

# Preparation and characterization of Sulfonated High Impact Polystyrene (SHIPS) ion exchange nanofiber by electrospinning

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## ABSTRACT

High impact polystyrene (HIPS) nanofiber was prepared by electrospinning overcoming brittleness of polystyrene (PS). HIPS nanofiber can be crosslinked after electrospinning with divinylbenzene as a crosslinking agent and heat. After thermal crosslinking, HIPS nanofiber was sulfonated by sulfuric acid. FT-IR, X-ray photoelectron spectroscopy (XPS), water uptake, ion exchange capacity (IEC), morphology and contact angle were used to characterize sulfonated HIPS nanofiber. According to XPS analysis, SO<sub>3</sub>H group was increased with sulfonation time and water uptake was increased with sulfonation time, due to the hydrophilic group (SO<sub>3</sub>H) introduced in the HIPS nanofiber.

*Keywords:* High impact Polystyrene (HIPS), nanofiber, electrospinning, Sulfonation, ion exchange capacity (IEC)

## 1 INTRODUCTION

The study of nanofibers has been a subject of intensive research because of their unique properties and widespread applications in many areas. Among the various methods used to prepare nanofibers, electrospinning has been very attractive in the past decade because it is a simple and versatile approach for producing a matrix of fibers with diameters ranging from a few nanometers to micrometers. To date, over 100 different polymers have been electrospun into nanofibers. Because of the very high aspect ratio, specific surface area, and porosity, electrospun fibers are used for various applications, including tissue engineering, wound dressings, drug delivery, and vascular grafts [1].

More recently fibers have been used for ion exchange and have the advantages of simplification of the preparation, fabrication, contact efficiency and physical requirements of strength and dimensional stability [2].

In this study, the electrospinning of solutions of HIPS dissolved in DCE and DMF was completed and nanometer fibers of HIPS were prepared by electrospinning. We obtained high capacity HIPS cation exchange nanofiber by sulfonation and evaluated the performance of HIPS cation exchange nanofiber. The chemical properties such as water uptake, ion exchange capacity (IEC), morphology and contact angle were evaluated FT-IR spectral analysis, XPS apparatus, via titration, scanning electron microscopy (SEM) observation and contact angle meter.

## 2 EXPERIMENTAL

### 2.1 Materials

The High Impact Polystyrene (HIPS) used in the study were obtained from Kumho petrochemical Co. Ltd. The 1,2-Dichloroethane (DCE, 99%) and N,N-Dimethylformamide (DMF, 99%) used as a solvent was obtained from Samchun Co. Ltd. The thermal initiator, benzoyl peroxide (BPO, 75%) from Lancaster Co. Ltd., was purified by recrystallization from water. As a cross-linking agent, divinylbenzene was high-purity grades purchased from Aldrich Co. Ltd. Sulfuric acid were from Duksan Co. Ltd.

### 2.2 Preparation of Sulfonated High Impact Polystyrene (SHIPS) Nanofiber

HIPS nanofiber was prepared by electrospinning of its solutions in 1,2-Dichloroethane (DCE) and N,N-Dimethylformamide (DMF). The process parameters studied in this work included the concentration of the polymer solution, the solvent (DCE:DMF) mixing ratios, the applied voltage, the flow rate. Figure 1 shows the

schematic diagram of electrospinning apparatus. Uniform HIPS nanofiber were prepared by this electrospinning with the following optimal process parameters: the concentration of HIPS in DCE and DMF was 23 wt%, the solvent (DCE:DMF) ratios was 30:70, the applied voltage was 15 kV, the flow rate was 1.5 ml/hr. The HIPS nanofiber was crosslinked by divinylbenzene at 90 °C and was treated by immersion in 95 % sulfuric acid (Aldrich) for 40-120 min at 60 °C. Finally the sulfonated HIPS nanofiber was treated to stepped dilution rinse (70%, 50%, 30% sulfuric acid) and followed by rinsing with deionized water [3]. Table 1 and Figure 2 show the reaction conditions and crosslinking and sulfonation mechanism used to prepare the HIPS cation exchange nanofiber.

