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Original article

Preparation of polystyrene nanofiber modified with Dithizone using electrospinning technique

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ABSTRACT

In this paper, polystyrene nanofiber were made using electrospinning polystyrene inside THF/DMF solvent. The major parameters such as voltage, distance between injection and collector, polystyrene concentration and rotating speed of collector were optimized in electrospinning technique. The results indicated that in specific range, with increasing voltage, high electrospinning distance, low flow of injection and high collector's speed, we could achieve to nanofiber having regular chain structure and less diameter. In optimal condition and unmodified surface, polystyrene fiber had average diameter of 82.1 nm. Finally polystyrene absorbent by dithizone were modified and through selecting best condition, the modified polystyrene nanofiber with 92.98 nm average diameter were obtained which although it has more diameter than unmodified nanofiber, it possesses properties which the unmodified nanofiber does not have those properties, for example property of absorbing metals.

1. Introduction

Nanomaterial is an increasingly important product of nanotechnology. During recent years, nanotechnology is developing with an ascending rate (Anwar, 2015). Nanotechnologies involve designing and producing objects or structures at a very small scale, on the level of 100 nanometers (nm) or less (1-100 nm).Really this technology is the efficient production of materials, systems and machines along with material control at nanometer scale and utilizing new properties and concepts which have been developed at nano scale (Ulrich et al., 1993). Nanomaterials were classified based on the various categories such as: nanoparticles, nanofibers, nanocoatings, nanocomposites, nanocrystals, nanocapsules and etc (Baumgarten, 1971). The fibers were those ultrathin filaments with high length to diameter ratio which have various and numerous applications.Nanofibers are defined as fibers with diameters less than 100 nm (Nanotechnology task force). In the textile industry, this definition is often extended to include fibers as large as 1000 nm diameter (Zhou et al., 2008). They can be produced by melt processing, interfacial polymerization, electrospinning, antisolvent-induced polymer precipitation and electrostatic spinning.Nanofibers may be made from various raw materials such as composites, ceramics or polymers. The high surface area to volume ratio and flexibility in surface properties could be pointed out as the typical properties of nanofibers. Nanofibers have been applied to various fields such as Hygiene and cosmetics, defense, tissue engineering, filtration, sensor and etc. There are numerous techniques for producing fibers but those techniques could be lead to fabrication of fibers having nano-meter diameters or nanofibers include: stretching, Frame Fabrication, phase separation, self-assembly and electrospinning. Electrospinning is one technique with electrostatic drive force for fabrication of nanofibers.

In this technique, nanofiber is formed from liquid solution or melt polymerwhich are fed from capillary tube to region with high electric field. When electrostatic forces dominate the surface tension of liquid, then Taylor cone will be formed and one narrow jet accelerates quickly toward ground-connected collector and or with opposite charge. Instability in this jet lead to hard collisions and as result, the jet will be lengthen and become thin and it allows to evaporate the solvent or to cool the melt and finally the nanofiber is formed on the target surface (Benicewicz et al., 1991; Yao et al., 2007). The factors effective on the fiber electrospinning generally could be applied to those factors related to polymer solving and factors related to operation conditions such as applied voltage, temperature, collector effect and environmental conditions could be classified. Recognizing these factors and then optimizing them cause to achieve the favorable dimensions of nanofiber during synthesis process (Chen et al., 2007; Um et al., 2004).Surface modification can improve the inherent characteristics of the nanofibers and serve to prepare nanocomposites inexistent in nature (Wang et al., 2001).In recent years modifying the nanomaterial surface by Dithizone has attracted the attention of researchers. For example in 2012, modification of gold (Au) nanoparticles surface by dithizone has been reported and the beneficial effects of surface modification was determined (Woznica et al., 2012).Dithizone (Figure .1) is a sulfur-containing organic compound. Dithizone may be prepared by reacting phenylhydrazine with carbon disulfide, followed by reaction with potassium hydroxide (Billman et al., 1955).Currently the available techniques for modifying and or changing the polymer surface include coating and copolymerization. The most common and simplest technique is the technique of physical coating and blending in order to modify the nanofiber.

