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ELECTROSPUN NANOFIBERS

Keywords: electrospinning, nanofibers, polymers.

Polymer nanofibers could have many extraordinarily properties including, small diameter (and the resulting large surface area to mass ratio), highly oriented crystalline structures (and the resulting high strength), etc. The recently fast developing technology "electrospinning" is a unique way to produce novel polymer nanofibers with diameters typically in the range of 50 nm to 500 nm. Electrospinning of polymer nanofibers attracted significant attention during the last several years as a simple and straightforward method to produce nanostructures, which are of interest in many applications. The process of electrospinning is a complicated combination of polymer science, electronics and fluid mechanics. To date, a fundamental mechanism of the process of electrospinning is still characterized only qualitatively. The absence of a comprehensive theoretical knowledge of the electrospinning has resulted in polymer nanofibers with less controllable morphology and properties. A study on this technique has been made in this paper. Based on this study, many challenges exist in the electrospinning process of nanofibers, and a number of fundamental questions remain open.

Ключевые слова: электропрядение, нановолокна, полимеры.

Полимерные нановолокна могут иметь множество свойств, включая чрезвычайно малый диаметр (и в результате большую величину отношения площади поверхности к массе), высоко ориентированные кристаллические структуры (и в результате высокую прочность) и т.д. Новая быстро развивающаяся технология «электропрядение» является уникальным способом получения новых полимерных нановолокон с диаметром обычно в диапазоне от 50 нм до 500 нм. Электропрядение полимерных нановолокон привлекло значительное внимание в течение последних нескольких лет как простой и прямой способ получения наноструктур, которые представляют интерес во многих применениях. Процесс электропрядения является сложным сочетанием науки о полимерах, электроники и механики жидкости. На сегодняшний день основной механизм процесса электропрядения по-прежнему характеризуется только качественно. Отсутствие всеобъемлющего теоретического знания электропрядения привело к тому, что нановолокна полимера имеют плохо контролируемые морфологию и свойства. Исследование по этой технике было проведено в данной работе. На основе этого исследования, многие проблемы, существующие в процессе электропрядения нановолокон, а также ряд фундаментальных вопросов остаются открытыми.

1. Introduction and background

Nanotechnology has become in recent years a topic of great interest to scientists and engineers, and is now established as prioritized research area in many countries. The reduction of the size to the nanometer range brings an array of new possibilities in terms of material properties, in particular with respect to achievable surface to volume ratios. Electrospinning of nanofibers is a novel process for producing superfine fibers by forcing a solution through a spinnerette with an electric field. An emerging technology of manufacturing of thin natural fibers is based on the principle of electrospinning process. In conventional fiber spinning, the mechanical force is applied to the end of a jet. Whereas in the electrospinnig process the electric body force act on element of charged fluid. Electrospinning has emerged as a specialized processing technique for the formation of sub-micron fibers (typically between 100 nm and 1 μm in diameter), with high specific surface areas. Due to their high specific surface area, high porosity, and small pore size, the unique fibers have been suggested for wide range of applications. Electrospinning of nanofibers offers unique capabilities for producing novel natural nanofibers and fabrics with controllable pore structure. Electrospinning is an economical and simple method used in the preparation of polymer fibers [1].

Outstanding properties make the polymer nanofibers to be optimal candidates for many important applications [2]. These include filter media, composite materials, biomedical applications (tissue engineering scaffolds, bandages, drug release systems), protective clothing for the military, optoelectronic devices and semi-conductive materials, biosensor/chemosensor [3].

It has been found that morphology such as fiber diameter and its uniformity of the electrospun polymer fibers are dependent on many processing parameters. These parameters can be divided into three groups: solution properties, processing conditions and ambient conditions. Under certain condition, not only uniform fibers but also beads-like formed fibers can be produced by electrospinning. Although the parameters of the electrospinning process have been well analyzed in each of polymers these information has been inadequate enough to support the electrospinning of ultra-fine nanometer scale polymer fibers. A more systematic parametric study is hence required to investigate [4-6].

2. Experimental

Polyacrylonitrile (PAN) fiber (Dolan) was from Hoechst. NMP (N-methyl-2-pyrolidon) was from Riedel-de Haën. The polyaniline used was synthesized in our laboratory. Polyaniline (PANi) was synthesized by the oxidative polymerization of aniline in acidic

media. 3 ml of distilled aniline was dissolved in 150 ml of 1N HCl and kept at 0°C, 7.325g of $(NH_4)_2S_2O_8$ was dissolved in 35 ml of 1N HCl and added dropwise under constant stirring to the aniline/HCl solution over a period of 20 mins. The resulting dark green solution was maintained under constant stirring for 4 hrs filtered and washed with methanol and then with water then it was dried before being added to 150 ml of 1N $(NH_4)OH$ solution. After an additional 4 hrs the solution was filtered and a deep blue emeraldine base form of polyaniline was obtained (PANiEB). Then it was dried and crushed into fine powder and then passed trough a 100 mesh.

