Effect of Different Salts on Electrospinning of Polyacrylonitrile (PAN) Polymer Solution

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ABSTRACT: Electrospinning is a relatively simple method to produce submicron fibers from solutions of different polymers and polymer blends. If the solution is absolutely insulating, or the applied voltage is not high enough that electrostatic force cannot overcome the surface tension, then no fiber can be produced by electrospinning; however, if some salt is added in the solution, the problem can be overcome. The effect of different salts on electrospinning of polyacrlonitrile (PAN) polymer solution was investigated in this article. The various inorganic salts used in this work include LiCl, $NaNO_3$, NaCl, and $CaCl_2$.The results show that when the salts were added, respectively, into different concentrations of PAN solution, the order of conductant was LiCl > $NaNO_3$ > $CaCl_2$ > NaCl > no salt added. Viscosity and shearing strength of electrospinning solutions are slightly affected by the adding of salts and mainly affected by the changes in concentration of PAN electrospinning solutions. The diameter of nanofibers electrospun by solutions with different salts size down as follows: LiCl > $NaNO_3$ > $CaCl_2$ > NaCl. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3865–3870, 2007

Key words: electrospinning; salts; PAN; nanofibers; nanotechnology; fibers; solution properties; viscosity

INTRODUCTION

Electrospinning is a process that produces superfine fibers. Electrospinning nanofibers are of interest in many applications.[1–6] These include filter media, composite materials, biomedical applications (tissue engineering, scaffolds, bandages, and drug release systems), protective clothing, optoelectronic devices, photonic crystals, and flexible photocells.

The procedure involves applying a very high voltage to a capillary and pumping a polymer solution through it. Superfine fibers of polymer collect as a nonwoven fabric on a grounded plate below the capillary. If the solution is absolutely insulating, or the applied voltage is not high enough that electrostatic force cannot overcome the surface tension, then no fiber can be produced by electrospinning; however, if we add some salt in the solution, the problem can be overcome because of enhancement of conductivity of solution, which is the factor that determine the spinning current and fiber diameter. Therona et al.[7] reported an experimental work on the electrospinning process in which the influence of different process parameters on the electric current and volume and surface charge density in the polymer jet was measured with different solutions of polyethylene oxide, polyacrylic acid, polyvinyl alcohol, polyurethane, and polycaprolactone, and they found that the addition of small amount of salt is observed to dramatically increase the mass flow, and an increase in solution concentration results in fibers with larger diameters; same phenomena were observed by Demir et al.[8] and Fong et al.[9]

We have analyzed the effect on the diameter and the stable length of nanofibers when LiCl was added to the PAN solution and found that the radius and the stable length of jet depends upon the content of LiCl involved.[10,11] In this article, the effect of different salts (LiCl, $NaNO_3$, NaCl, $CaCl_2$, or no salt) on electrospinning of PAN polymer solution was investigated.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN) with a molecular weight of 75,000 was purchased from Shanghai Chemical Fibers Institute. *N*,*N*-Dimethylformamide (DMF) was purchased from Shanghai Chemical Co., and LiCl, $NaNO_3$, NaCl, and $CaCl_2$ were purchased from Pinjiang Chemical Co. The experiments were carried out at room temperature in air.

Electrospinning setup

Experimental set-up device used for electrospinning process is shown in Figure 1. Variable high voltage power supply was used for the electrospinning. It was used to produce voltages ranging from 0 to 50 kV; the

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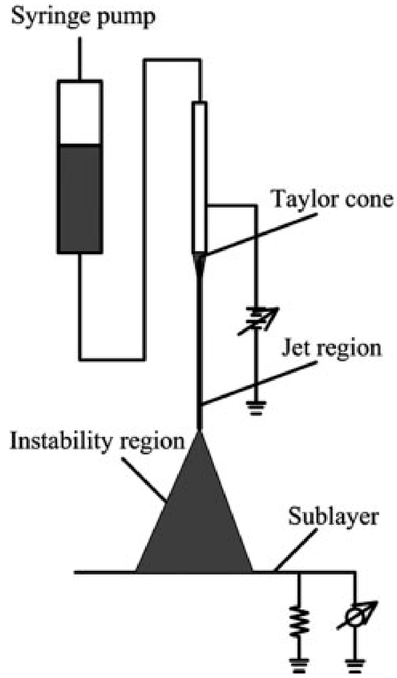

Figure 1 Experimental set-up.

voltage used in the experiment was about 40 kV, and the current was adjusted to be constant. PAN solution was poured in a syringe attached with a capillary tip of 0.5 mm diameter, and the flow rate was uniform, 0.5 mL/h.