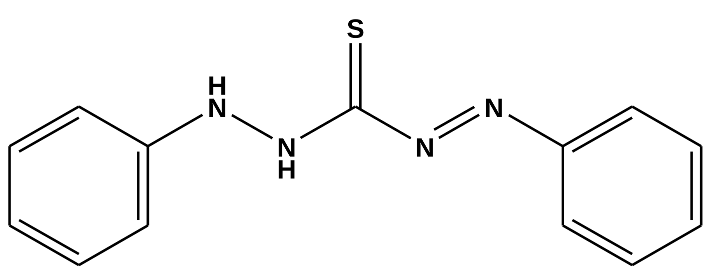

Fig. 1. Molecular structure of Dithizone

In this paper, polymer nanofiber (polystyrene nanofiber) were made through modification by dithizone and optimization of parameters effective on the electrospinning.

2. Experimental

2.1. Materials and apparatuses

The chemicals used for the research including polystyrene (PS), dithizone, dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Merck ltd. Also the used devices included the optic microscope made by Nikon co, electrospinner made by Iran, ultrasonic device made by ULTRA (Model VGT-1730QTD), Scanning Electron Microscope (SEM) made by KYKY ltd (Model EM3200) and electric agitator model HP-3000.

2.2. Preparing polymer solution

Firstly the given amount of PS were poured into atest tube, then DMF and THF were added so that all PS has well been solved in itself and become as the form of viscous solution. The solution were maintained for 3 hours in room temperature and then were placed in ultrasonic bath for 15min and at 20 ℃ tempreture in order to being further made uniform. After that, the solution was injected inside the 5ml plastic syringes on which angiographic needle had been inserted.

2.3. Modifying the PS surface

The physical coating technique is the simplest and most common technique for modifying nanofiber which in the paper, this technique was utilized. Having prepared the PS solution, the given amount of dithizone was added to the solution and in order to well progress the reaction among polymer and modifier, the solution was transferred into the small beaker and was agitated for 5 min at room temperature by agitator. Therefore full coating was made and one homogeneous solution was obtained. Then the solution was transferred into the ultrasonic bath and was placed for 15 min at 20℃temperature to completely eliminate the air bubbles.Then this modified polymer solution was transferred to electrospinning device for electrospinning process.

2.4. Optimizing the parameters effective on electrospinning

In this step, the parameters effective on structure changes and average diameter of fiber including polymer solution concentration, distance of nozzle to collector, voltage, flow of injection, collector speed and the amount of used dithizone in modifying the solvent were studied and optimized. After applying any change at effective parameters, it needs to see the result of these changes in order to decrease diameter of nanofiber. For the same reason, we regularly should use SEM images after every stage of experiment. Because of cost and time savings, firstly the process was following by the optic microscope and after the conditions fall into the right path, diameter values of final samples were read through SEM images.

