

FABRICATION AND CHARACTERIZATION OF PVA/ZINC ACETATE NANOFIBRES BY ELECTROSPINNING METHOD

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Abstract

Local-made electrospun machine is firstly constructed. Poly Vinyl Alcohol /Zinc acetate (PVA/Zinc acetate) composite fibres, different molarities of (0.2 M, 0.3 M, 0.4 M, 0.5 M) are formed on Al-foil substrate by electrospinning technique. Electrospun Poly Vinyl Alcohol/Zinc Oxide (PVA/ZnO) submicron fibres of (0.2 M–0.5 M) are successfully formed by calcinations at high temperature. Scanning Electron Microscopy (SEM) analysis is carried out to examine the fibre diameter and microstructural properties of both submicron fibres.

Keywords: Electrospinning Machine, Nanofibres, Precursor Solution

Introduction

Engineers have successfully created polymer fibres using mechanical methods for several decades using mechanical processes. Conventional mechanical fibre spinning techniques cannot produce fibres with diameters smaller than about 2 μm robustly. Although conventional methods of producing polymer fibres are capable of producing fibres with diameters in the (μm) range, many applications require nm range (1).

Production of synthetic filaments using electrostatic forces has been known for more than one hundred years. The process of spinning fibres with the help of electrostatic forces is known as electrospinning. It has been shown recently that electrospinning process is capable of producing fibres in the submicron range.

Recently a process called electrospinning has been developed. This process has produced fibres as small as 5nm in diameter and is appropriately called nanofibres (2).

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clothing" for military, filters, sensors, nanocomposites, nanoelectronic devices, wound dressing etc. In normal conventional spinning techniques, the fibre is subjected to a group of tensile, gravitational, aerodynamic, rheological and inertial forces [Brain P Sautter].

Electrospinning traces its roots back to electrostatic spray painting, which has been in operation for almost 100 years. In 1934, a process for the production of polymer filaments using electrostatic force was patented by Formhals. Formhals encountered a number of problems early in his work, but by 1940 he had not only overcome those initial problems, he had developed methods of producing composite fibres using multiple polymers and for producing fibres that were aligned parallel to one another. Although the fibres produced by Formhals were much larger than the nanofibres, his work set the stage for the production of these structures. Taylor did a study of the polymer droplet at the end of the needle in an electrospinning setup in 1969. This study led to a better understanding of the process by which the polymer solution streams from the needle.

In 1987, the experimental conditions and factors that cause highly conductive fluids exposed to increasing voltages to produce unstable streams was studied by Hayati et al. These conditions cause the fluid stream to whip around in different directions as it leaves the needle. The work of Doshi and Reneker explored how changing the concentration of the polymer solution and the voltage applied to the solution affected the formation of nanofibres [Bibekananda Sundaray].

Research and development of nanofibre products is very active over the world producing fibre with diameter in nanometer range. Many types of polymers were processed into nanofibres of 50 to 1000 nanometers in diameter, several orders of magnitude smaller than conventional fibre spinning [Oldrich JIRSAK].

The nonwoven industry generally considers nanofibres as having a diameter of less than one micron, although the National Science Foundation (NSF) defines nanofibres as having at least one dimension of 100 nanometer (nm) or less [<http://www.engr.utk.edu/mse/pages/Textiles/Nanofiber%20Nonwovens.htm>].

The sol-gel process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Applying the sol-gel process, it is possible to fabricate ceramic or glass

materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibres, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials [<http://www.sol-gelTechnology.com>].

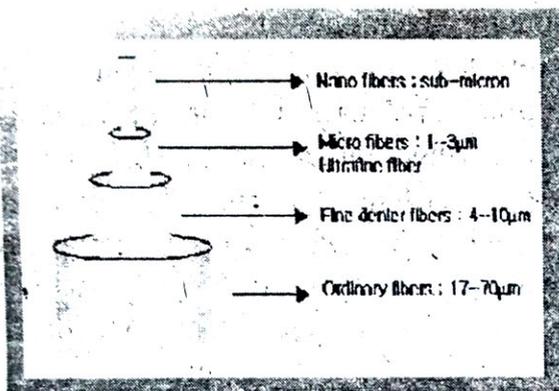


Fig.1 Fibre diameter comparison



Fig. 2 SEM of Nanofibres and human hair

Material and Setup

Zinc acetate and polyvinyl alcohol was chosen as the polymer. This polymer was best suited for the goal of this project. The electrospinning process takes place in a cylindrical shape of Plexiglas tube.