Measurements

DDSJ-308A Intelligent Conductivity Meter was used to measure the conductance of PAN polymer solution. HAAKE RS150 Rheometer was used to measure the rheological property. Before measuring, the samples were put into rheometer for 20 min at constant temperature. Measuring method of balance flow curve was used (Equilibrium time of each measured value was set as 5 s). At the same shear rate range, the method that shearing rate changed was used. The process was set that shearing rate increases from low to high gradually and then decreases gradually. Variation curve of shearing strength and apparent viscosity of specimens change along with the change of shearing rate is measured.

JSM-5600LV Digital Vacuum Scanning Electron Microscope, produced by Japan Electron Optical Laboratory, was used to observe the morphology of nanofiber mats.

RESULTS AND DISCUSSION

The PAN PAN/DMF solutions prepared for electrospinning are at the concentration of 4, 6, 8, and 10 wt % with different salts such as LiCl, $NaNO_3$, NaCl, $CaCl_2$, or no salt. The experiment parameters of electrospinning are shown in Table I.

Test of conductance

The conductance of spinning solutions with different kinds of concentration and added salts are compared in Figure 2. The concentration of added salts is 1 wt %. The values of experiment show that the conductance is almost zero when salt is not added in the solution, whereas the conductance has notable change when salt is added in the solution.

In pure PAN/DMF solution, the conductance of different concentration is almost zero as shown in Figure 2. But the conductance is improved remarkably after adding different kinds of salts in the solutions. LiCl has the greatest influence degree of conductance; the influence of $NaNO_3$ and $CaCl_2$ takes the second place; the influence of $NaCl_2$ is the smallest. That is to say, the big to small order of conductance is LiCl $>$ $NaNO_3$ $>$ $CaCl_2$ $>$ NaCl $>$ no salt. The fluctuation in conductance of PAN solutions with different kinds of concentration and the same salts has not been researched thoroughly.

The effect of added salts on viscosity and shearing strength of solution

Viscosity is one of the most important parameters in the manufacture of chemical fiber. In general, the viscosity of PAN copolymer solution depends on the molecular weight of PAN copolymer, the concentration, and the solvent of solution. To improve capabilities of fiber, the method that content and molecular weight of acrylic copolymer are increased is usually used. The result is that solution viscosity increases greatly; the feeding and filtration of solutions are difficult. So the result that adding some inorganic salts into the solution of acrylic copolymer can decrease viscosity may be very important for the production of PAN. Predecessors use that theory to research is the influence of salt to acrylic spinning solution of dry and wet spinning and properties of finished fiber, but they all considered acrylic solution concentration in excess of 30 wt %. The PAN concentration discussed in this

TABLE I
The Experiment Parameters of Electrospinning

PAN/DMF concentration (wt %)	Kinds of the added salts	Concentration of salt (wt %)	Voltage (kV)	Diameter of needle (mm)	Distance (cm)
4, 6, 8, 10	No salt : LiCl : $NaNO_3$: NaCl : $CaCl_2$	1	40	0.5	25

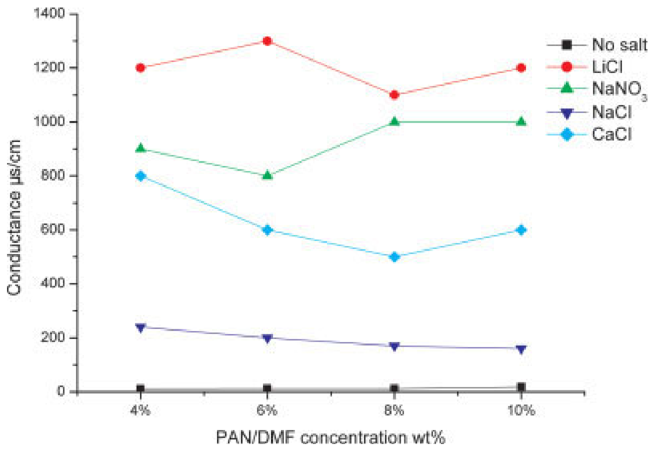

Figure 2 Comparison of conductance of solutions with different kinds of concentration and added salt.

