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Preparation of Porous Polyacrylonitrile/Poly (vinylidene fluoride) Nanofibers via Selective Dissolution of Electrospun PAN/PVdF/PMMA Nanofibers

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ABSTRACT

In order to prepare porous PAN/PVdF nanofibers, PAN/PVdF/PMMA blend nanofibers were electrospun and then the PMMA was removed via a selective dissolution technique with chloroform. After extraction of the PMMA, the resulting PAN/PVdF nanofibers had highly porous surface. The surface morphology was characterized using scanning electron microscopy (SEM). The Brunauer-Emmett-Teller (BET) surface area of porous PAN/PVdF nanofibers made from PAN/PVdF/PMMA blend precursors is higher than that of PAN/PVdF nanofibers.

Key words: Porous, Nanofibers, Selective Dissolution, PAN/PVdF

INTRODUCTION

Electrospinning is a unique technique for the preparation of ultrafine polymer fibers with diameter in the range of micrometer to nanometer. Since electrospun fiber mats have high specific surface area and high porosity, they can be applied for many applications such as scaffolds, membranes, wound dressings, sensors, electrical energy storage, etc. [1-5]. Poly (vinylidene fluoride) (PVdF) and polyacrylonitrile (PAN) have been intensively studied because of their excellent electrochemical properties for using as polymer electrolyte in lithium batteries.

Porous structure nanofibers have been of significant interest because of their ultrahigh surface areas as compared to nonporous nanofibers with similar diameters. Porous nanofibers with high surface area may have many potential applications in which web morphology and controlled pore structure are strongly required. Porous nanofibers as polymer electrolyte can absorb a lot of electrolytes in lithium batteries and show good electrochemical properties. There are different approaches to prepare porous nanofibers. Porous ultrafine fibers can be prepared via electrospinning of polymer blends, followed by selective thermal or photo degradation of one component, or by selective dissolution of one component [6-7]. Porous nanofibers were also obtained by exploiting the phase separation process of different polymers [8- 9]. Other researchers have reported the production of porous nanofibers through calcinations [10].

In this study, ultrafine PAN/PVdF nanofibers with a highly porous structure were prepared via selective dissolution technique. PAN/PVdF/PMMA blend solutions in N, N-dimethylformamide (DMF) were electrospun and most of PMMA was selectively extracted with chloroform.

MATERIAL AND PROCEDURE TECHNIQUE

Materials

PVdF (Solef 1010), PAN and PMMA were purchased from Solvay Co. France, Isfahan Polyacryl Inc. Iran, and Sigma Aldrich respectively. N, N dimethylformamide (DMF), and chloroform were purchased from Merck Co. Germany and Sigma-Aldrich Co. USA respectively.

Solution Preparation and Electrospinning

The PVdF, PAN and PMMA were vacuum dried at 60°C for 12h. Necessary amount of PVdF, PAN and PMMA were added to DMF at ambient conditions and stirred until homogeneous solution was formed. 1 ml Hamilton syringe was used as injector. The needle diameter was 0.41 mm. Electrospinning were carried out on a horizontal

setup. The electrospinning setup consisted of a syringe, a syringe pump (New Era Pump System, NE1000, USA), a grounded electrode (Aluminum sheet as collector), and a high voltage power supply (Gamma High Voltage Research, RR60, USA) which could generate positive DC voltages up to 60 kV. Then the electrospun nanofibrous membranes were finally dried under vacuum at 60°C for 12h.

Some preliminary experiments were conducted to obtain bead-free, stable, and continuous nanofibers. The value of electrospinning parameters were chosen as follows: voltage 21kV, solution concentration 16wt%, and PAN/PVdF/PMMA ratio in the polymer part of the solution 25/25/50, distance between the tip of the spinneret and collector 17cm, solution feed rate 200µl/h. Electrospinning was performed at room temperature and the syringe set up was enclosed in a chamber for adjusting and controlling the temperature.

Preparation of porous PAN/PVdF nanofibers

To extract the PMMA, the PAN/PVdF/PMMA nanofibers was treated in chloroform and then vacuum dried. Most of the PMMA component was extracted from the nanofibers by this treatment.

Morphology studies

Samples were gold coated prior to morphology studies. Thereafter, micrographs of the electrospun PAN/PVdF/PMMA and PAN/PVdF nanofibers were obtained by field emission scanning electron microscopy (FESEM, Phillips XL-30, Netherlands). 8-10 images were taken for each sample.

BET measurements

Surface area analysis was carried out using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method. The samples were degassed under flowing UHP grade nitrogen for 2 h at a temperature of 100ºC. Nitrogen gas adsorption measurements were taken at 0.05, 0.1, 0.15, 0.2, and 0.25 of saturation pressure using a Micromeritics Gemini 2360 instrument capable of measuring surface area from 0.01 m^2g^{-1} and higher.

RESULTS AND DISCUSSION

The morphology of porous PAN/PVdF nanofibers was characterized using SEM technique. Fig. 1 shows the SEM image of nanofibers before and after treating with chloroform. The surface morphology of the nanofibers becomes rough and irregular after the chloroform treatment.

