

# Electrospinning of Poly(Dimethyl Siloxane) by Sol–Gel Method

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**ABSTRACT:** Crosslinked poly(dimethyl siloxane) (PDMS) fibers were fabricated by electrospinning in combination with a sol–gel process followed by heat treatment. Before and after heat treatment, the changes in the chemical and thermal properties of the electrospun PDMS fibers were examined by differential scanning calorimetry (DSC), equilibrium swelling tests, and contact angle measurements. There was no significant change in morphology

and average diameter of the as-spun PDMS fibers after heat treatment. The tensile properties of the as-spun PDMS fibers mat increased with increasing heat treatment temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3870–3874, 2009

**Key words:** poly(dimethyl siloxane) (PDMS); electrospinning; crosslinking; tetraethoxy orthosilicate (TEOS)

## INTRODUCTION

Poly(dimethyl siloxane) (PDMS) is a rubbery, highly hydrophobic, and thermally and mechanically stable polymer. The features of PDMS were attributed to the nature of the Si–O bonds, which have higher bond strength, longer bond length, and larger bond angle than C–C bonds.<sup>1</sup> Therefore, PDMS is used widely in a variety of fields, such as high performance sealants, separating membranes, and biomedical devices.<sup>2–4</sup> The PDMS elastomer is generally produced by crosslinking PDMS prepolymers with reactive groups at their ends. As an example, PDMS networks can be prepared using a multifunctional crosslinking agent, such as tetraethyl orthosilicate (TEOS).<sup>5</sup>

Electrospinning has been studied extensively because of its simplicity and efficiency in the fabrication of fibrous structures with microscale to nanoscale dimensions. Over a last decade, although a number of synthetic and natural polymers have been studied for electrospinning, there have been fewer studies on rubbery polymers (elastomers) with a very low glass transition temperature ( $T_g$ ).<sup>6–9</sup>

Compared with other elastomers, PDMS is more difficult to electrospin because the electrospinning process should be combined with the sol–gel process of a relatively low molecular weight PDMS prepolymer and crosslinker. The electrospinning process, in combination with a sol–gel process, has been used to fabricate ceramic and metal oxide nanofibers, which are particularly useful in high temperature applications.<sup>10–15</sup>

In this study, the PDMS prepolymer with hydroxyl end groups and TEOS crosslinker were used for electrospinning and sol–gel process. The as-spun PDMS fibers were further heat treated to induce a polycondensation reaction between the PDMS prepolymer and TEOS. The chemical, thermal, and mechanical properties of as-spun and heat-treated PDMS fibers were compared using an equilibrium swelling tests, contact angle measurements, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile tests.

## EXPERIMENTAL

### Materials

Hydroxyl terminated PDMS ( $M_n = 46,000$ ) was purchased from Aldrich Co. TEOS was obtained from Junsei Co. Tetrahydrofuran (THF) (Samchun Chemical Co., Seoul, Korea) and nitric acid ( $\text{HNO}_3$ ) (Duk-san Pure Chemical, Seoul, Korea) was used as the solvent and acid catalyst for the hydrolysis of TEOS,

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respectively. All chemical reagents were used without further purification.

### Electrospinning

A PDMS prepolymer solution was prepared using TEOS and THF based on a sol-gel procedure. A 0.13M PDMS was dissolved in 30 mL of THF, and TEOS (2 mL) and nitric acid (200  $\mu$ L) were added. This mixed solution was stirred and aged at 80°C, resulting in a viscous transparent PDMS sol through a hydrolysis reaction and evaporation of the solvent (THF). The viscosity of the sol was adjusted for electrospinning by adding THF (15 mL). The PDMS fibers were prepared by electrospinning the viscous PDMS sol.