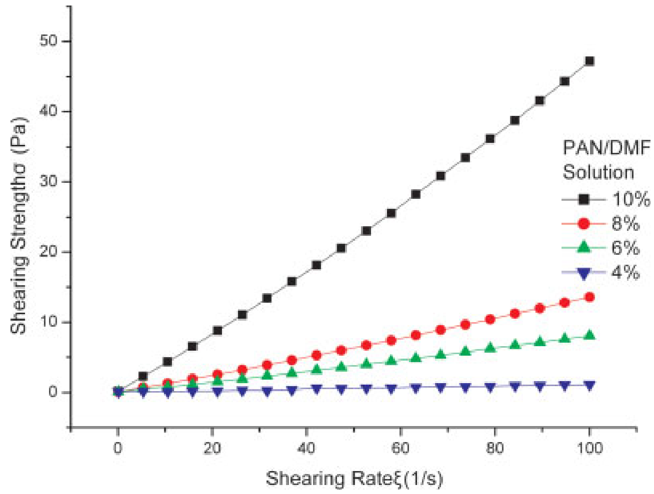

Figure 4 Comparison of shearing strength of PAN/DMF solution at different concentration.

paper is less than 16% that is suitable for electrospinning.

It is shown in Figure 3 that flow curve describes viscosity of spinning fluid at larger shearing rate range. That kind of flow curve is used to compare viscosity of different kinds of solutions and the change in shearing strength.

In Figure 4, shearing strength is increased with the increase in shearing rate; shearing viscosity is decreased with the increase in shearing rate at preliminary stage of test. The main reason is that the concentration of entwisted points decreases. High molecular polymer can be regarded as instantaneous network structure. Homeostasis moves accordingly along with the change in shearing strength. When shearing rate increases, some of entwisted points are removed. The decrease of entwisted points leads to the decrease of fluid viscosity. A majority of entwisted points in the system are removed when the shearing rate comes to a stated value, and so between liquid flow layers there are only friction force and applied shearing strength. The viscosity presents gently. The fluid viscosity researched in the range of this study is at stable condition. This study will omit original transilient situation in the flow curve figure at other conditions. We will mainly research the over all trend.

It is obvious from Figures 3 and 4 that viscosity increases with the increase of concentration, and shearing strength also increases with the increase of concentration at the same shearing rate. Meanwhile, the shearing strength increases with the increase of shearing rate. It is known from equation $\sigma = \eta\xi$ that shearing strength σ is proportional to shearing rate ξ and the slope of flow curve is the solution viscosity η. Meanwhile, we can know from Figure 3 that solution viscosity would not change with the change in shearing strength or shearing rate at stable condition.

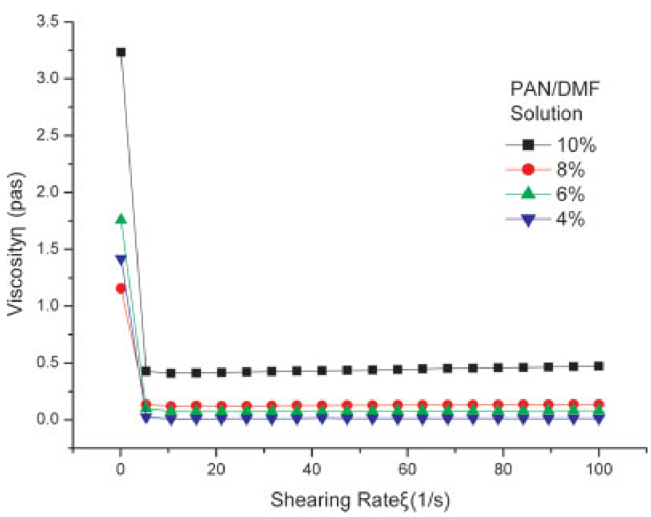

Figure 3 Comparison of solution viscosity of PAN/DMF at different concentration.

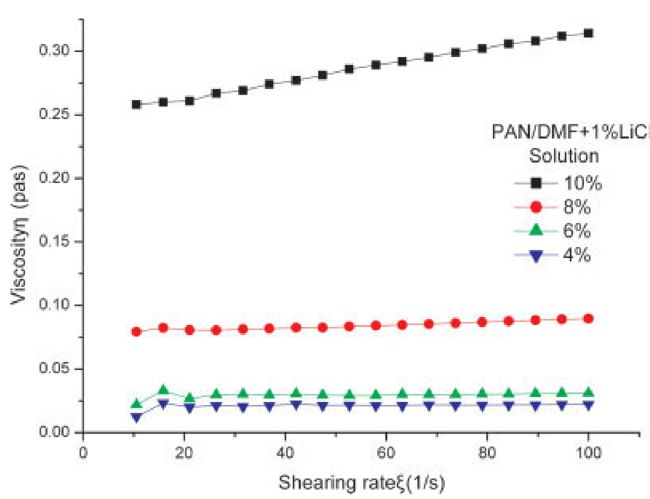

Figure 5 Comparison of viscosity of PAN/DMF solutions added with LiCl at different concentration.

