by electrospinning to investigate the effect of viscosity on the morphology of PAN fibers. Experimental results revealed that higher viscosity is critical for the formation of unbeaded nanofibers because

the surface tension is almost constant throughout the experiment. Also, the fiber diameter rose while increasing the viscosity of the precursor solution. Uniform, smooth, and continuous fibers with diameters of about 700 nm were achieved for the 10 wt% PAN fibers at a flow rate of 0.5 mL/h and an electric field of 0.875 kV/cm.

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