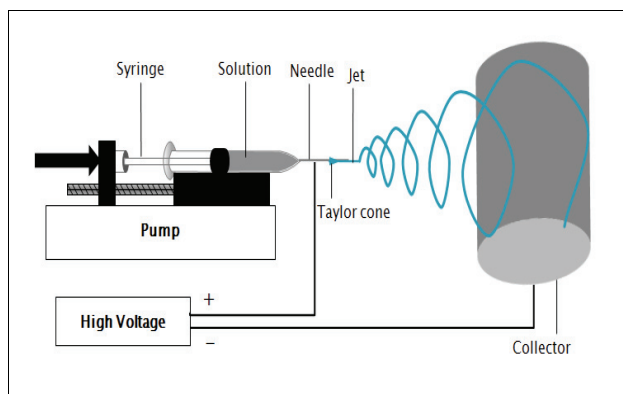


Figure 1: Schematic diagram of electrospinning apparatus.

| Solvent Mixing ratio (DCE:DMF) | Condition of electrospinning |           |                   |          | Crosslinking agent (wt%) | Sulfonation time (min) |
|--------------------------------|------------------------------|-----------|-------------------|----------|--------------------------|------------------------|
|                                | Conc. (%)                    | Volt (kV) | Flow rate (ml/hr) | TCD (cm) |                          |                        |
| 30:70                          | 23                           | 15        | 1.5               | 15       | 5                        | 40                     |
|                                |                              |           |                   |          | 7.5                      | 80                     |
|                                |                              |           |                   |          | 7.5                      | 120                    |
|                                |                              |           |                   |          | 10                       | 200                    |

Table 1: Preparation conditions of SHIPS ion exchange nanofiber.

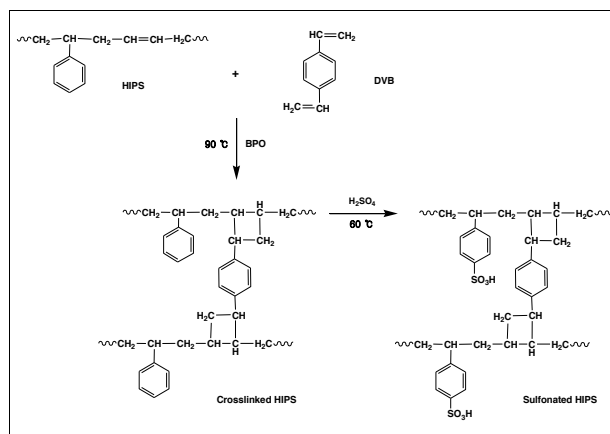


Figure 2: Mechanism of crosslinking and sulfonation on HIPS ion exchange nanofiber.

## 2.3 Characterization

The chemical structures of HIPS cation exchange nanofiber was characterized by Fourier transform infrared spectrometry (FT-IR).

X-Ray photoelectron spectroscopy (XPS) with Al Ka (1486.6 eV) X-rays evaluated the amount and state of nitrogen and sulfur ions doped into HIPS cation exchange nanofiber.

The swelling behavior of the sulfonated HIPS caion exchange nanofiber was measured by water uptake (WU). The water uptake was calculated as the ratio of the weight of the absorbed water to the dry membrane weight using the following equation.

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

Here,  $W_{wet}$  and  $W_{dry}$  are the wet and dry weights of the samples, respectively.

The ion exchange capacity (IEC) of the sulfonated HIPS nanofber were determined by Fisher's titration method. The experimental ion-exchange capacity (IEC) values were calculated from the following equation.

$$IEC(\text{meq/g} \cdot \text{dry}) = \frac{(V_{\text{NaOH}} \times N_{\text{NaOH}}) - (V_{\text{HCl}} \times N_{\text{HCl}})}{\text{Weight of sample}} \quad (2)$$

$V_{\text{NaOH}}$  is the volume of the NaOH standard solution,  $V_{\text{HCl}}$  is the volume of consumed HCl standard solution, and

$N_{\text{NaOH}}$  and  $N_{\text{HCl}}$  are the concentrations of the NaOH and HCl solutions, respectively.

The surface morphology of nanofiber before and after sulfonation reactions was observed by scanning electron microscopy (SEM).

The contact angle measurements were performed at room temperature (25 °C) using a commercial contact angle meter. All measurements were performed with deionized water.