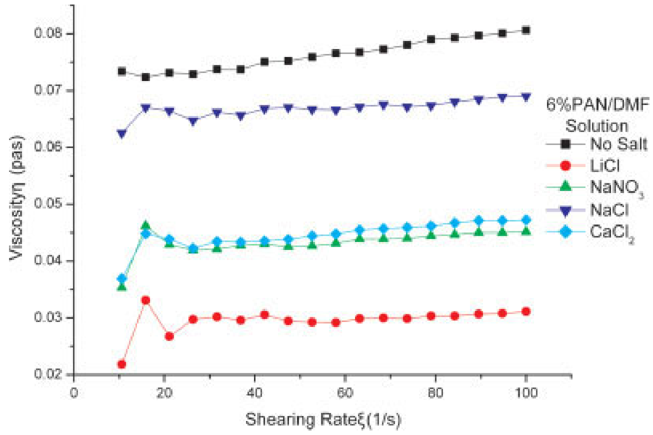

Figure 6 Comparison of viscosity influence of 6 wt % PAN/DMF electrospinning solutions with different salts.

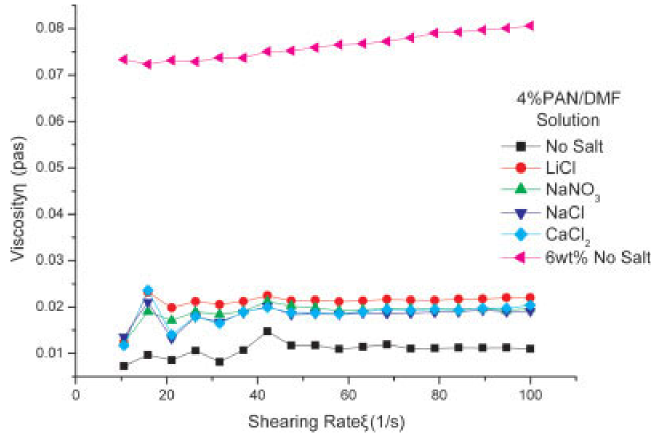

Figure 8 Comparison of viscosity influence of 4 wt % PAN/DMF electrospinning solution with different salts to 6 wt % PAN/DMF solution viscosity.

Meanwhile, the change in viscosity when the solutions are added with 1 wt % LiCl at different concentration is measured in the experiment. The result is showed in Figure 5. The sequence of viscosity is 10 wt % > 8 wt % > 6 wt % > 4 wt %. The same results appear when solutions are added with $NaNO_3$, NaCl, or $CaCl_2$.

A set of comparative experiments is done in this study. The change in solution concentration is measured when 6 wt % solutions are added with the four kinds of salts mentioned earlier.

It is shown in Figures 6 and 7 that viscosity and shearing strength of solutions will reduce along with the adding of salts when solution concentration increases. Viscosity and shearing strength of solutions reduce at different degrees after the addition of LiCl, $NaNO_3$, NaCl, and $CaCl_2$, when concentration of solutions is 6 wt % and influence degree of LiCl is especially obvious.

The same phenomenon is observed at 8 and 10 wt % PAN/DMF solutions. It can be discovered that NaCl is difficult to be dissolved in DMF during experiment. $NaNO_3$ and $CaCl_2$ have certain solubility, but the solubility is less than that of LiCl.

Meanwhile, we found an interesting thing. The change of solution concentration is measured when 4 wt % solutions are added with the four kinds of salts mentioned earlier. Moreover, the concentration of 6 wt % solution is compared in Figure 8. The experiment led up to the fact that the viscosity of PAN solution increase rather than decrease when the concentration is as low as 4 wt %. It can be observed from the figure that the greatest effect to solution viscosity is LiCl. It also can be observed that although viscosity of 4 wt % PAN/DMF solution has somewhat increased after adding salt, it still cannot outstrip the viscosity of 6 wt % PAN/DMF without salt. The same phenomenon happens in the change of shearing strength (Fig. 9). It can be discovered clearly from experiment that the viscosity is slightly influenced by the adding of salts and the PAN solution viscosity changes on the whole along with the change in concentration of solution itself.