3. Results and discussion

3.1. The effect of polymer solution concentration on the nanofiber diameter

Electrospinning fibers have different diameter and homogeneity with change at device, medium and solution parameters. Viscosity (as solution parameter) depends on the molecular mass and polymer concentration and will increase as these two factor rise. Also as viscosity rise then fiber diameter will increase and surface tension results in to generate bead on the fiber. Therefore forming uniform and without bead fiber require to decrease the surface tension. Having increased the conductivity and di-electric constant of the solution, the produced fiber diameterwillbe decreased. The voltage applied to device is set at critical value which the fiber diameter will increase at less and more than this value. In order to establish mass equilibrium, the feed rate must be equal to solution transfer rate from needle. In this condition, as the feed rate increase, then chargeson the jet will rise. Outlet diameter decreasing to specific value could decrease the fibber diameter. Low distance between collector and needle results in to generate bead on the fiber. In investigating the effect of polymer solution concentration, four first solutions comprised the various concentrations of polystyrene polymer. Firstly polymer solution 10%w/vwas examined which re-examination of this solution was withdrawn due to its low viscosity and generating bead among fiber. Then polymer solution 15% w/v was examined. When primary sample was placed under the optic microscope, simply similar to previous sample, tie among polymer fibers was found. The solution 20% w/v was sampled and primary samples were placed under the microscope.The formed nanofiber had properties such as uniformity and low diameter. In following stage, the solvent was prepared but due to low viscosity, polymeric powder was placed on the collector surface instead of form nanofiber. Therefore it did not fit for forming solvent. The polymer solution 25% w/v was tested and primary sample exhibited reasonable result under the microscope and so having the favorable viscosity make possible to produce suitable solvent at large scale with this concentration. Figure .2 shows the fiber average diameter changes with solution concentration changes. Also it is found that in 25% mass concentration, lowest value had been obtained for the average fiber diameter.

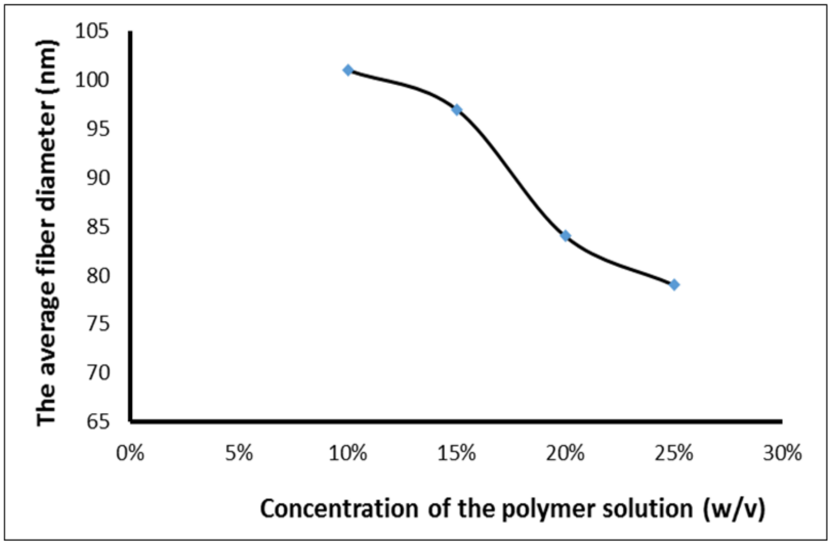

Fig. 2. Changes of average diameter of fiber by changes of polymer solution concentration.
(Voltage: 10 kV, Distance: 12 cm, Collector speed: 200 rpm)

Table 1
Technological parameters during electrospinning process.

Distance (cm)	Voltage (kV)	Average diameter (nm)
16	13	88
	14	85
	15	85
17	13	85
	14	85
	15	83
18	13	82
	14	82
	15	81
	16	78
19	13	78
	14	75
	15	75
	16	72
20	13	75
	14	71
	15	71
	16	68

3.2. The effect of voltage, electrospinning distance, injection flow and collector speed on the nanofiber diameter

In this stage, electrospinning distance and voltage were considered as variables and concurrently, fiber structure and diameter changes were investigated. Then using one-variable technique, the effect of injection flow and collector speed was investigated on the fiber diameter. With considering to respectively table 1, Figure .3 and Fig. 4 and their investigations it is found that in specific range, with increasing voltage, high electrospinning distance, low injection flow and high collector speed, the nanofiber having regular chain structure and lower diameter could be achieved. In Figures 3 and 4, the curves of average fiber diameter changes have respectively been showed with injection flow and collector speed changes. Though optimizing these effective parameters during synthesis process, fiber having average diameter 82.1nm could be obtained (at best condition).

