Needleless electrospinning of PAN/SBA-15 for the preparation of nanofibers membranes

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Abstract. Polycrylonaitrile is one of the few waterproof polymers that can be spun from relatively safe solvents, facilitating the use of PAN nanofibers membranes in medical, filtration and biological applications. In this study PAN nanofiber membranes containing SBA-15 nanoparticles were prepared by the process of electrospinning in needless electrospinning machine and DMSO was used as solvent. A small amount of dispersing agent BYK W-9010 was added for a better deagglomerating of SBA-15 nanoparticles in the PAN/DMSO solution. The influence of rod like SBA-15 type ordered mesoporous silica particles as filler on the morphology and textural parameters of electrospun PAN nanofibers was studied. The effect of concentration, applied voltage, distance and feed rate on nanofibers diameter was investigated. The results obtained demonstrated that by increasing the concentration, applied voltage and feed rate, the number of nanofibers was increased and thicker nanofibers were obtained. Viscosity increased by increasing the concentration of polymer and it increased further by imparting small amount of silica nanoparticles. The SEM images of nanofibers were taken and their morphology explains that presence of silica nanoparticles in the nanofibers increases the specific surface area and makes the surface rough.

1. Introduction
Nanofibers can be produced by different methods like jet blowing, melt blowing, co-extrusion, interfacial polymerization, electrospinning and many others. Among these, electrospinning is a versatile and well organized technique that is used to produce very fine homogeneous micro fibers or nanofibers. There are many advantages of the electrospinning process including being a relatively quick, simple, economical and efficient way to produce nanofibers. The applications of electrospun products are mainly in electronics, automotive, cosmetics, filtration and healthcare sectors [1].

In the process of electrospinning, usually polymer is dissolved in a solvent to make a solution and the selection of solvent is very important as it should be not toxic, corrosive or dangerous to be used [2]. In this work polycrylonitrile (PAN) is the selected polymer with ordered mesoporous silica SBA-15 particles as
inorganic fillers dissolved and suspended, respectively, in dimethyl sulphoxide (DMSO) to make a suspension to be electrospun. PAN is one of the few water resistant polymers which is semi crystalline and well resistant to degradation by sunlight, and in addition fibers of PAN are thermal insulators [3].

The addition of SBA-15 particles in the nanofibers provides increase in specific surface area of nanofibers [1]. Mesoporous silica materials have a great interest that continues to grow in emerging applications such as drug delivery system, catalysis, sensors, filtration etc., that benefit from the properties of these materials [4]. There are many specific cases where ordered mesoporous technology is urgently needed. These include ultrapure water purification and reuse in semiconductor industry, treatment of pharmaceutical waste water discharge and recovery of toxic homogeneous catalyst used in fine chemical production [5]. Nanocomposites filled with nanofibers show enhanced mechanical properties in contrast to unfilled composites [6].

Dispersion of silica nanoparticles by adding some surfactant implies the modification of surface energy of the silica particles that results in disrupting the Van der Waals forces that attract the silica particles to each other and thus hindering the SBA-15 particles to reaggregates [7].

This study gives an overview of the effect of the different PAN concentrations in DMSO, the effect of incorporating SBA-15 particles and the effect of dispersing agent in PAN/SBA-15/DMSO solutions, variation of electrospinning parameters on the process and resulting nanofibers.

2. Material and Methods

2.1. Materials
Polyacrylonitrile with Mw = 150,000 g/mol and DMSO (99.9% pure) were purchased from Sigma-Aldrich. SBA-15 has been synthesized according to S. Almuhamed et al [6] and Y. Belmoujahid et al [7] procedure. Dispersing agent BYK-W 9010 was obtained from BYK Company (Germany).

2.2. Preparation of solution
PAN solutions of 7, 8.5 and 10wt% were prepared in DMSO and 2wt% SBA-15 was added in all three solutions. A dispersing agent (1 wt% with respect to SBA-15) was also added in the SBA-15 containing suspension. Each SBA-15 containing suspension was stirred for 30 minutes by IKA® T18 digital Ultra Turrax to make the suspension homogeneous and obtain well deagglomeration of (SBA-15) silica particles.