In the electrospinning process, a high electric potential was applied to a droplet of the sol at the tip (ID = 0.838 mm) of a syringe needle. The electrospun fibers were collected on a target placed 10 cm from the syringe tip. A voltage of 10.5 kV was applied to the collecting target using a high voltage power supply (Chungpa EMT, CPS-40K03). The mass flow rate of the sol was 15 mL/h. All electrospinning procedures were carried out at room temperature.

### After treatment of PDMS fibers

To induce crosslinking reaction between PDMS and TEOS, the as-spun PDMA fibers were heat treated at 200, 250, 300°C for 3 h.

### Equilibrium swelling test<sup>16</sup>

The equilibrium swelling experiment in toluene at room temperature was carried out to confirm the degree of crosslinking of the as-spun and after-treated PDMS fibers. The equilibrium swelling ratio (ESR, %) was calculated as follows:  $ESR (\%) = (W - W_0)/W_0 \times 100$ , where  $W$  and  $W_0$  are the weight of the sample before and after immersion in toluene for 24 h, respectively.

### Characterization

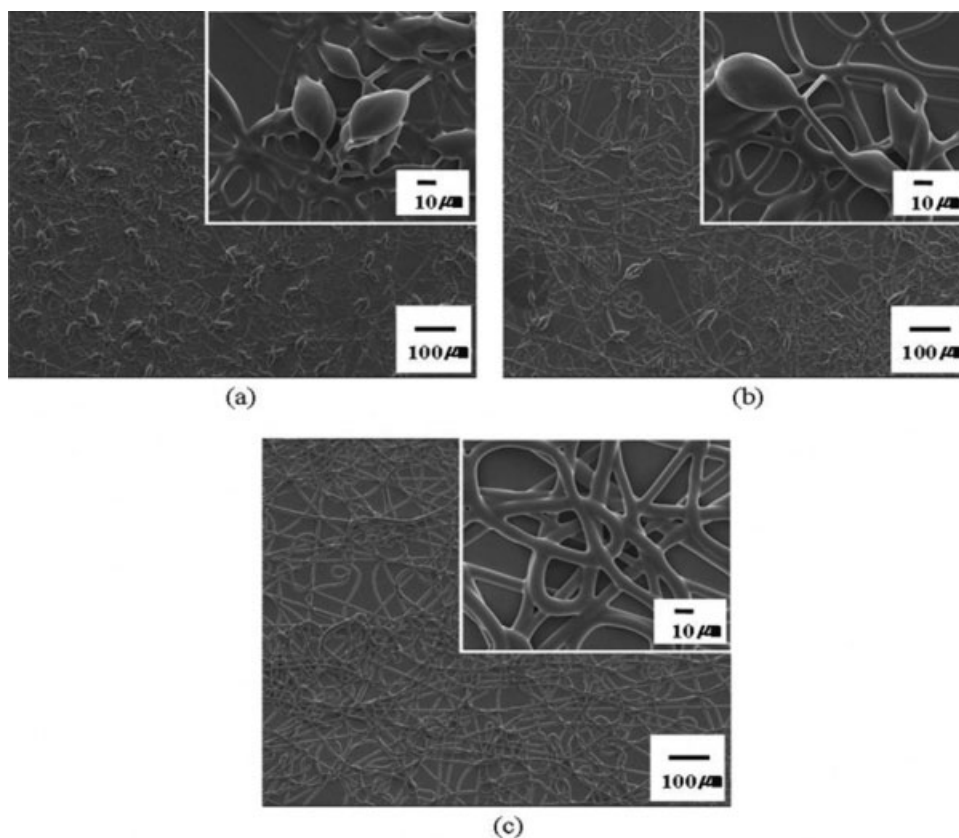
The morphology of the as-spun and after-treated PDMS fibers was observed by field emission scanning electron microscopy (FE-SEM, JSM-6335F, JEOL, Tokyo, Japan). The average fiber diameter was determined by analyzing the SEM images using a custom code image analysis program (Scope Eye II, Korea). DSC was performed using a Perkin Elmer DSC7 instrument (Waltham, MA) in a nitrogen atmosphere. About 10-mg sample was sealed in an aluminum pan for the measurement. The sample was heated from -150 to 100°C at a rate of 10°C/min. The thermal stability of the PDMS fibers was

measured by thermogravimetric analysis (TGA) (Perkin Elmer TGA-7). The sample was heated from 30 to 800°C at a rate of 20°C/min under N<sub>2</sub> atmosphere. The tensile properties of the electrospun PDMS fiber mat were measured 10 times on an Instron tensile tester (Instron 4467) according to the ASTM D-638.