There are basically three components to fulfill the process: high voltage supplier, capillary tube and a metal collecting screen. In the electrospinning process a high, voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidifies, and is collected as an interconnected web of small fibres. One electrode is placed into the spinning solution/melt and the other attached to the collector. The collector is simply grounded.

A DC voltage in the range of several to several tens of kVs is necessary to generate the electrospinning. Polymers, molten in high temperature, can also be made into nanofibres through electrospinning. However, different from the case of polymer solution, the electrospinning process for a polymer melt has to be performed in vacuum condition. Namely, the capillary tube, the traveling of the charged melt fluid jet, and the metal collecting screen must be encapsulated within a vacuum [<http://www.elsevier.com/locate/compscitech>]

Experimental

The local-made electrospinning apparatus contains a needle or spinneret, high voltage power supply, and a grounded collector. Horizontal experimental setup was chosen for electrospinning process. High voltage power supply, which was transferred from 21"TV fly pad (219x6M, Toshiba) indirectly. To obtain the capable of producing the high voltage in the range of 10 kV~30 kV, 60 of 10MΩ resistors were used in series connection. It was known by using high voltage probe that produces maximum voltage 27.32 kV but the operating voltage was 25.19 kV. A syringe holder and a collector were kept in the cylindrical shape of Plexiglas tube, length of 36.3cm and inside diameter was 8.45 cm, 9 cm apart from each other. DC voltage generator of positive terminal was connected with hypodermic needle (0.55x25 mm) and the circular shape of Al collector which were covered with Al foil is connected by negative terminal of Power Supply as system ground.

ZnO fibres were formed by calcinating the precursor PVA/Zinc acetate composite fibres and for the preparation of composite fibre, sol-gel process was used. In this study, zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), distilled water and PVA(Polyvinyl alcohol) were used as raw materials for the preparation of PVA/Zinc acetate composite fibre. Firstly, Zinc acetate powder is dissolved in water and Zinc acetate solution was obtained after stirring for an hour. Polyvinyl alcohol was added in it by the equal ratio and it was stirred vigorously about 3 hours and highly concentrated zinc acetate solution was obtained. Then, it was kept in a constant temperature bath at 80 °C for 6 h, a viscous gel of PVA/Zinc acetate composite was obtained. In this process, there are different molarities of gel such as 0.2 M, 0.3 M, 0.4 M and 0.5 M are used for different samples.

Table 1 Concentration of composite

Sr No	Molarity (M)	Zinc acetate (g)	PVA (g)	Water (ml)
1.	0.2	43.874	43.874	1000
2.	0.3	65.811	65.811	1000
3.	0.4	87.748	87.748	1000
4.	0.5	109.685	109.685	1000

Sample preparation for Fibres

Before setting the vacuum glass-ambient, the experimental setup was prepared. PVA/Zinc acetate precursor solution about 20 cc was put into the syringe. The projectile of colloidal solution and target aluminium foil was apart 9 cm. after that the glass tube was pumped out until the expected value of the atm pressure was about 0.1 mm Hg by pumping motor. In the electrospinning process, a high voltage was applied to create an electrically charged jet of colloidal solution which solidified to leave a fibre. One electrode was placed into the spinning solution and the other attached to a colloidal solution. This induced a charge on the surface of the liquid. In this way, a charged jet of liquid was ejected from the tip of the capillary tube. The ejected liquid lay itself randomly on a grounded collecting target aluminium foil. The resultant Al-foil was examined with microscope. The comparison of original plane of Al-foil and the electrospun surface of Al-foil is shown. The resultant Al-foil was divided into two parts and one was calcined at 80 °C for 6 h each respectively. The surface morphology of each PVA/Zinc oxide coated Al-foils of before and after calcination were examined by scanning electron microscopy (SEM).