2.3. Electrospinning
For electrospinning, the needleless nanospinning machine “Nanospider Lab” (Elmarco, Czech Republic) was used. The spinning parameters such as voltage, electrode-substrate distance, nozzle diameter, carriage speed etc. were varied to find optimum conditions. The optimized parameters are given in table 1.

| PAN Concentration in DMSO (wt %) | Voltage (KV) | Distance (mm) | Feed rate (mL/h) |
|---------------------------------|--------------|---------------|------------------|
| 7%                              | 20           | 200           | 0.5              |
| 8.5%                            | 30           | 200           | 0.6              |
| 10%                             | 40           | 190           | 0.6              |

2.4. Electrospinning conditions
The prepared PAN and PAN/filler solutions were electrospun directly by means of nanofibers machine “nanospider” by (Elmarco, Czech Republic). Temperature of the spinning chamber was 22-24 °C and
relative humidity was 38% to 40%. Carriage speed was 190 mm/sec and each sample was electrospun for 20 minutes. The electrospinning process is carried out between two high voltage wires, i-e the bottom rotating wire (electrode) in which polymer solution carriage is moved and it produces nanofibers, whereas the top wire (electrode) that is connected to nanofibers collector sheet.

2.5. Characterization

The viscosity of PAN/DMSO, PAN/SBA-15/DMSO and PAN/SBA-15/BYK-W 9010/DMSO solutions were measured using Anton Paar Modular Compact Rheometer 502 on “plan plan mode”. SBA-15 particles sizes were measured by ZETASIZER nano series in DMSO. The surface morphology of nanofibers was examined using scanning electron microscopy JEOL JSM-IT100. Images obtained by SEM were analyzed by Image J 1.45S software to obtain the average fibers diameter. Three images were taken by sample to get the mean values of diameter of fibers. On each image, 25 measurements of fibers diameters were taken and average value of all measurement were determined.

3. Results and Discussion

3.1. Effect of PAN concentration on PAN/DMSO solution viscosity

The viscosities of all the solutions were measured at constant temperature of 20 °C and before each measurement solutions were mixed by Ultra Turrax at $1 \times 10^4$ r.p.m for 20 minutes to make solutions homogeneous. The viscosities are mentioned in table 2.

| Sr. No. | PAN concentration in DMSO (wt%) | Viscosity mPa/sec |
|--------|---------------------------------|-------------------|
| 1      | 7                               | $9.62 \times 10^2 \pm 45$ |
| 2      | 7+2%SBA-15                      | $1.5 \times 10^3 \pm 145$ |
| 3      | 7+2%SBA-15+1% BYK               | $1.65 \times 10^3 \pm 212$ |
| 4      | 8.5                             | $2.55 \times 10^3 \pm 294$ |
| 5      | 8.5+2%SBA-15                    | $3.25 \times 10^3 \pm 217$ |
| 6      | 8.5+2%SBA-15+1% BYK             | $3.47 \times 10^3 \pm 188$ |
| 7      | 10                              | $3.93 \times 10^3 \pm 161$ |
| 8      | 10+2%SBA-15                     | $5.87 \times 10^3 \pm 408$ |
| 9      | 10+2%SBA-15+1% BYK              | $6.3 \times 10^3 \pm 175$ |

The results show that an increase in concentration of PAN in DMSO will increase the viscosity. The increase in viscosity is ascribed to the increase of intermolecular interactions. In the same way, dispersion, stronger polarization and hydrogen bonding between the solvent and the polymer affects the solubility and the viscosity, where continuously increase in viscosity is observed by increasing the concentration from 7%wt to 8.5%wt and then 10%wt. Similarly by imparting the 2%wt of silica nanoparticles increases the viscosity of solution to much extent and it is observed that same behavior of increasing the viscosity in small impact is seen by adding BYK W-9010 (1%wt of total weight of silica particles) (figure 1).
The viscosity of solution has great impact on the electrospinnability of the solution and on the morphology of the resulted nanofibers. If the solution has less viscosity only beads and beads on nanofibers will be obtained. This is due to the number of chains entanglements of polymers that are lower than the critical point. This lack in viscosity gives the place to the solvent surface tension to be dominant and thus to break up the jet into individual droplets and electrosprying or beads on nanofibers takes place [7]. Further increase in the solution concentration yields higher number of chains entanglement which is high enough to resist the jet breakage and also to withstand further elongation the solvent evaporation. Thus bead free nanofibers were collected.

