

Nanofibrous Ion Exchangers

Jaromír Marek, Jakub Wiener, Yan Wang

Abstract—The main goal of this study was to find simple and industrially applicable production of ion exchangers based on nanofibrous polystyrene matrix and characterization of prepared material. Starting polystyrene nanofibers were sulfonated and crosslinked under appropriate conditions at the same time by sulfuric acid. Strongly acidic cation exchanger was obtained in such a way. The polymer matrix was made from polystyrene nanofibers prepared by Nanospider™ technology.

Various types postpolymerization reactions and other methods of crosslinking were studied. Greatly different behavior between nano- and microsize materials was observed. The final nanofibrous material was characterized and compared to common granular ion exchangers and available microfibrinous ion exchangers. The sorption properties of nanofibrous ion exchangers were compared with the granular ion exchangers. For nanofibrous ion exchangers of comparable ion exchange capacity was observed considerably faster adsorption kinetics.

Keywords—Electrospinning, ion exchangers, nanofibers, polystyrene.

I. INTRODUCTION

THE study was inspired by the work [1]-[4] which firstly described the possibility of preparation of high capacity and very fast ion exchange nanofibrous material. For the preparation of the material both of authors used “jet” (or “nozzle”) electrospinning of polystyrene. In the second step of preparation they functionalized it by sulfuric acid. By this method they obtained polystyrene nanofibrous cation exchangers with strongly acidic sulfogroups.

The very beginning of this study was to proof work [1]-[4]. However the mentioned methods did not provide preparation samples desirable for industrial purpose. The effort was to simplify the preparation of these ion exchangers, to obtain material with required parameters and to find more environmental friendly agents which could approach the industrial scale of mass production.

For the preparation of nanofibrous matrix it was used different technology which enables preparation of bigger samples and is easily transferable to the larger production.

Functionalization of polystyrene nanofibres needs to be performed with the crosslinked material otherwise water soluble material is obtained. In the [2], [3] was omitted the crosslinking and the result was melted polystyrene membrane far from the original form of nanofibers. The methods used in this work for crosslinking were derived from the known

J. Marek is with Department of Textile Material Engineering, Technical University of Liberec, 461 17 Czech Republic (phone: 00-420-485-353-730; e-mail: jaromir.marek@tul.cz).

J. Wiener and Y. Wang are with Department of Textile Material Engineering, Technical University of Liberec, 461 17 Czech Republic (e-mail: jakub.wiener@tul.cz, yan.wang@tul.cz)

methods [5]-[9]. But, the polystyrene nanofibers compared to another polystyrene material (like foams, beads or microfibers) exhibited essentially different behaviour.

The final functionalization is represented by sulfonation i.e. wet treatment while obtaining cation exchange nanofibrous polystyrene membrane.

II. EXPERIMENTAL PART

A. Electrospinning

The starting polymer matrix for preparation of nanofibrous ion exchangers was readily available polystyrene analogously to the common particular ion exchangers based on this polymer [1], [2]. The nanofibers of polystyrene were prepared by Nanospider™ technology [10].

In principle the electrospinning by Nanospider™ is a modified process for the production of nanofibers and nanofiber layers via the electrostatic fiber spinning of polymer solutions [10], [11].

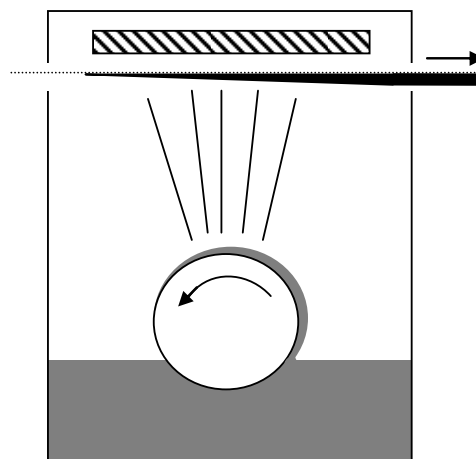


Fig. 1 Spinning from the free liquid layer [10]. The spinning cylindrical electrode partially submerged in polymer solution due to rotating enables to form Taylor cones from the free liquid layer. The polymer jets heading to collecting electrode form nanofibrous layer onto the surface of supporting layer.