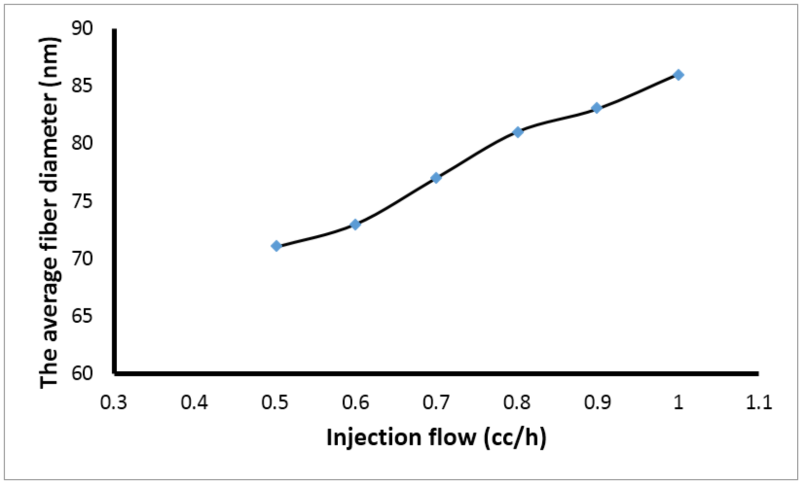

Fig. 3. Changes of average diameter of fiber by changes of injection flow.(Concentration: 25% w/v, Voltage: 16 kV, Distance: 20 cm, Collector speed: 200 rpm, Syringe diameter: 13 mm)

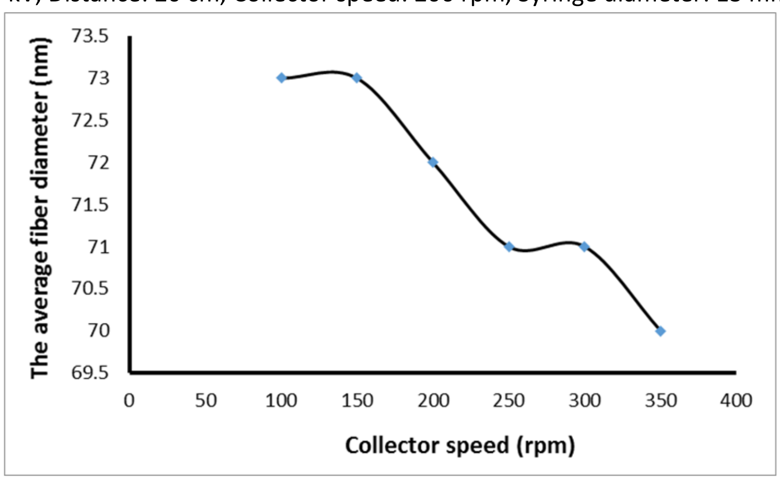

Fig. 4. Changes of average diameter of fiber by changes of collector speed.(Concentration: 25% w/v, Voltage: 16 kV, Distance: 20 cm, injection flow: 1 ml/h, Syringe diameter: 13 mm)

3.3. Studying the modified polystyrene Nanofiber diameter

In Figure 5, fiber diameter changes are found due to dithizone locating among fiber. Though optimizing and selecting best condition, the modified polystyrene nanofiber with average diameter 92.8 nm could be achieved (Figure .6).Although average diameter at modified mode is more than unmodified mode, the polystyrene nanofiber modified with dithizone has the unique properties such as metals absorption which the unmodified fiber does not have these properties.