The polymer solutions were prepared by first dissolving exact amount of PANi in NMP. The PANi was slowly added to the solvent with constant stirring at room temperature. This solution was then allowed to stir for 1 hour in a sealed container. PAN/NMP solution was prepared separately and added dropwise to the well stirred PANi solution and the blend solution was allowed to stir with a mechanical stirrer for an additional 1 hour.

By mixing different solution ratios (0/100, 50/50, 60/40, 75/25) of 5% PANi solution and 20% PAN solution various polymer blend solutions were prepared with the concentration of polyaniline ranging from 5 wt% to 42 wt%. The fiber diameter and polymer morphology of the electrospun polyaniline/polyacrylonitrile NMP solution were determined using an optical microscope Nikon Microphot-FXA. A small section of the non-woven mat was placed on the glass slide and placed on the microscope sample holder. A scanning electron microscope (SEM) Philips XL-30 was used to take the SEM photographs to do more precise characterization. A small section of the web was placed on SEM sample holder and coated with gold (BAL-TEC SCD 005 sputter coater).

3. Results and Discussion

In our first experiment we tried to find out whether electrospinning of PANi pure solution can result in a web formation or not. Without the addition of PAN to PANi dissolved in NMP, no web formation occurred, because the concentration and viscosity of the solution was not high enough to form a stable drop at the end of the needle and just some dispersed drops were formed on the collector. Adding more polyaniline can not increase the solution viscosity and just resulted in gelation of the solution.

Based on these results the blend solution was electrospun the initial results showed that in room temperature fine fibers are formed. In these blends the concentration of PANi ranged from 5 wt% to 42 wt%. The potential difference between the needle tip and the electrode was 20 Kv. Optical microscope photomicrographs (Fig. 1) showed that the fibers are formed but they are entangled to each other also the bead forming is observed. In order to get more uniform webs we tried to obtain the webs at the gap between two metal stripes which were placed on the collector plate, and it was seen that webs got more uniform but yet the entanglement and beads were observed (Fig. 2).

For examining the web formation of PAN it was electrospun from NMP at different concentrations. (10% and 15%) webs were formed at voltages between 17 and 20. PAN web showed an excellent webforming behavior and the resulted webs were uniform (Fig. 3).

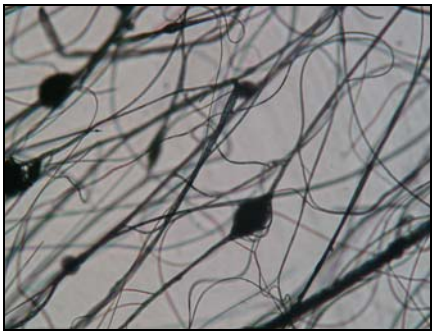

Fig. 1 – Optical microscope micrograph of 16% PANi blend solution, beads can be observed clearly.

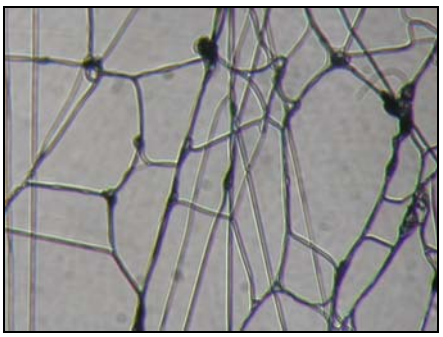

Fig. 2 – Optical microscope micrograph of 16% PANi blend solution caught in air.

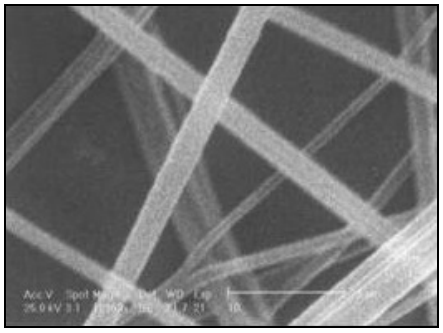

Fig. 3 – SEM photomicrograph of pure PAN.

After that optical microscope micrographs confirmed that the fibers are formed; higher concentrations of PANi were used and the resulted webs were examined by SEM for studying their diameter and morphology more precisely. The SEM photomicrograph revealed that the diameter of fibers in non-woven mat ranged from minimum 160 nm to maximum 560 nm, with an average fiber diameter of 358 nm.