In comparison with other available methods, this technology does not use jets or capillaries for the formation of fibers, but utilizes a rotating drum partially submerged in a polymer solution. The main advantage of this technology is the significant increase in production capacity. The throughput for the spinning of polystyrene was $0.4\text{g}\cdot\text{m}^{-1}\cdot\text{min}^{-1}$ which means that 1m long spinning electrode produce 0.4g of polymer per 1minute. The average output of nozzle electrospinning is usually $0.002\text{g}\cdot\text{min}^{-1}$ [12]. This means that it is possible to prepare samples of industrial format allowing simplified

experimental work.

In comparison with classical electrospinning, the polystyrene nanofibers prepared by this technology can be spun only from few specific solvents. In this work were used aromatic solvents based on the natural terpenoids [13] in mixture with polar aprotic solvents and polystyrene with molecular weight 260 000. These solvents are environmental friendly [14].

B. Cation Exchangers

Cation exchangers were prepared by sulfonation of polystyrene nanofibrous membrane due to simple chemical reaction

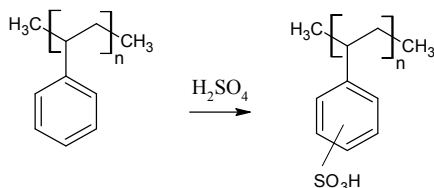
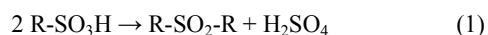


Fig. 2 Preparation of nanofibrous polystyrene cation exchangers by sulfonation

To improve the stability of nanofibrous material was used above mentioned crosslinking. Usually, the step of crosslinking precedes functionalization. But, under appropriate conditions [5] it is also possible to achieve functionalization and crosslinking in one step.

The methods used unsuccessfully for the polystyrene nanofibrous membrane included crosslinking during the electrospinning [11], crosslinking by radiation [6], suspension polymerization by Friedel-Crafts catalyst [7]-[9].

Study [5] mentioned crosslinking of polystyrene material by sulfobridges due to simple equation



together with sulfonation. This is the only method successfully used for polystyrene nanofibers. Application of this method is proved with the infrared spectrum of the final nanofibrous crosslinked and functionalized membrane (Fig. 5).

C. Characterization of Material

Scanning electron microscope (FEI Quanta 200 with ETD detector and high voltage of 15 kV) with the 5000 times magnification was used for the determination of morphology and control of structural changes of the nanofibrous materials as in Figs. 3 and 4.

Infrared spectroscopy with Fourier transformation (FTIR Bruker IFS 66v) was used to analyze the chemical structure of final material.

Method for measuring ion exchange capacity was acid-base titration. Ion exchange capacity (IEC) is the measure of the number of replaceable H^+ ions per unit mass of the exchange material. The effluent was collected in a flask, and measured by titration to a phenolphthalein end-point against a known molarity solution.

III. RESULTS AND DISCUSSION

Following figure shows quality of nanofibrous polystyrene layer. The fiber diameter starting polymer matrix was between 90 and 350 nm with good uniformity of the layer.

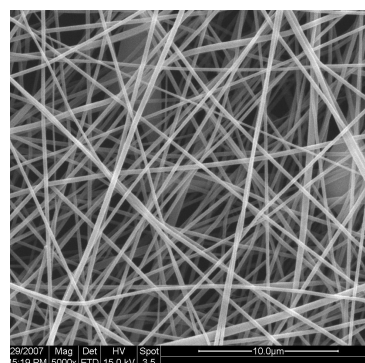


Fig. 3 Polystyrene nanofibers prepared by free liquid layer electrospinning (Nanospider™ technology [10], [13]), scale represents diameter of 10μm and corresponding fiber diameter is 90 to 350nm

After successful crosslinking and sulfonation the nanofibers increased their diameter range to 290-500 nm. The weight of nanofibrous samples increased to 150%.