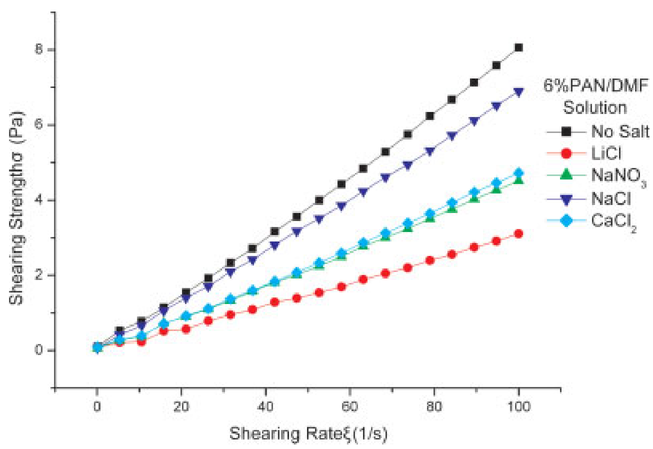

Figure 7 Comparison of shearing strength influence of 6 wt % PAN/DMF spinning solutions with different salts.

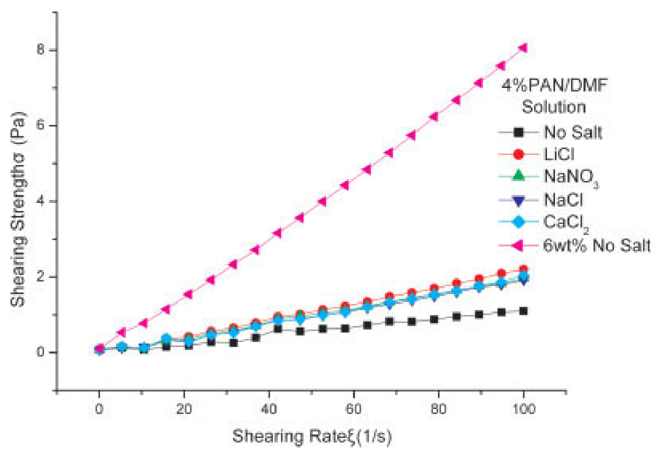

Figure 9 Comparison of shearing strength influence of 4 wt % PAN/DMF electrospinning solutions with different salts to 6 wt % PAN/DMF solution.