### 3 RESULTS AND DISCUSSION

To confirm the change in the chemical structure of the HIPS ion exchange nanofiber, FT-IR spectra of the HIPS nanofiber before and after the sulfonation reaction were analyzed. Figure 3 shows the FT-IR spectra of HIPS and SHIPS, which were prepared with varying sulfonation times. In the sulfonated HIPS nanofiber, the absorption bands assigned to sulfonic acid groups were observed at 1250~1150 and 1060~1030  $\text{cm}^{-1}$ . The strong band in the frequency range of 1250~1150  $\text{cm}^{-1}$  can be ascribed to the stretching vibration of S=O, and the absorption band around 1060~1030  $\text{cm}^{-1}$  is assigned to the symmetric (O=S=O) stretching band.

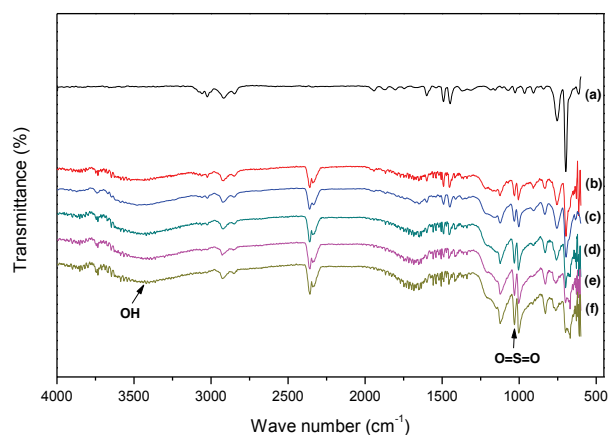


Figure 3: FT-IR spectra of HIPS nanofiber and sulfonated HIPS ion exchange nanofiber on 7.5% DVB content at sulfonation time (min): (a) 0, (b) 40, (c) 80, (d) 120, (e) 160 and (f) 200.

The composition of the surface layers of sulfonated HIPS cation exchange nanofiber was investigated by XPS. Figure 4 shows XPS wide scan spectra of sulfonated HIPS cation

exchange nanofiber having various sulfonation time. All nanofiber show three primary characteristic peaks corresponding to O1s, C1s, and S2p at binding energies of 532.5 eV, 284.9 eV, and 169.7 eV respectively.

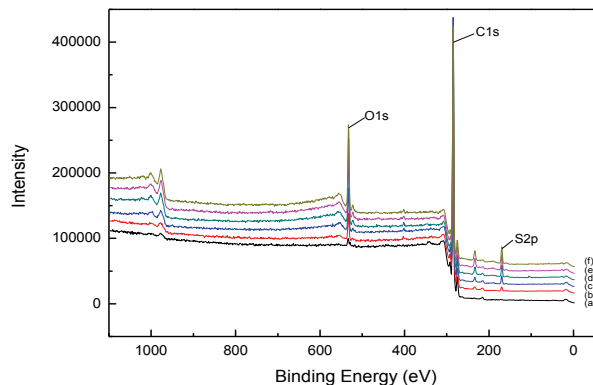


Figure 4: XPS spectra of HIPS nanofiber and sulfonated HIPS ion exchange nanofiber on 7.5% DVB content at sulfonation time (min): (a) 0, (b) 40, (c) 80, (d) 120, (e) 160 and (f) 200.

The water uptake is the most important property for ion exchange nanofiber in terms of their application. As shown in Figure 5, the water uptake decreased with increasing DVB contents. The maximum water uptake was 75.6 %, which was found for nanofiber prepared with 5 wt% of DVB and 200 min of sulfonation time. From this result, it can be concluded that DVB contents as crosslinking agent was an important factor for the water uptake.

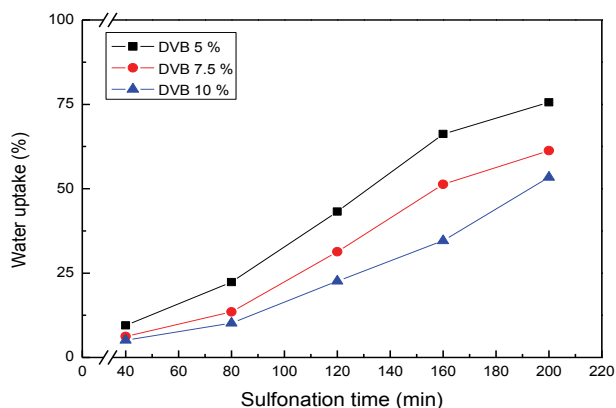


Figure 5: Effect of DVB contents on the water uptake.

