



## Preparation and Morphological Characteristics of Fluoroelastomer Electrospun Fibers†

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AJC-13172

Electrospinning is a unique and versatile process for fabricating ultrathin fibers in the form of nonwoven meshes or as oriented arrays from a range of polymers. In this study, a fluoroelastomer mat was prepared by electrospinning and then irradiated with UV radiation for crosslinking. The electrospinning of fluoroelastomer produced nonwoven uniform layers of fibers. The prepared fluoroelastomer mat exhibited reasonably good mechanical properties. Morphological analyses showed that the fibers were small in diameter with a more regular fiber distribution. An ion-transportable stretchable membrane was prepared from these fluoroelastomer mats *via* a direct sulfonation reaction. The structural properties of these individual and sulfonated nanofibers mats were compared using scanning electron microscopy and Fourier transform infrared spectroscopy.

**Key Words:** Electrospinning, Fluoroelastomer, Membrane, Morphology, Sulfonation.

### INTRODUCTION

Electrospinning is a versatile technique that allows the fabrication of very fine intrinsically charged fibers. Using this process, ultrathin fibers in the form of nonwoven meshes or as oriented arrays from a range of polymers can be fabricated. In this process, a high voltage is applied to a polymer solution when it is forced through a nozzle. Nanofibers can be produced from a wide range of polymers. These fibers have extremely high specific surface areas owing to their small diameters, high surface per weight ratio, high surface energy, good strength per unit weight and good barrier characteristics against the micro-organism<sup>1</sup>. The electrospinning process uses an electrostatic force to destabilize the surface of a polymer liquid droplet, creating a charged jet that elongates and solidifies to form an electrospun fiber<sup>2-4</sup>. When the electric potential is sufficiently high to overcome the surface tension of the liquid, a charged jet is ejected toward a grounded or oppositely charged counter electrode. The diameter of electrospun fibers are typically in the range of tens to a few hundreds of nanometers for solution electrospinning to hundreds of nanometer to a few micrometers for fibers electrospun from molten polymers<sup>2-4</sup>.

The geometry of the spinner, applied voltage, humidity, temperature, distance between spinning unit and collector are

known as the process parameters<sup>5</sup>. The system parameters are related to the properties of the polymer solution that can be specified as solvent, solution concentration, electrical conductivity, viscosity, surface tension, additives, intermolecular interactions, molecular weight distribution<sup>6</sup>. The concentration of the polymer solution is the most important system parameter in an electrospinning system. The diameter of the electrospun fibers is determined by the following: viscosity, conductivity and surface tension of the solution; molecular weight and concentration of the polymer; electric field strength and flow rate, *etc.*<sup>7-11</sup>. Electrospinning has many advantages because it can produce materials with a large surface area to volume ratio<sup>11</sup>. This process can be used for a variety of applications, such as membranes, filters, catalysts, composite reinforcements, bio-engineering and electronic devices<sup>12</sup>.

Plastics are polymers with a higher glass transition temperature ( $T_g$ ) than room temperature and are relatively easy to be made into electrospun fibers, whereas rubbery polymers are difficult to electrospin due to the low  $T_g$ . The  $T_g$  values of elastomers, such as natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR), are far below 0 °C. The shape of the fiber can be formed from a rubber solution by electrospinning but it tends to be destroyed immediately by

†Presented to the International Rubber Conference (IRC-2012), May 21-24, 2012, Jeju, Republic of Korea

cold flow due to the lower  $T_g$  than room temperature<sup>13</sup>. For this reason, the crosslinking of electrospun fibers is an essential method. On the other hand, the crosslinking methods of rubber include sulfur vulcanization, peroxide cure or resole curing<sup>13</sup>. These methods require high temperatures and pressures, which is unsuitable in this case. This can be solved using a UV curing system. This system can produce a highly crosslinked polymer within few seconds at room temperature. In this method, irradiation produces an initiating species, such as free radicals or cations, by photolysis of radical type or cationic-type photoinitiators.