Table 2 Typical range of operating parameters used for electrospinning experiments with PVA/Zinc Acetate ultrafine fibre

Syringe Capacity	20 cc
Electrode Spacing	9 cm
Capillary Diameter	0.55 mm
High Voltage Power Supply (DC)	25.19 kV
PVA/Zinc Acetate Concentration	0.2 M, 0.3 M, 0.4 M, 0.5 M
Running Time	1 h
Cooling Time	10 h
Annealing Temperature	80 °C
Annealing Time	6 h

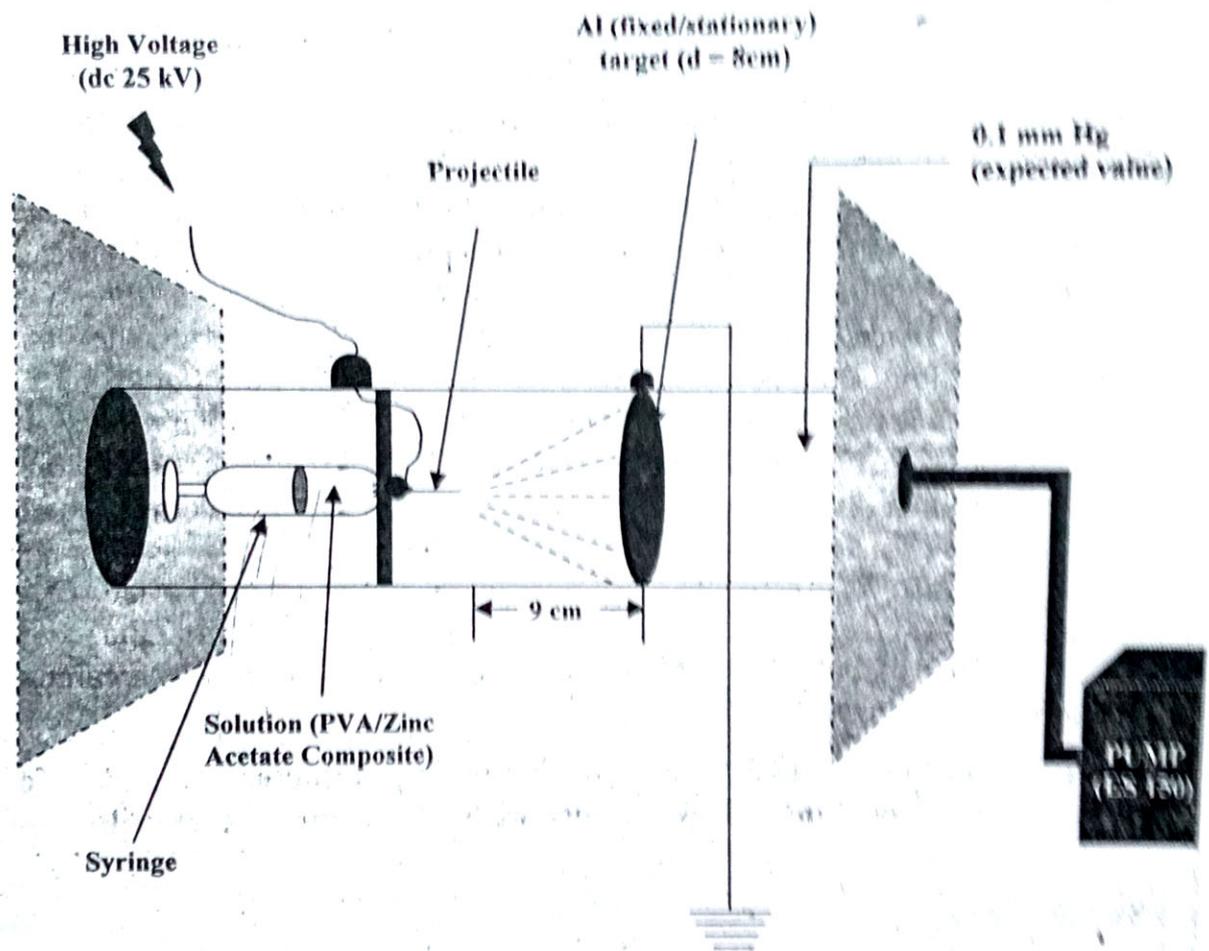


Fig. 3 Experimental set-up for electrospinning process

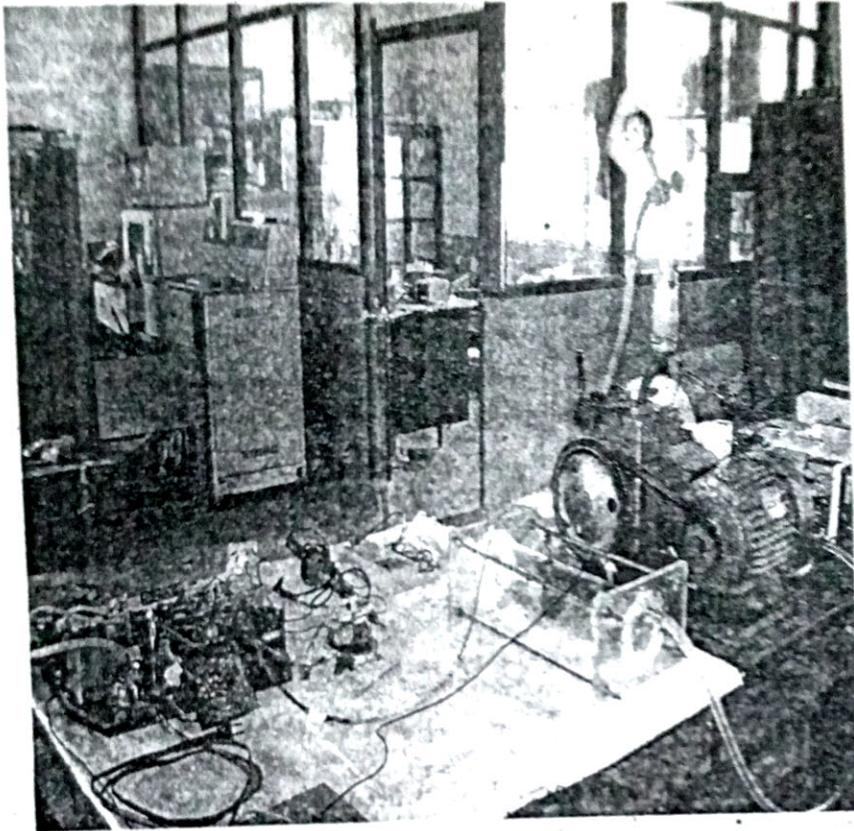


Fig. 4 Experimental setup for Electrospinning system



Fig. 5 Polymer solution is ejected when High Voltage is applied.