It was noticed that by increasing amount of PAN the fiber formation enhanced and more uniform fibers were obtained; also the fiber diameter variation is smaller, it can be related to intrinsic fiber forming behavior of PAN as it is used widely as the base material for producing fibers and yarns. By increasing

PANi ratio amount of beading increased and fibers twisted to each other before reaching the collector, in some parts a uniform web was formed. It seemed that the fibers were wet and it is the cause of sticking of fibers together. In 42% of PANi the webforming was not seen and instead we had an entangled bulk with some polymer drops. Actually with increasing the PANi ratio the fiber diameter decreased as it can be noticed clearly from the results indicated in Table 1.

Table 1 – Fiber diameters in different PANi ratios.

PANi percent (blend ing ratio)	0% (0/100)	20% (50/50)	27% (60/40)
Fiber diameter	445 nm	372 nm	292 nm

By increasing the temperature of electrospinning environment to 75°C in order to let the solvent evaporate more rapidly the problem of twisted fiber was overcame and more uniform webs and finer nanofibers were formed but yet the beading problem was seen. More research is in progress to enhance the web characterization and decreases the fiber diameter to real nanometer size.

4. Conclusion

Nanoibers of pure PAN dissolved in NMP was prepared, but pure PANi /NMP solution did not show the web forming. By adding PAN fiberforming was observed. Different PANi/PAN blends were electrospun, the average diameter of nanofibers were 385 nm. It was seen that by increasing the PANi amount the resulted nanofibers diameter decreased; also with increasing the amount of PANi the web becomes more irregular and nonuniform.

The electrospinning technique provides an inexpensive and easy way to produce nanofibers on low basis weight, small fiber diameter and pore size. It is hoped that this article will pave the way toward a better understanding of the application of electrospinning of nanofibers. There are three categories of variables that influence the electrospun fiber diameter, including (1) polymer solution variables, (2) process variables, and (3) environmental variables. Examples of solution variables are viscosity or polymer concentration, solvent volatility, conductivity, and surface tension. Process variables consist of electric field strength, fluid flow rate, and distance between electrodes. Low molecular weight fluids form beads or droplets in the presences of an electric field, while high molecular weight fluids generate fibers. However, an intermediate process is the occurrence of the "beads on a string" (Fig. 4, 5) morphology. In many instances, bead formation is also observed in addition to fiber growth. This morphology is a result of capillary break-up of the spinning jet caused by the surface tension. Solution conductivity is another polymer solution property that greatly influences electrospun fiber diameter. The addition of salts to polymer solutions has been shown to increase the resulting net charge density of the electrospinning jet. The surface tension of the polymer solution also influences the resulting fiber morphology because large surface tensions promote the formation of polymer droplets. The surface tension of the fluid must be overcome by the electrical voltage in order for emission of an electrified jet from the syringe. Process variables also control the morphology of fibers during the electrospinning process. In general fiber diameter is rather insensitive to process conditions when compared to varying the polymer solution properties, however extensive work has been published on the influence of voltage, flow rate, and working distance on electrospun fiber morphology. The distance between the electrodes or the working distance influences the electrospinning process. Generally as the working distance decreases, the time for the flight of path for the fluid jet decreases.

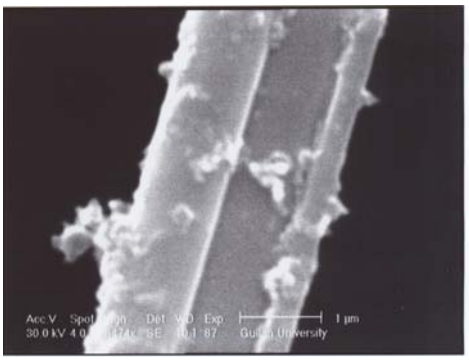

Fig. 4 – Formation of "beads on a string"

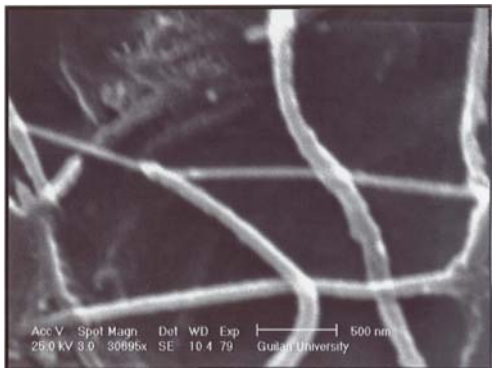

Fig. 5 – Formation of "beads on a string"

Moreover, it should be noted that temperature is a convoluted variable when attempting to discern its influence on electrospun fiber formation. Increasing the solution temperature causes (1) a change in chain conformation in solution, (2) a decrease in solution viscosity, and (3) an increase in rate of solvent evaporation. Thus, quantifying the effect of temperature on electrospinning proves difficult since all of the above can influence fiber morphology. Humidity has been shown to control the surface morphology of electrospun fibers.

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