This paper reports the preparation, properties and morphological characterization of fluoroelastomer (FKM) electrospun fibers. The electrospinning conditions were optimized by the selection of a suitable solvent and polymer concentration. The morphology of the electrospun fibers was evaluated under different experimental conditions. Finally, an ion-transportable stretchable membrane was prepared from these fluoroelastomer mats by direct sulfonation. The structural properties of these individual and sulfonated nanofibers mats were examined by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

## EXPERIMENTAL

Commercial grade fluoroelastomer, Viton F605C, was chosen as the base polymer to prepare the fluoroelastomer mat. Fluoroelastomer was obtained from DuPont Performance Elastomers L.L.C (USA). Acetone was used as a solvent for fluoroelastomer and was purchased from Daejung Chemical & Metals Co., LTD (Korea). The photoinitiator 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (max = 310 nm) and crosslinking agent trimethylolpropane *tris*(3-mercaptopropionate) were acquired from Sigma-Aldrich, USA. Magnesium oxide (MgO, Osaka) and calcium hydroxide (Showa) were used as additives agent for curing fluoroelastomer. A UV lamp (306 nm, 8 W) was used for the radiation curing of fluoroelastomer. Aluminum foil (Lotte Aluminium Co., Ltd.) was used to collect the electrospun fibers. A Profi syringe (50 mL, Shinchang medical Co., Ltd, Korea) was used to fill the polymer solution. The needle (Bectom Dichinson Medical(s) Pte Ltd, Singapore) was used to produce nanofibers with a very low production rate. Chlorosulfuric acid (Aldrich, USA) was used for the sulfonation of fluoroelastomer.

**Preparation of the electrospun nanofibers:** For the preparation of electrospun fibers 13-20 wt % of fluoroelastomer solution in acetone was prepared. This was combined with 1 wt % photoinitiator and 3 wt % crosslinking agents, respectively. A 50 mL Profi syringe (for single use) was used. The needle was changed for each solution. The electrospinning process was performed using an Electraris apparatus. Fig. 1 shows the electrospinning apparatus with a UV lamp for curing. A syringe with a metal needle (2.0 cm of length and 0.4 mm of diameter) was used as the solution reservoir. A drum-shaped counter electrode was located below the reservoir. The electrospun fibers were collected on the tubular layer. The distance between the capillary tip and counter electrode (tip-to-collector distance, TCD) was 30 cm and the applied

voltage was 25 kV. The drum was spun at 100 rpm. The distance between the collector and UV lamp was 10 cm. The sample was irradiated with UV immediately after electrospinning. The electrospun fibers were collected on the top of the drum collector and the bottom side of the drum was irradiated with UV light to avoid UV-irradiation of the solution reservoir. A UV lamp was supplementary irradiated on the electrospun fibers for 0.5 h after electrospinning.

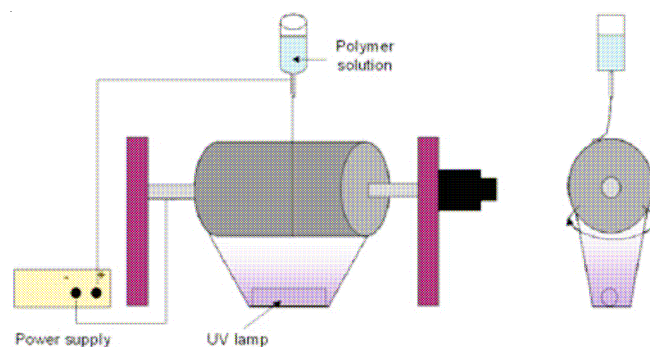


Fig. 1. Electrospinning apparatus with *in situ* UV irradiation system

## Testing and characterization

**Curing of samples:** Two methods were used for curing the electrospun mat. Firstly, the electrospun mat was dipped into an aqueous solution of MgO and Ca(OH)<sub>2</sub> for 1 h. It was then taken out and dried for 1 day at room temperature and finally it was heated at 180 °C for 0.5 h for making the mat to be crosslinked. Secondly, the electrospun fibers were exposed to UV light for 0.5 h after finishing the electrospinning process.

**Morphological analysis:** Scanning electron microscopy (SEM, JEOL JSM 5900, Japan) was used to examine the morphology and surface textures of various electrospun fibers samples. The images were obtained at a tilt angle of 0° with an operating voltage of 20 kV and an average beam current of 90 mA. Field emission SEM (FE-SEM, Hitachi S-4800) was also used for morphological characterization. For SEM analysis, the nanofibers were coated with a thin layer of platinum.