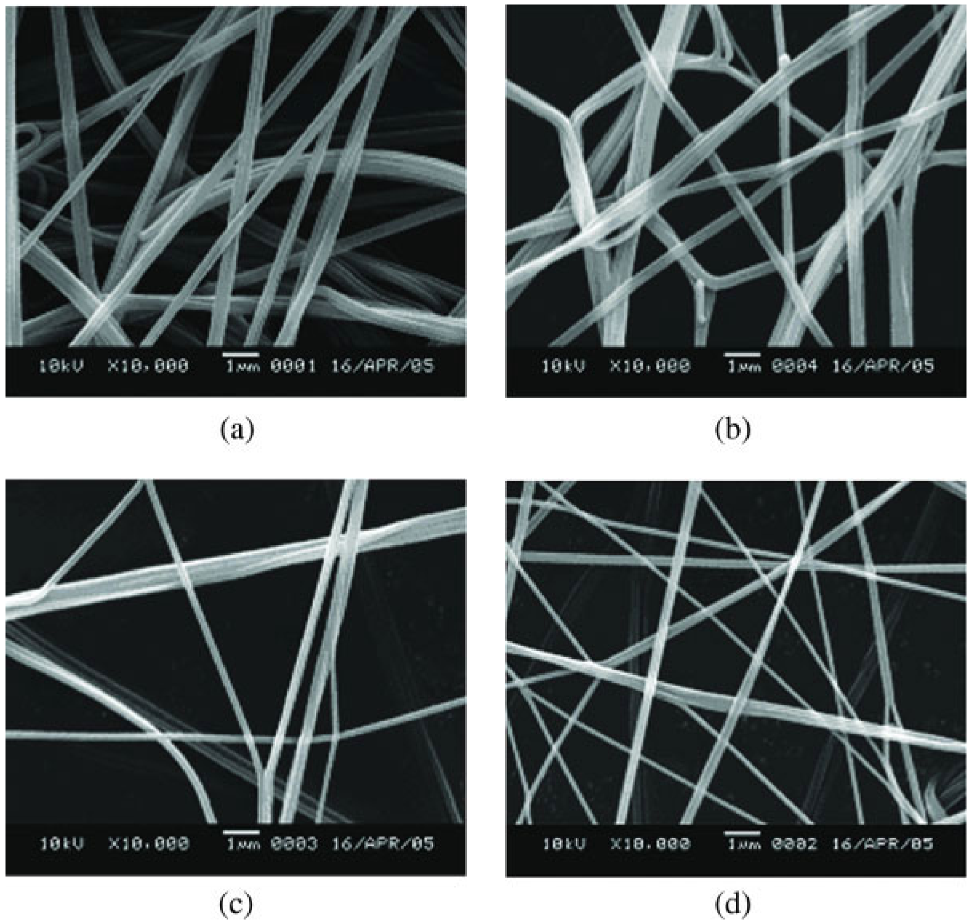

Figure 10 Electrospinning SEM figures of solutions with different salts. (a) 10 wt % PAN/DMF + 1% LiCl solution, (b) 10 wt % PAN/DMF + 1% $NaNO_3$ solution, (c) 10 wt % PAN/DMF + 1% $CaCl_2$ solution, and (d) 10 wt % PAN/DMF + 1% NaCl solution.

All the experiments show that viscosity and shearing strength of solutions are slightly affected by the addition of salts. The viscosity and shearing strength of electrospinning solutions all decrease slightly by the addition of salts when the concentration of electrospinning solutions is more than 4 wt %, whereas they increase slightly by the addition of salts when the concentration of electrospinning solutions is 4 wt %. It can be also discovered that the effect of salts on viscosity of electrospinning solutions and shearing strength is much less than that of concentration of electrospinning solutions itself. In a word, the viscosity of PAN electrospinning solutions changes along with the changes of concentration. The law is quite different from great changes in viscosity after the addition of salts on producing traditional acrylic fiber.[12,13]

Effect of adding inorganic salts on fineness of electrospinning nanofibers

Nanofibers are elctrospun at the condition of 10 wt % concentration and addition of different salts (1 wt %). The morphology is observed by SEM and fiber diameter is measured by related software. Fifty comparatively homogeneous fibers are measured for diameter in each SEM figure and mean value is obtained. The SEM morphology of fibers is shown in Figure 10. The diameter of fibers is shown in Table II.

Nanofibers diameter is comparatively made clear in Table II when different salts are added. The diameter of fibers that are added with LiCl is a little larger than those with other salts. According to theoretical research, the increase of electric conductivity of high polymer solution leads to the increase of surface

TABLE II
Mean Values of Fibers Electrospun by Solutions with Different Salts

Kinds of salts	Mean diameter of fibers (nm)
LiCl	473
$NaNO_3$	462
$CaCl_2$	444
NaCl	410

charge of spinning jet, which makes the spinning more fluent, jet quantity of solution increased, and at last diameter of fibers increased. Among influence degree of conductivity, LiCl is maximal; $NaNO_3$ and $CaCl_2$ are smaller; NaCl is the smallest. So diameter of nanofibers electrospun by solutions with different salts size down as follows: LiCl > $NaNO_3$ > $CaCl_2$ > NaCl. Meanwhile, it can be observed from experiments that the dissolution of LiCl is easier than other salts and the process is smoother when LiCl was added to the electrospinning solution.

CONCLUSIONS

The study investigated the effect of different salts on electrospinning of polyacrlonitrile (PAN) polymer solution.

1. When LiCl, $NaNO_3$, NaCl, and $CaCl_2$ were, respectively, added into different concentration of PAN solution, the order of conductant was LiCl > $NaNO_3$ > $CaCl_2$ > NaCl > no salt added.
2. Viscosity and shearing strength of electrospinning solutions are slightly affected by the adding of salts and mainly affected by the changes in concentration of PAN electrospinning solutions. The viscosity and shearing strength of electrospinning solutions all decrease slightly by the addition of salts when the concentration of electrospinning solutions is more than 4 wt %, whereas they increase slightly by the addition of salts when the concentration of electrospinning solutions is 4 wt %; but it can be also discovered that the effect of salts on viscosity of electrospinning solutions and shearing strength is much less than that of concentration of electrospinning solutions itself.
3. The diameter of nanofibers electrospun by solutions with different salts size down as follows: LiCl > $NaN0_3$ > $CaCl_2$ > NaCl.

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