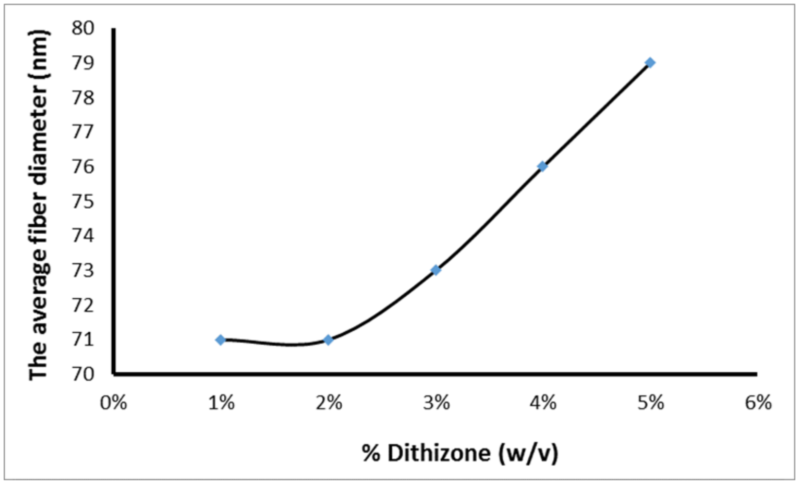

Fig. 5. Changes of average diameter of fiber by changes of Dithizone% w/v.
(Concentration: 25% w/v, Voltage: 16 kV, Distance: 20 cm, Syringe diameter: 13 mm)

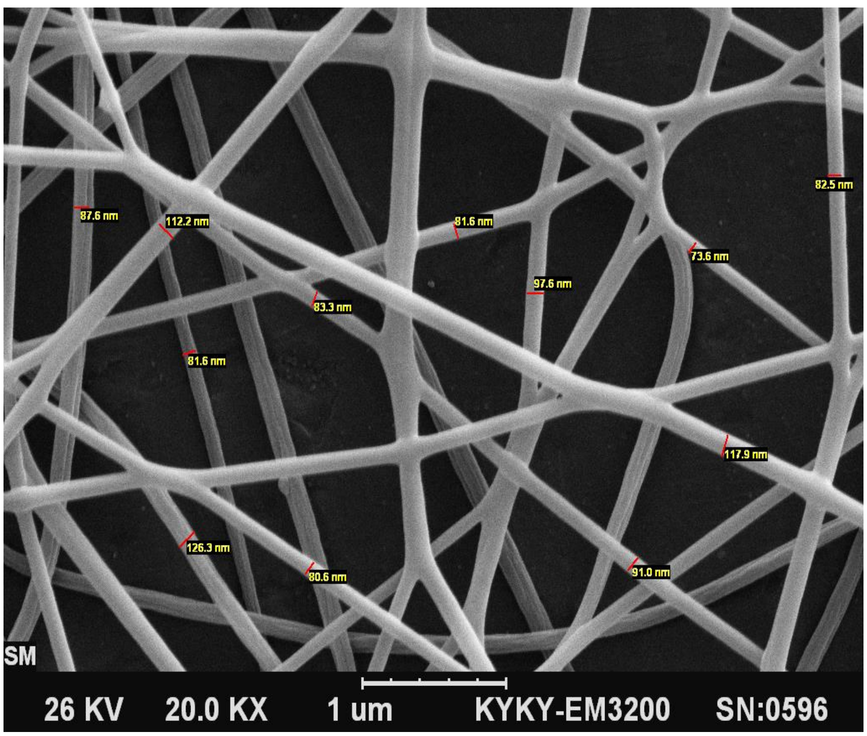

Fig. 5. SEM image of modified nanofibers.(Concentration of polymer solution: 25% w/v, Voltage: 16 kV, Distance: 20 cm, Collector speed: 350 rpm)

4. Conclussion

In the paper, polystyrene nanofiber were produced using polystyrene electrospinning in THF/DMF. Through studying the parameters effective on the electrospinning it become clear that if polymeric solution concentration is very low, then drop is formed rather than fiber formation and as polymer solution concentration increase then fiber diameter rise. Therefore optimal concentration (25% w/v) was detected and used.Due to results of optimizing effective factors it revealed that with increasing voltage, high electrospinning distance, low injection flow rate and high collector speed, nanofiber with regular chain-structure and lower diameter could be reached. Through optimizing effective parameters and at best conditions, polystyrene fiber had average diameter 82.1 nm. At last, polystyrene nanofiber were modified with dithizone and the modified polystyrene nanofiber having 92.8nm average diameter were synthesized using optimal conditions.

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