**Swelling test:** An electrospun mat, 5 mm × 5 mm in size, was fabricated and immersed in acetone. The morphology of the electrospun fibers were examined by SEM over a 4 week period.

**Sulfonation of fluoroelastomer mat:** 1 g of the fluoroelastomer mat was soaked with 99.9 % methanol for 10 min at 60 °C. The sample was centrifuged (5000 rpm for 10 min) at room temperature and dried at 60 °C for 10 min before adding 10 mL of chlorosulfuric acid in a glass centrifugation tube. The reaction was carried out at 60 °C for various times and stopped by separating the mat sample from chlorosulfuric acid. The sample was washed with 20 mL of 1,2-dichloroethane and centrifuged as above. The sample was washed again with 20 mL of 99.9 % methanol followed by washing with distilled water. Finally, the sample was dried at 60 °C in a vacuum oven for 15 h.

## RESULTS AND DISCUSSION

**Morphological analysis:** Fig. 2 presents SEM images of the electrospun fluoroelastomer fibers. Electrospun fluoroelastomer fibers exhibited a circular fiber morphology. Fig.

2(a) shows the uncured surface electrospun fibers. The mean diameter of the uncured-electrospun fibers was 0.7-1  $\mu\text{m}$ . This diameter was somewhat thicker than the usual submicron diameters for common plastic polymer materials, possibly due to the single filament formation. The cross section of the uncured fibers showed severe deviation from a circular shape (Fig. 2b). Fig. 3(a-h) presents the deformation of uncured electrospun fibers as a function of time. Initially, a circular fiber morphology was observed. The surface of the uncured electrospun fibers tended to deform to become flat and finally lost their initial circular fiber morphology (Fig. 3). This might be due to viscous cold flow originating from its low  $T_g$ . The uncured fiber samples morphology was changed to films with flat, smooth surfaces. This type of fiber deformation has been observed on both the surface and cross section.

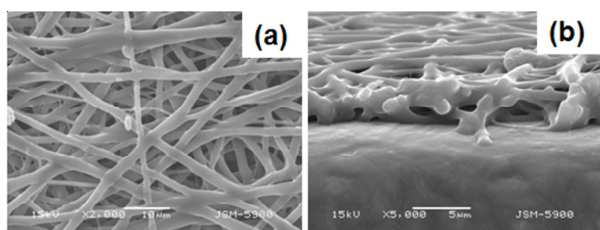


Fig. 2. Uncured electrospun mat of fluoroelastomer: (a) surface and (b) cross section