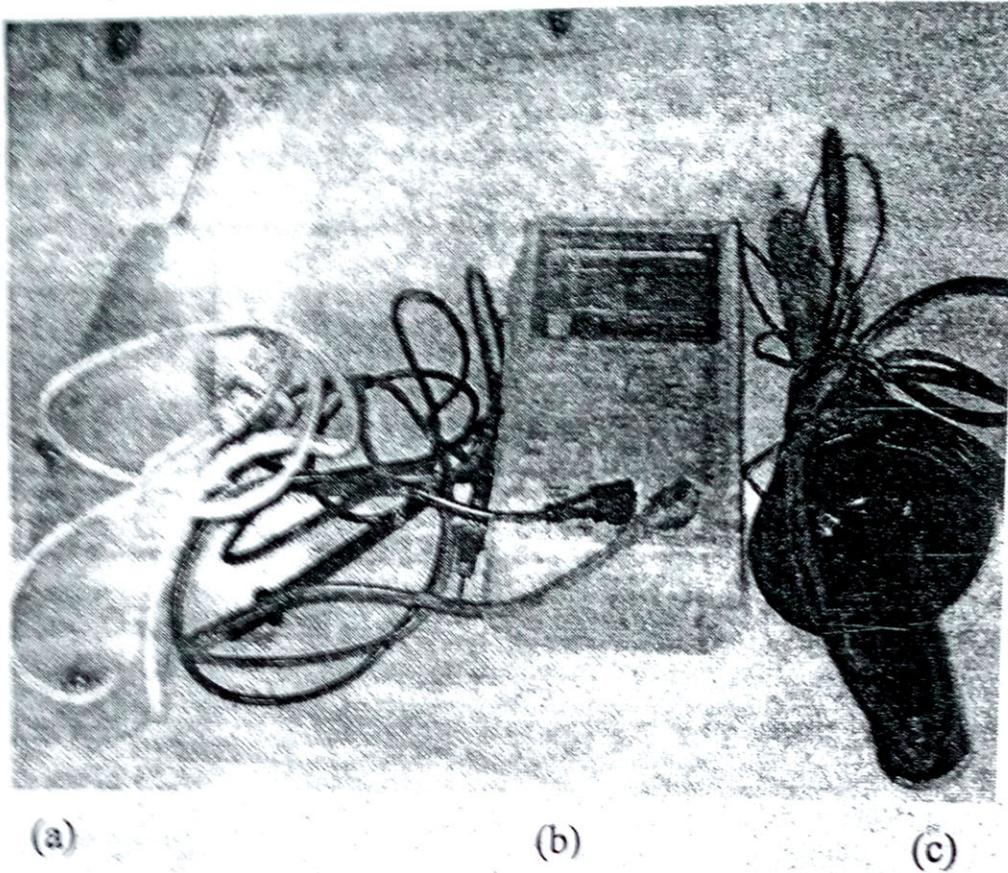


Fig. 6 Equipments used to detect High Voltage'

- (a) Vacuum Tester
- (b) Digital Multimeter
- (c) High Voltage Probe

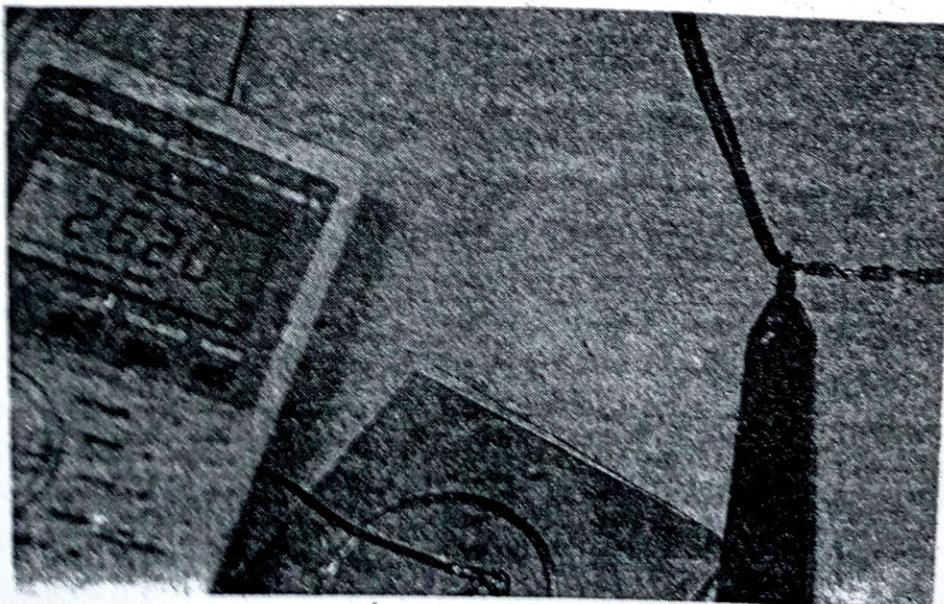


Fig. 7 Detecting system with Digital Voltmeter

Results and Discussion

SEM Analysis of PVA/Zinc acetate Composite Fibres

The PVA/Zinc acetate composite fibre was formed on Al-foil ($0.5 \times 0.5 \text{ cm}^2$) and SEM was employed to characterize these fibres. The set of SEM images for PVA/Zinc acetate composite fibre was recorded at Fig 8-11 (a). Fig 8(a) showed the SEM picture of PVA/Zinc acetate composite fibre with 0.2M. As it was seen in Fig 8(a), it was obvious that sub-micro fibres were appeared by splitting of bicomponent fibres. The shape of this fibres was segmented pie structure. Bicomponent fibres were split with the help of high forces of air or water jets. Eight fibres were significantly formed. Fig 9(a) gives the SEM plot of PVA/Zinc acetate composite fibre with 0.3 M. Different lengths of fibres were produced. The fibres orientation was randomized. The fibre used in this electrospinning technique looked islands-in-a-sea. Number of filament of a pack in single islands could not divided/counted. The fibre diameter was approximately equal to $1.87 \mu\text{m}$. The SEM plot of PVA/Zinc acetate composite fibre was given as Fig 10(a). Non-uniform fibre distribution was observed. Fibre length was also different. Film surface was smooth, low density; high pore volume and tight pore size were formed. The fibre diameter was $2.123 \mu\text{m}$. Fig 11(a) described the SEM micrograph of PVA/Zinc acetate composite fibre. Non-uniformed fibre length was obviously formed. Some fibres were separated by pores and some was in continuity. The fibre diameter was seemed to be $1.494 \mu\text{m}$.