## RESULTS AND DISCUSSION

In electrospinning, the morphology of the electrospun products varied according to the concentration of the polymer solution or precursor sol. Figure 1 shows SEM images of the PDMS fibers electrospun from the PDMS precursor sol with different concentrations ranging from 29 to 38% by volume. At concentrations up to 33 vol %, large irregular beads or beaded fibers were generated by electrospinning [Fig. 1(a,b)]. Continuous fibers were obtained at concentrations above 38 vol % [Fig. 1(c)], which correspond to the onset of proper chain entanglement. However, at 45 vol %, continuous and uniform electrospinning was inhibited by high viscosity (1050 cP) of the PDMS sol at that concentration. The average diameter of the as-spun PDMS fibers was 11.4  $\mu$ m (Table I). Therefore, a sol concentration of 38 vol % was chosen as the optimal concentration to fabricate PDMS fibers.

In this study, the polycondensation/crosslinking reactions of the as-spun PDMS fibers were induced by a thermal treatment ranging from 200 to 300°C. The crosslinking reaction between the hydroxyl terminated PDMS and TEOS usually involves two steps. The first step is the hydrolysis of TEOS with an acid catalyst. In the second step, the hydrolyzed TEOS diffuses into the PDMS chains, followed by polycondensation between the terminal Si-OH groups of the PDMS and the OH groups of the partially hydrolyzed TEOS. The thermal transition behavior of the as-spun and heat-treated PDMS fibers was examined by DSC. Figure 2 shows DSC thermograms of the as-spun and after-treated PDMS fibers. As shown in Figure 2(a), the as-spun PDMS fibers did not exhibit glass transition because they were composed mainly of short linear chains (i.e., low molecular weight). In addition, the as-spun PDMS fibers have a melting point at -41°C but do not have a glass transition temperature ( $T_g$ ), which can be observed in the polymer with a long molecular chain (i.e., high molecular weight). The PDMS fibers heat treated at 200 or 250°C for 3 h showed crystallization peaks at approximately -100°C. However, the PDMS fibers at heat-treated at 300°C for 3 h did not exhibit crystallization and melting peaks around -100 and -40°C, respectively, indicating that the polycondensation and/or crosslinking reaction between the PDMS prepolymer and hydrolyzed



**Figure 1** SEM images of the PDMS fibers electrospun at different concentrations; (a) 29%, (b) 33%, and (c) 38%.

TEOS occurred significantly in the chain backbone (dimethyl siloxane group) as well as the chain ends (hydroxyl group). The  $T_g$  values ( $\sim -124^\circ\text{C}$ ) observed for the heat-treated PDMS fibers were identical to the value given in previous work.<sup>17</sup>

Figure 3 shows TGA thermograms of the as-spun and heat-treated PDMS fibers. The thermal degradation of the as-spun PDMS fibers began at  $\sim 380^\circ\text{C}$ , whereas the thermal degradation of the PDMS fibers heat treated at 200 and  $250^\circ\text{C}$  began at  $\sim 426$  and  $\sim 436^\circ\text{C}$ , respectively. On the other hand, thermal degradation of the PDMS fibers heat treated at  $300^\circ\text{C}$  began at  $\sim 440^\circ\text{C}$ , and their weight loss at  $800^\circ\text{C}$  was only 38 wt % because of severe crosslinking.