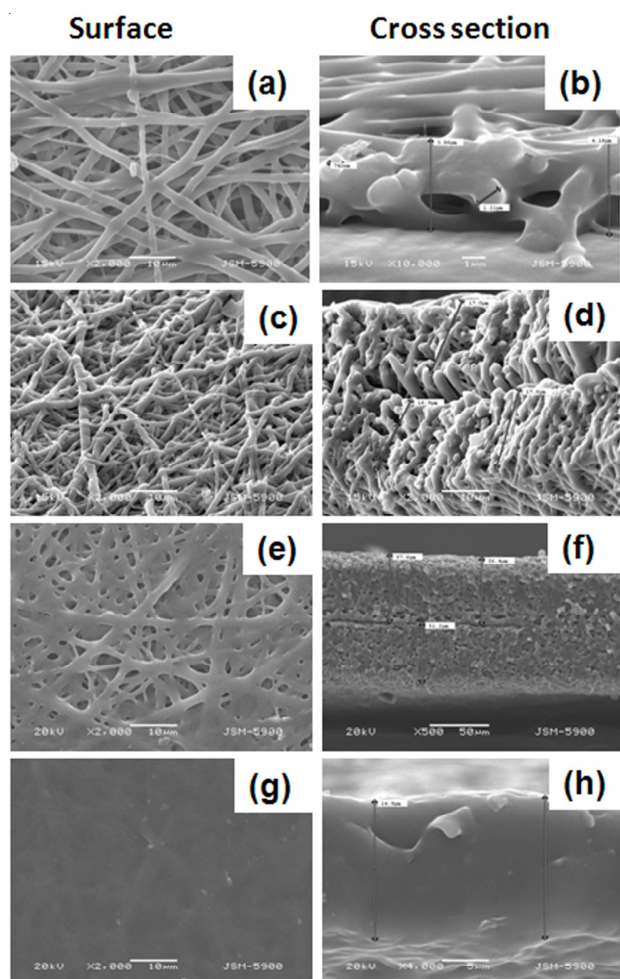


Fig. 3. Deformation of an uncured fluoroelastomer electrospun mat by times: (a-b) after 1 day, (c-d) after 14 days, (e-f) after 50 days and (g-h) after 70 days

**Effect of phase morphology on curing system:** Various electrospun fibers samples were observed by SEM to examine the change in morphology and surface textures with different curing agents. Fig. 4 shows SEM images of the uncured mat, MgO, Ca(OH)<sub>2</sub> and UV cured mat, respectively. The uncured electrospun fibers were more regular and smaller in diameter. On the other hand, no fiber was obtained from the mat cured with MgO and Ca(OH)<sub>2</sub>. The sample was cured but the fiber morphology changed to a dispersed phase film morphology. In contrast, the morphology of the mat was maintained in the UV cured system. The fibers were more regular and uniform but were larger than the uncured fluoroelastomer electrospun fibers. Therefore, UV curing is the most favourable curing method for this type of electrospun fiber.

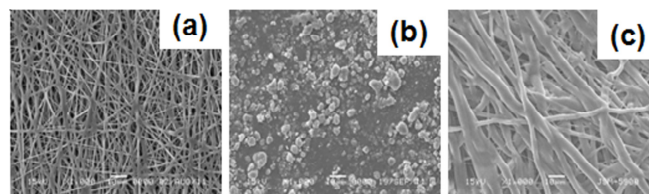


Fig. 4. Surface morphology of fluoroelastomer with different curing systems: (a) Uncured mat, (b) Curing with MgO, Ca(OH)<sub>2</sub> and (c) UV cured mat

#### Swelling study of cured fluoroelastomer mat:

Fluoroelastomer was dipped into acetone to assess its swelling behaviour and fiber stability in a solvent. The sample cross-linked by UV irradiation did not dissolve in acetone. Fig. 5(a-e) shows SEM images of the UV-cured fluoroelastomer mat before and after swelling. The fiber morphology was not affected, even after a long duration of swelling. On the other hand, after swelling, some of the fibers stuck together. The electrospun fluoroelastomer fiber mats exhibited considerable shrinkage under physiological conditions. As shown in Fig. 5(a), immediately after electrospinning, the fibers appeared fairly straight, detached from each other and with ample space between the individual fibers. They evenly overlapped to form a nonwoven network structure. The fiber structure became irregular. After swelling, the nanofibers appeared bulkier and considerably closer together. As a result, with the elimination of space between the fibers, the size of the unwoven sample was reduced significantly. The results also showed that the electrospun fiber diameters increased with increasing swelling time.

**ATR-FTIR spectroscopy:** ATR-FTIR was used to characterize the untreated and treated fluoroelastomer mat to obtain more insight on the surface functional groups of the fluoroelastomer. Fig. 6 shows FTIR spectroscopy of the fluoroelastomer mat before and after sulfonation. The broad band ranging from 1000 to 1400  $\text{cm}^{-1}$  was assigned to the stretching vibration of the C-F bond. This was common for all spectra but the intensity and sharpness decreased with increasing treatment time. After a potential treatment time of 20 min, some new peaks were observed due to the generation of new functional groups. Two peaks were observed at 2920 and 2850  $\text{cm}^{-1}$ , which was common in all spectra and were assigned to asymmetric and symmetric C-H stretching, respectively. The intense band at 1750-1735  $\text{cm}^{-1}$  corresponds to the stretching