SEM Analysis of PVA/ZnO Fibres

Pure ZnO (or) PVA/ZnO fibre was obtained by calcination at temperature of 80°C for 6 h. The set of SEM images of PVA/ZnO fibres with different molarities were shown in Fig 8-11(b). In the epitaxial film with 0.2M, crystalline was highly oriented, normally vertical and parallel with each fibre. It was crack-free and that in microstructure. The fibre diameter was estimated to be $2.95 \mu\text{m}$. The fibre distribution was non-uniform and little amount of pore was observed on this micrograph. Eight fibres were significantly formed. The mean pore size was examined to be $1.77 \mu\text{m}$. Fig 9(b) showed the SEM picture of PVA/ZnO fibres with 0.3M. non-uniform fibre distribution was clearly observed. The mid-zone of film was relatively dense. The film morphology looked like a mat. It was non-cracked and flat. Fig 10(b) gives the SEM micrograph of PVA/ZnO fibres with 0.4M. As

described in figure, the fibres were formed by splitting of component fibres. The fibre orientation was formed right. The fibre length was examined to be different. The fibre diameter was about 1.82 μm . Fig 8(b) described the SEM plot of PVAc/ZnO fibres with 0.2M. Non-uniform fibre distribution was clearly formed in this picture. The fibre length was also different. The fibre diameter was 0.26 μm .

Table 3 Diameter dependence of molarity of PVAc/Zinc acetate composite

SrNo.	Molarity(M)	Before Calcination	After Calcination
		Diameter(μm)	Diameter(μm)
1.	0.2	1.898	2.959
2.	0.5	1.3687	2.796
3.	0.4	1.725	1.874
4.	0.5	1.404	1.258

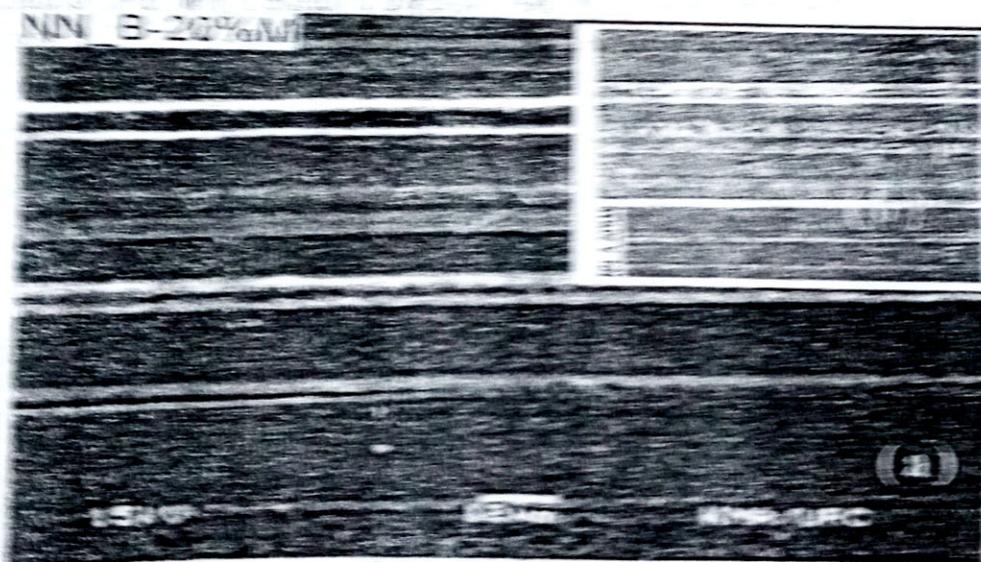


Fig. 8(a) Continuous as-spun nanofibres deposited 40-50l of PVAc/Zinc acetate composite: 0.2M