3.2. Particles size measurement
The particles size of SBA-15 in DMSO was measured by light scattering, with and without BYK-W 9010, and results are given in table 3.

| Sample Name | Poly dispersity index (PDI) | Mean Diameter (nm) |
|-------------|-----------------------------|--------------------|
| 2wt%SBA-15+ BYK-W-9010 (1wt% vs SBA-15 wt) in DMSO | 0.945 | 110 |
| 2wt%SBA-15/DMSO | 0.641 | 250 |

The dispersing agent causes deagglomeration of silica particles in the solution by coating the surface of the inorganic filler. Dispersing or deagglomeration of silica nanoparticles by introducing the dispersing agent was a physical treatment which was pretreated by mechanical shear mixing. Mechanical shear mixing had the role of creating high local shear stress, which produced the tinny gap in the aggregates and the dispersing agent diffused into those gaps and started to disperse the nanoparticles by steric or electrostatic repulsions and as a result the previously formed gaps propagate, leading to ultimately separating the silica nanoparticles from their aggregates.

3.3. Nanofibers surface morphology
The nanofibers morphologies are shown in figure 1. For all three different solution concentrations, voltage was increased gradually 20, 30 and 40kV and feed rate of 0.5mL/h for low concentration (7wt% PAN) was used whereas for higher PAN concentrations (8.5, 10wt% PAN) it was increased to 0.6mL/h to make the feed rate convenient with electric field and concentration, so that droplets suspended at the needle tip must be drawn away with equilibrium mass balance and as a result nanofibers with uniform diameter were
obtained. The distance was fixed at 200mm for 7, 8.5wt% and 190mm for 10wt% of PAN in DMSO concentration. SEM images of different PAN concentrations with different diameters are shown in figure 2.

The SEM images show that at low PAN concentration, there are very few nanofibers and with small average diameter of 520nm. By increasing the polymer concentration, voltage and feed rate, the amount of nanofibers increased and their diameter also increased to 830 nm and 840nm for 8.5 and 10wt% of PAN in DMSO, respectively. Similarly, by introducing silica nanoparticles in PAN/DMSO solution the viscosity behavior is much increased because the introduction of silica nanoparticles increased the resistance in flow of solution. And increase in viscosity resulted in thick nanofibers of 890nm, 1090nm and 1150nm for 7%wt, 8.5%wt and 10%wt of PAN concentration respectively, so high viscosity resulted in nanofibers of larger diameter. The impact of PAN concentration on nanofibers diameter is shown in figure 3.

![Figure 2. SEM images of nanofibers of different PAN/DMSO concentrations.](image)

![Figure 3. Impact of PAN concentration on nanofibers diameter.](image)

In the case of applied voltage, as it is increased for 7%wt to 8.5%wt and then for 10%wt concentration from 20kV to 30kV and 40kV, the quantity of nanofibers is increased and their diameter is also increased. The reason behind it is that low voltage electrospinning does not occur because the magnitude of generated
electric field has not enough power to overcome the surface tension of the solution, whereas at higher voltages, the electric field overcomes the surface tension of the solution and droplets take the shape of typical Taylor cone and it will accelerate the jet, reduce the flight time. Shorter flight time will offer less time for the fiber to be stretched and the defect free cylindrical thick nanofibers are obtained [7]. The decrease in distance between electrodes to 190mm in case of 10wt% PAN concentration resulted in an increased in the electrical field and a reduction in flight time, which caused thick nanofibers. By adding the silica particles in the nanofibers, a few agglomerates are observed on the surface of nanofibers and their diameter also increased. Silica particles make the surface of nanofibers rough and increase the specific surface area.

4. Conclusion
For needleless electrospinning, finding the best parameters is very important, as voltage, PAN concentration and feed rate give the significant effect on electrospinning results. High voltage accelerated the jet and reduced the flight time, which allowed less time for fibers stretching and elongation, resulting in thicker nanofibers. High concentration of polymer solution resulted in higher number of polymer chains entanglement which led to the formation of larger diameter nanofibers. Whereas higher feed rate, due to large nozzle, coated more polymer solution on the electrical wire, which resulted in more fibers and increased fibers’ diameter. The addition of silica particles increased the viscosity of PAN/DMSO solution. The dispersing agent BYK W-9010 was successfully used to promote the deagglomeration of silica particles in the PAN/DMSO solution. BYK W-9010 has also small impact on solution viscosity. The introduction of silica particles make the surface of nanofibers rough and increase the nanofibers diameter.

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