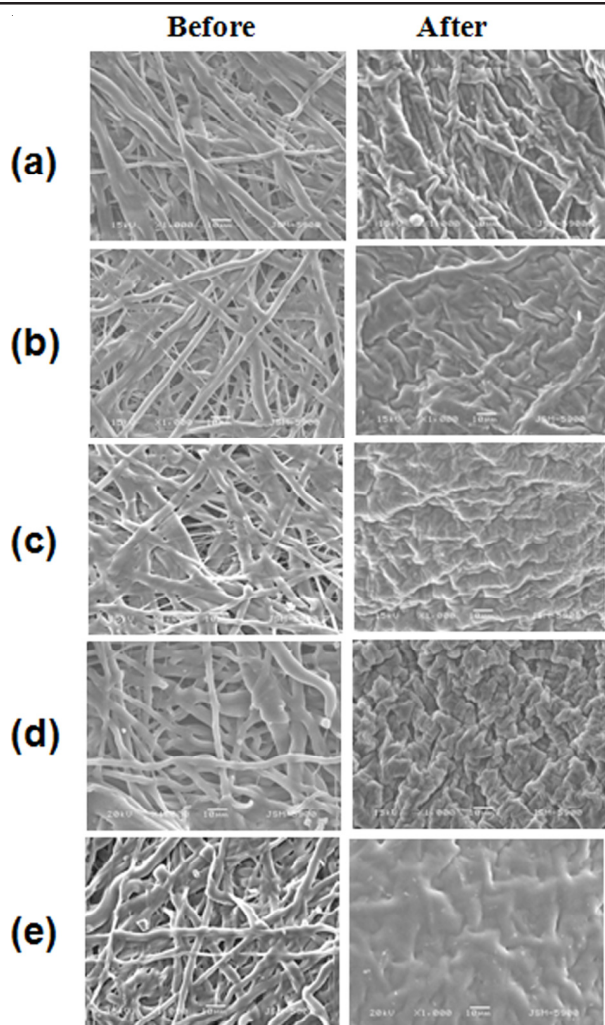


Fig. 5. 0.5 h UV irradiated electrospun mat and immersed in acetone for (a) 0 week, (b) 1 week, (c) 2 weeks, (d) 3 weeks and (e) 4 weeks

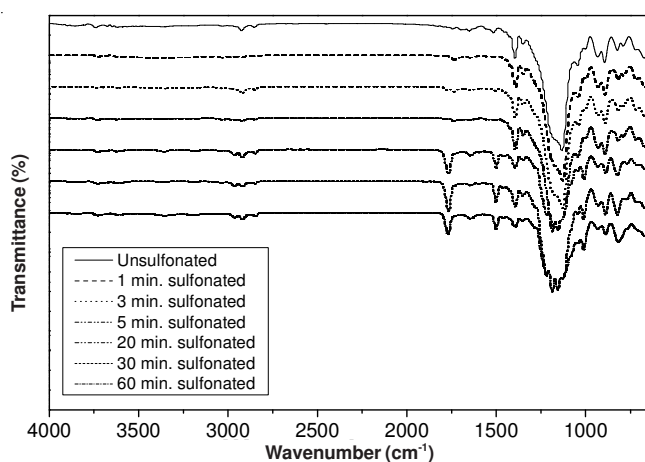


Fig. 6. ATR-FTIR spectrum of the sulfonated electrospun fluoroelastomer mat

vibration of the C=O group. The broad and slightly less intense bands at 1090-990 and 870-810  $\text{cm}^{-1}$  were assigned to the stretching vibration of the S=O and S-O bond, respectively. The C-F bond and S=O double bond range overlapped making it difficult to distinguish. This shows that the treatment allows the grafting of sulfonated groups on the surface of the fluoroelastomer mat. The appearance of characteristic

peaks due to the symmetric stretching of  $\text{SO}_3^-$  at 1035  $\text{cm}^{-1}$  confirmed the introduction of sulfonic groups.

**Observation of sulfonated fluoroelastomer mat by SEM:** Before and after treatment (sulfonation), the fluoroelastomer mat was analyzed by SEM. As shown in Fig. 7, both the surface and cross section of the electrospun fluoroelastomer mat was deformed. As the treatment time increased, the sample morphology was changed to a film with a flat, smooth surface. This type of fiber deformation was observed on both the surface and cross section.