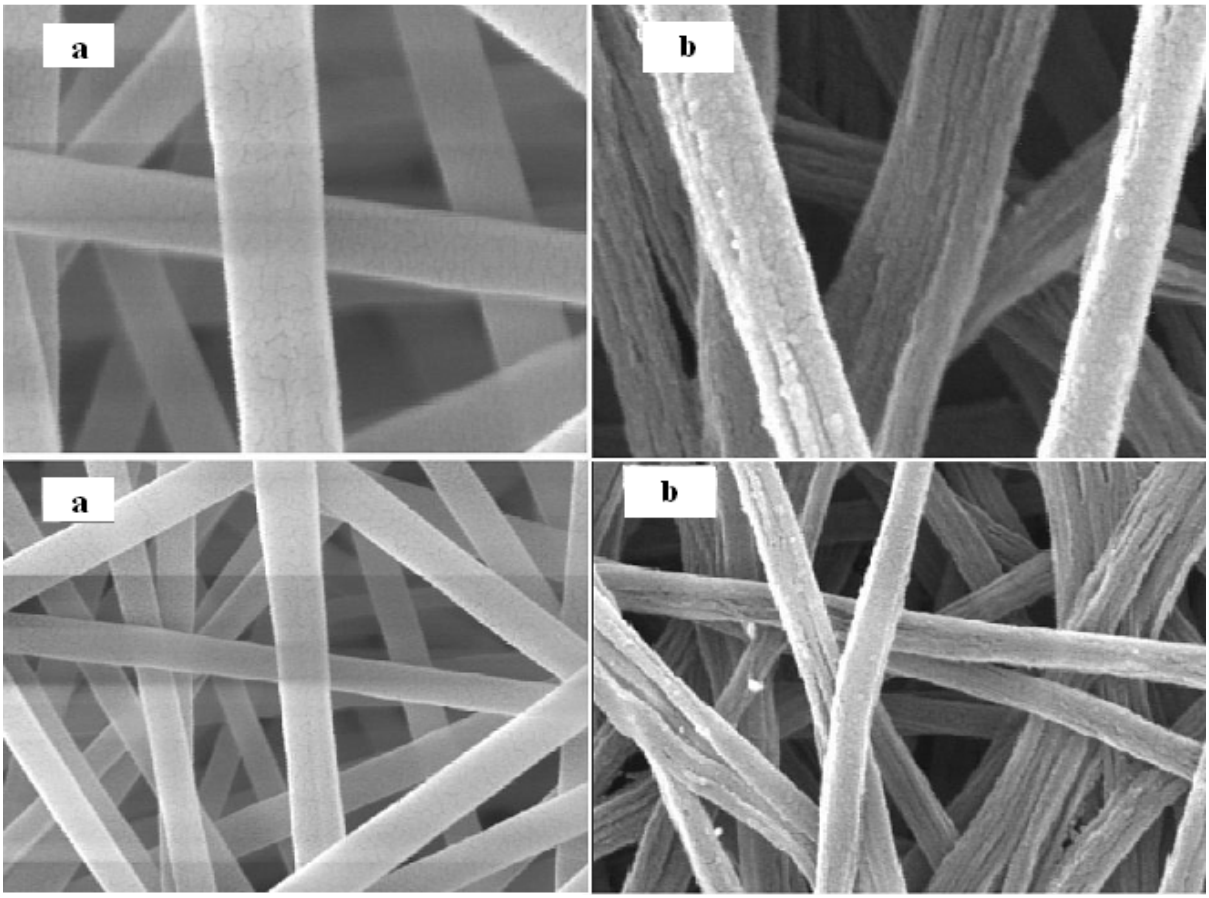

Fig. 1 SEM images of (a) PAN/PVdF/PMMA and (b) PAN/PVdF (after removal of PMMA)

The weight percentages of the remaining PAN/PVdF nanofibers after selective dissolution of the PMMA with chloroform are listed in Table 1, which were determined by weighing the dried fibers before and after dissolution of the PMMA for 2 h. Most of the PMMA was dissolved and extracted by chloroform.

Table -1 Weight percentage of the remaining fibers after extraction of the PMMA

Fibers	Remaining fibers (%)
PAN/PVdF/PMMA (25/25/50)	54.3

The solubility parameters of PVdF, PMMA and chloroform have been reported 10, 9.1, and 9.3 respectively. Surface area measurements of porous nanofibers were carried out using the BET nitrogen adsorption method. Porous nanofibers obtained after removing of PMMA have a BET surface area of 24.32. In comparison, PAN/PVdF nanofibers with similar diameters have a BET surface area of only 20.05. Therefore, the surface area of porous nanofibers increased by 21%, complementing the findings obtained from SEM analyses.

CONCLUSION

Porous PAN/PVdF nanofibers were obtained by removing the PMMA in PAN/PVdF/PMMA nanofibers using chloroform. ATR-FTIR spectra and TGA thermograms show that the PMMA has been removed from PAN/PVdF/PMMA nanofibers after chloroform treatment. SEM results demonstrate the formation of a porous structure in chloroform-treated nanofibers. The BET surface area of chloroform-treated PAN/PVdF nanofibers is 20% higher than that of PAN/PVdF nonporous nanofibers.

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