The ion-exchange capacity (IEC) of the sulfonated HIPS nanofiber prepared with different sulfonation time and

DVB content as crosslinking agent were investigated by titration methods. Figure 6 shows the ion exchange capacity for HIPS nanofiber with different sulfonation reaction time and DVB content. The highest IEC value occurred for the sulfonated HIPS nanofiber prepared with 7.5 wt% of DVB and 200 min of sulfonation reaction time, having 2.53 meq/g.

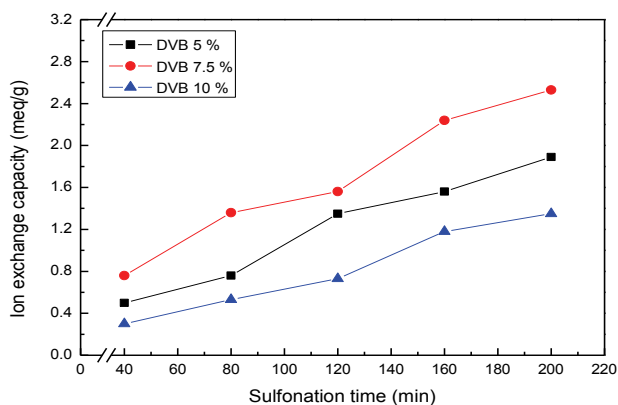


Figure 6: Effect of DVB contents on the ion exchange capacity.

The morphology of the nanofiber influences the sulfonation reaction. The SEM images of HIPS and SHIPS nanofiber prepared with various sulfonation reaction times are shown in Figure 7. As shown in Figure 7, the SHIPS nanofiber surface is rougher than the HIPS nanofiber due to the increased sulfonation time.

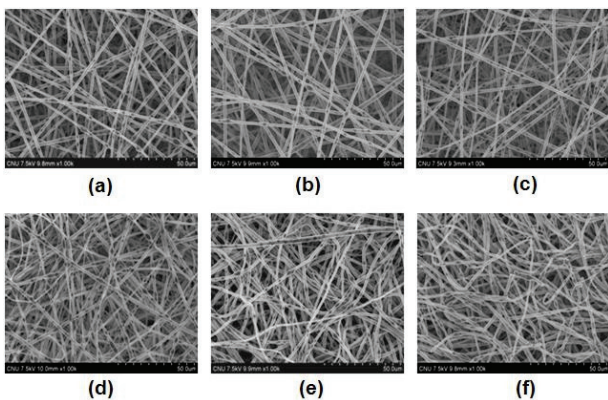


Figure 7: SEM images of sulfonated HIPS ion exchange nanofiber (original magnification = 1000x) at sulfonation time (min): (a) 0, (b) 40, (c) 80, (d) 120, (e) 160 and (f) 200.

The relationship between the hydrophilicity of nanofiber and the sulfonation reaction time is shown in Figure 8. It can be found that the contact angle decreases, implying the hydrophilicity of the nanofiber increases with the increase of sulfonation time.

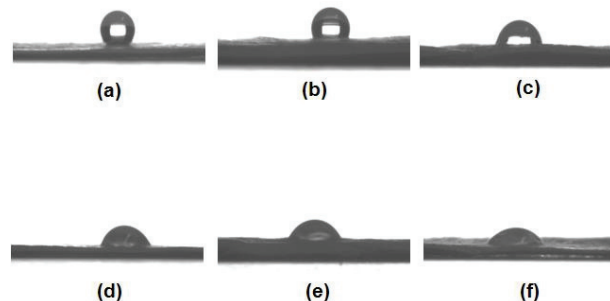


Figure 8: Contact angle of sulfonated HIPS ion exchange nanofiber (original magnification = 1000x) at sulfonation time (min): (a) 0, (b) 40, (c) 80, (d) 120, (e) 160 and (f) 200.

## REFERENCES

- [1] Y. Lin, Y. Yao, X. Yang, N. Wei, X. Li, P. Gong, R. Li, D. Wu, "Preparation of Poly(ether sulfone) Nanofibers by Gas-Jet/Electrospinning," *Journal of Applied Polymer Science*, 107, 909, 2008.
- [2] L. Dominguez, K.R. Benak, "Design of High Efficiency Polymeric Cation Exchange Fibers," *Polymers for Advanced Technologies*, 12, 197, 2001.
- [3] H. An, C. Shin, G.G. Chase, "Ion exchanger using electrospun polystyrene nanofiber," *Journal of Membrane Science*, 283, 84, 2006.