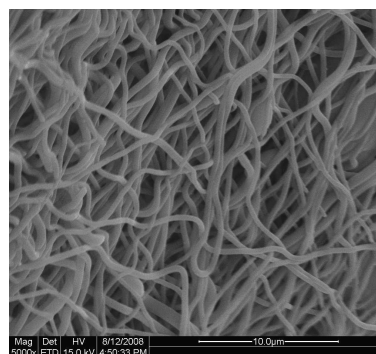


Fig. 4 Nanofibrous polystyrene sulfonated and crosslinked by sulfobridges; explicated scale represents 10μm and corresponding fiber diameter range from 290 to 500nm

The infrared spectra of strong acid nanofibrous polystyrene cation exchanger exhibit crosslinking by sulfobridges and sulfone groups as in Fig. 5. The characteristic peaks for sulfobridges ($\text{Ar-SO}_2\text{-Ar}$) are $1360\text{--}1335\text{cm}^{-1}$, $1170\text{--}1160\text{cm}^{-1}$ and for sulfone groups ($\text{SO}_3\text{-H}^+$) it is 1680cm^{-1} , $1230\text{--}1120\text{cm}^{-1}$ and $1120\text{--}1025\text{cm}^{-1}$. Compared to infrared spectrum of polystyrene standard and starting polystyrene nanofibrous matrix it is indicated significant move of peaks denoting new chemical bond in spectra.

Sulfones are very stable compounds. The nanofibrous polystyrene is then insoluble in common organic solvents like toluene or acetone even under heating. Their decomposition can be achieved only by melting with alkaline hydroxides [15], [16].

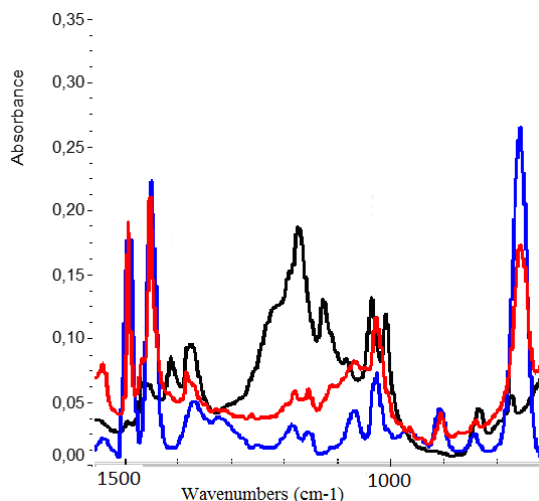


Fig. 5 Infrared spectra of polystyrene standard (spectrum with lowest absorbance around 1200cm^{-1}), nanofibrous polystyrene (middle spectrum), nanofibrous strong acid cation polystyrene exchanger with sulfone groups and sulfone bridges (strong peaks around 1200cm^{-1})

The main goal of this study was to demonstrate the advantages of nanofibrous ion exchangers compared with the microfibrinous and granular ion exchangers. In the following table we can see the comparison of ion exchange capacity of these materials.

TABLE I
COMPARISON OF ION EXCHANGE CAPACITY BETWEEN GRANULAR AND FIBROUS ION EXCHANGERS

Competitive ion exchanger	Type	Functional group	Ion exchange capacity ^b (meq.g ⁻¹)
Granular cation exchanger	resin	-R-SO ₃ ⁻	5.0
Microfibrinous ^a cation exchanger	microfibers	-R-SO ₃ ⁻	2.4
Nanofibrous cation exchanger ^d	nanofibers	-R-SO ₃ ⁻	5.2

^a Institute of Physical Organic Chemistry, National Academy of Science of Belarus;

^b Evaluated as dry matter in MEGA a.s., Czech Republic

The capacity of nanofibrous ion exchangers is two times higher than microfibrinous and comparable to the capacity of granular ion exchangers. So in this point of view the properties of nanofibrous ion exchangers are better than microfibrinous. It is because, in contrast to microfibrinous grafted exchangers, no inert polymer backbone, which lowers the portion of polymer available for functionalization, is present.

IV. CONCLUSION

This study describes simple and environmental friendly preparation of nanofibrous cation exchangers suitable for industrial mass production.

Compared to the granular ion exchangers, fibrous sulfonic

cation exchanger exhibited excellent kinetic features. These features are expressed by no lag in acid-base titration in comparison with granular ion exchangers. The time of saturation indicated by steady state of sorption and desorption of captured ions by nanofibrous ion-exchangers is 2 seconds while for granular ion exchangers 300 seconds.