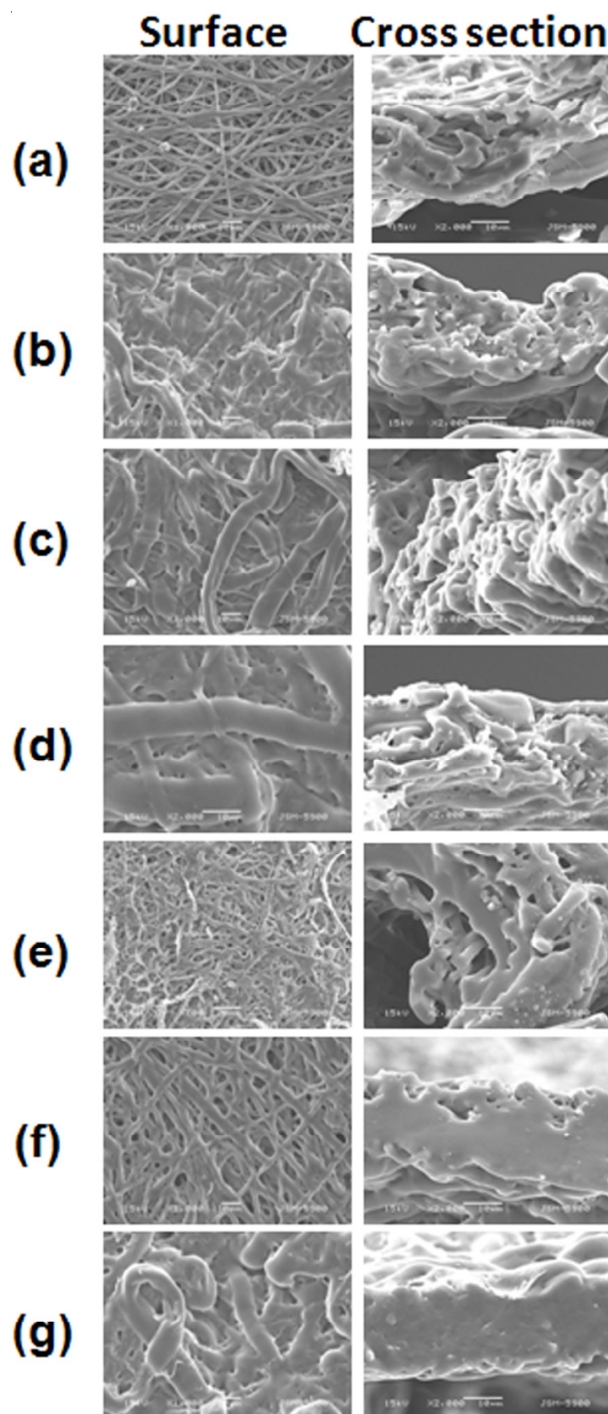


Fig. 7. Surface and cross section morphologies of an electrospun fluoroelastomer mat deformed at different sulfonation times. (a) unsulfonated mat, (b) 1 min, (c) 3 min, (d) 5 min, (e) 20 min, (f) 30 min and (g) 60 min

## Conclusion

Electrospinning is a simple and versatile method for creating fluoroelastomer-based high functional structural materials. The fibrous mat was prepared successfully by electrospinning. The concentration of fluoroelastomer and crosslinker play a significant role on the fibers morphology. A major challenge is the long term stability of the fiber morphology. As a result, the electrospun fibers have a high specific surface area. The uncured electrospun mat morphology was changed to a flat film. UV curing using a photoinitiator is a suitable method for maintaining this fiber morphology. The cured fibers mats were insoluble, even in acetone. The sulfonation of a fluoroelastomer mat was confirmed by ATR-FTIR. The fibrous structure was disturbed after sulfonation. This jagged morphology of nanofibers indicated a high surface to volume ratio, making them ideal candidates for many applications. This assembly approach can be expanded even to the hierarchical assembly of nanofibers to other well-defined functional nanostructures.

## ACKNOWLEDGEMENTS

This study was carried out under the World Class University Program of the Korea Science and Engineering Foundation, funded by the Ministry of Education, Science and Technology (R33-2008-000-10016-0).

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