Fig. 8(b) Aligned electrospun ultrafine fibres of 0.2 M

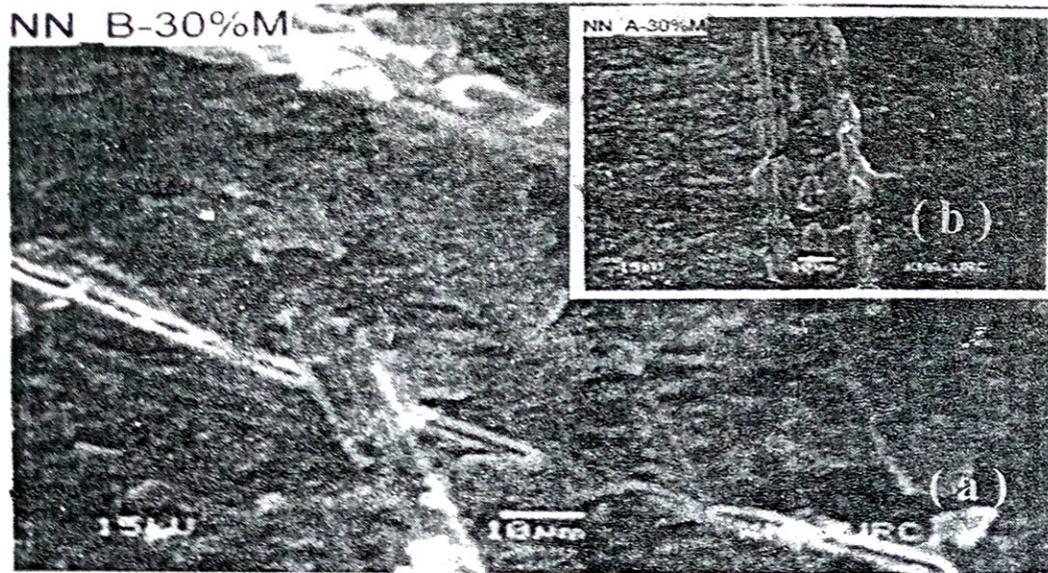


Fig. 9(a) SEM image (magnification = 10,000) of polymer solution 0.3 M

Fig. 9(b) Fibre scaffolds electrospum of 0.3 M at annealing temperature 500°C for 1 h