ACKNOWLEDGMENT

This work was supported by ESF operational program "Education for Competitiveness" in the Czech Republic in the framework of project "Support of engineering of excellent research and development teams at the Technical University of Liberec" No. CZ.1.07/2.3.00/30.0065.

REFERENCES

- [1] H. An, C. Shin, G. G. Chase, "Ion exchanger using electrospun polystyrene nanofibers," *J. Membr. Sci.*, vol. 283, pp. 84–87, 2006.
- [2] H. Matsumoto, Y. Wakamatsu, M. Minagawa, A. Tanioka, "Preparation of ion-exchange fiber fabrics by electro-spray deposition," *J. Colloid Interface Sci.*, vol. 293, pp. 143–150, 2006.
- [3] Y. Wakamatsu, H. Matsumoto, M. Minagawa, A. Tanioka, "Effect of ion-exchange nanofiber fabrics on water splitting in bipolar membrane," *J. Colloid Interface Sci.*, vol. 300, pp. 442–445, 2006.
- [4] C. Shin, H. An, G. G. Chase, "Comparison of ion exchange performance of ion-exchange nanofiber cation exchanger and glass fibers coated with poly(styrene-co-divinylbenzene)," *Chem. Eng. Technol.*, vol. 29, pp. 364–367, 2006.
- [5] F. Kučera and J. Jancar, "Homogeneous and Heterogeneous Sulfonation of Polymers: A Review," *Polym. Eng. Sci.*, vol. 38, no. 5, pp. 785–792, May, 1998.
- [6] R. Gopal, M. Zuwei, S. Kaur, and S. Ramakrishna, "Surface modification and application of functionalized polymer nanofibers," in *Molecular Building Blocks for Nanotechnology*, vol. 109, G. A. Mansoori, T. F. George, L. Assoufid, G. Zhang, Ed. Springer New York, 2007, pp. 72–91.
- [7] N. A. Peppas, K. P. Staller, "Friedel-Crafts crosslinking methods for polystyrene modification," *Polym. Bull.*, vol. 8, pp. 233–237, 1982.
- [8] F. P. Regas, C. J. Papadoyannis, "Suspension crosslinking of polystyrene with friedel-crafts catalysts," *Polym. Bull.*, vol. 3, pp. 279–284, 1980.
- [9] N. P. Valkanas, V. D. Vrekou, A. G. Theodoropoulos, G. N. Valkanas, I. C. Konstantakopoulos, "Cross-linking regulators in one-step synthesis of macronet ion-exchangers," *J. Mater. Sci.*, vol. 31(18), pp. 4831–4836, 1996.
- [10] O. Jirsák, F. Sanetník, D. Lukáš, V. Kotek, L. Martinová, J. Chaloupek, Patent CZ 294 274, 14.09.2004, WO/2005/024101, (2005)
- [11] Bin Ding, Hak-Yong Kim, Se-Chul Lee, Douk-Rae Lee and Kyung-Ju Choi, "Preparation and characterization of nanoscaled poly(vinyl alcohol) fibers via electrospinning," *Fibers and polymers*, vol. 3(2), pp. 73–79, 2002.
- [12] Y. Yamashita, H. Miyake, A. Higashiyama, A. Tanaka, "Practical use of nanofiber made by electro-spinning process" 140.134.132.124., 2007.
- [13] Ch. Shin, G. G. Chase, "Nanofibers from recycle waste expanded polystyrene using natural solvent," *Polym. Bull.*, vol. 55 (3), pp. 209–215, 2005.
- [14] T. Noguchi, M. Myachita, Y. Inagaki, H. Watanabe, "Method and apparatus for recycling styrene resin," *Sony Corporation; US Pat. 6169121*, Jan. 2001.
- [15] J. Economy, L. Dominguez, K. Benak, "Polymeric ion exchange fibers," *US Pat. 6706361 B1*, Mar. 2004.
- [16] D. Agostino, G. E. Cooley, M. Newton, K. Bouchal, "Method for the preparation of cation exchange membranes doped with insoluble metal salts," *US Pat. 5705534*, Jan. 1998.