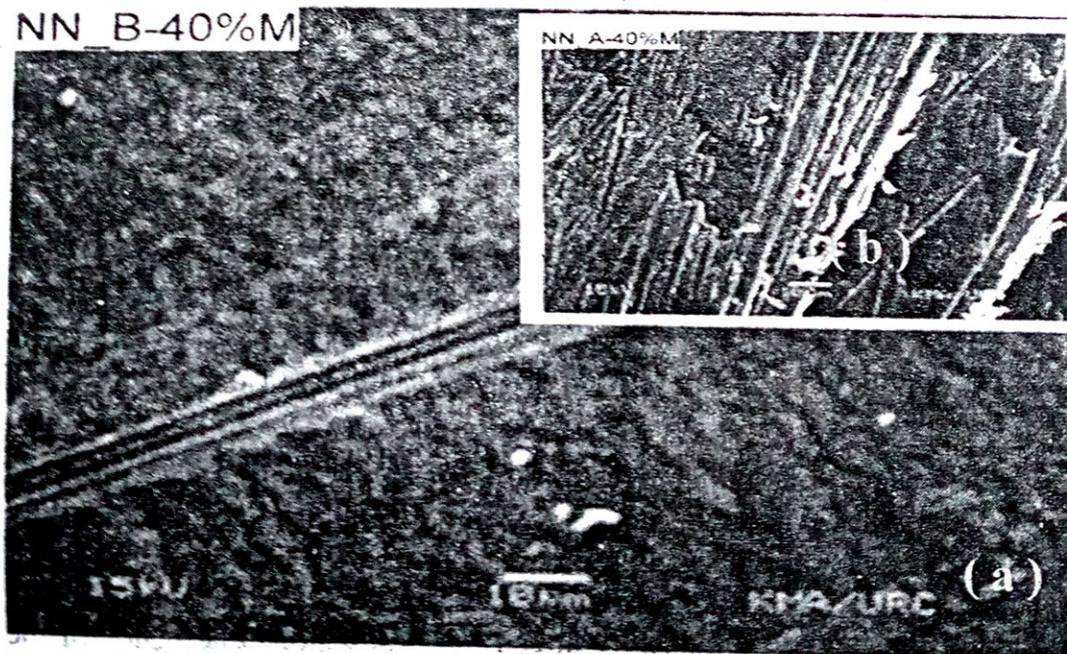


Fig. 10(a) Typical SEM image of PVA/ZnO acetate composite, 0.4 M

Fig. 10(b) Surface morphology of PVA/ZnO fibre with concentration 0.4 M

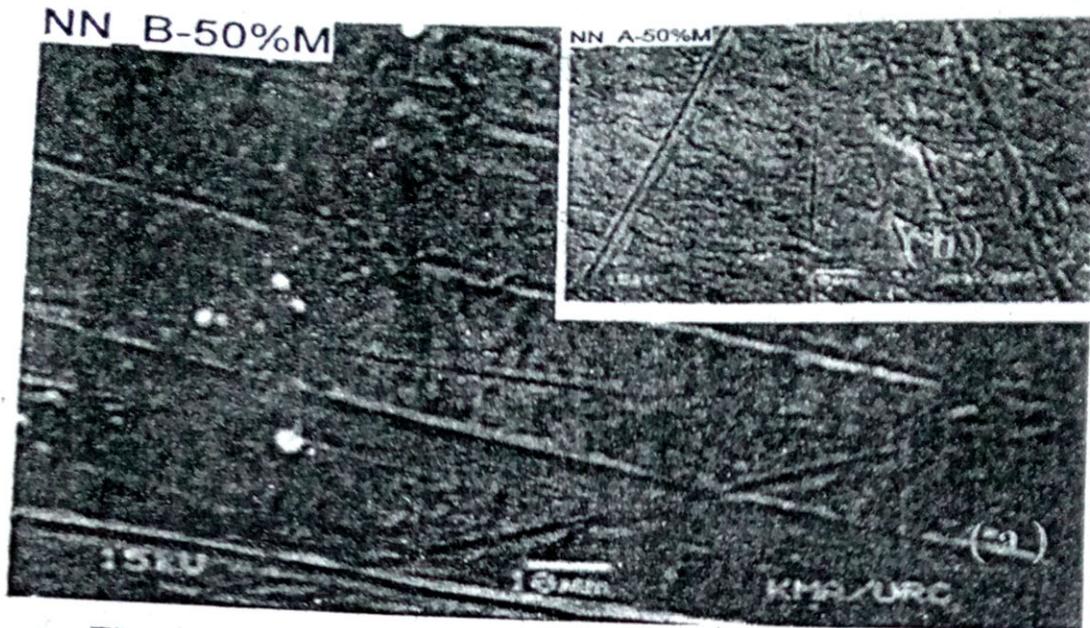


Fig. 11 (a) Image reported from SEM graph of 0.5 M

Fig. 11 (b) SEM micrograph of electrospun fibre

Conclusion

The micron fibres have been prepared by the following sequential steps:

- (1) Preparation of a solution with suitable inorganic precursor.
- (2) Mixing inorganic solution with a polymer template to get the solution for electrospinning with appropriate viscosity.
- (3) Electrospinning of the solution to obtain inorganic/ organic composite fibres.
- (4) Calcination of the prepared composite fibres to yield pure metal oxide fibres.

The electrospinning process took place in cylindrical shape of Plexiglas tube that had very limited exposure to elements exterior to the tube. This tube helped control the environment in which the electrospinning was taking place namely the unpredictable air converts in an uncontrolled environment that could dramatically alter fibre production. The inside of the tube also reached vacuum condition that was ejected from the needle during the experiments. We have implemented to fulfill the process as three components : high voltage supplier, syringe of small diameter and grounded Al-foil.

In this process, a high voltage was needed to create an electrically charged jet of polymer solution or melt out of needle. Before reaching the collecting screen, the solution jet evaporated or solidified and was collected as an interconnected web of small fibres. From the SEM results, it was concluded strongly that all fibres before and after calcinations were said to be "submicron fibres". The SEM images for both PVA/Zinc acetate composite fibre (before calcinations) and PVA/ZnO fibre (after calcinations) were not remarkably different in micro structures the smallest value of fibre diameter was found of PVA/ZnO submicron fibre (after calcinations) with 0.5M.

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