Figure 4 shows SEM micrographs of the as-spun and heat-treated PDMS fibers. Before and after heat

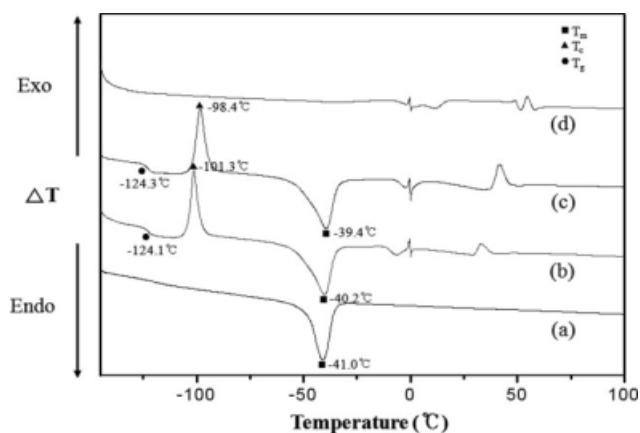
treatment, there was no significant change in fiber morphology and average fiber diameter (AFD) (Fig. 4 and Table I). However, there were some cracks in the PDMS fibers heat-treated at  $300^\circ\text{C}$ , indicating that they had become brittle as a result of the severe crosslinking. As shown in Figure 4, the slightly collapsed fiber morphology was observed. Interestingly, joint welding of the fibers at their neighboring points and at their cross-points was observed in the PDMS sample. This welding played an important role in improving the mechanical stability of PDMS.

The PDMS is quite hydrophobic. The water contact angle (WCA) of the as-spun PDMS fibers mat was increased from  $128^\circ$  to  $137^\circ$  by heat treatment ( $200$  and  $250^\circ\text{C}$ ), which is possibly due to a decrease in the hydrophilic hydroxyl end groups by the

**TABLE I**  
Characterization Results of the As-Spun and After-Treated PDMS Fibers

	PDMS (As-Spun)	PDMS ( $200^\circ\text{C}$ , 3 h)	PDMS ( $250^\circ\text{C}$ , 3 h)	PDMS ( $300^\circ\text{C}$ , 3 h)
AFD ( $\mu\text{m}$ )	$11.4 \pm 2.6$	$12.4 \pm 3.5$	$12.7 \pm 3.0$	$12.9 \pm 2.6$
WCA ( $^\circ$ )	128.0	137.5	137.3	–
ESR (%)	443	294	281	91

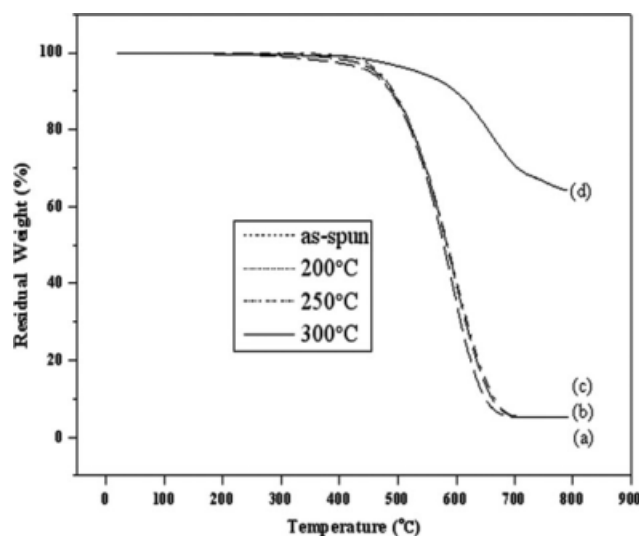
AFD, average fiber diameter; WCA, water contact angle; ESR, equilibrium swelling ratio.



**Figure 2** DSC thermograms of the as-spun and heat-treated PDMS fibers; (a) as-spun, (b) 200°C, (c) 250°C, and (d) 300°C.

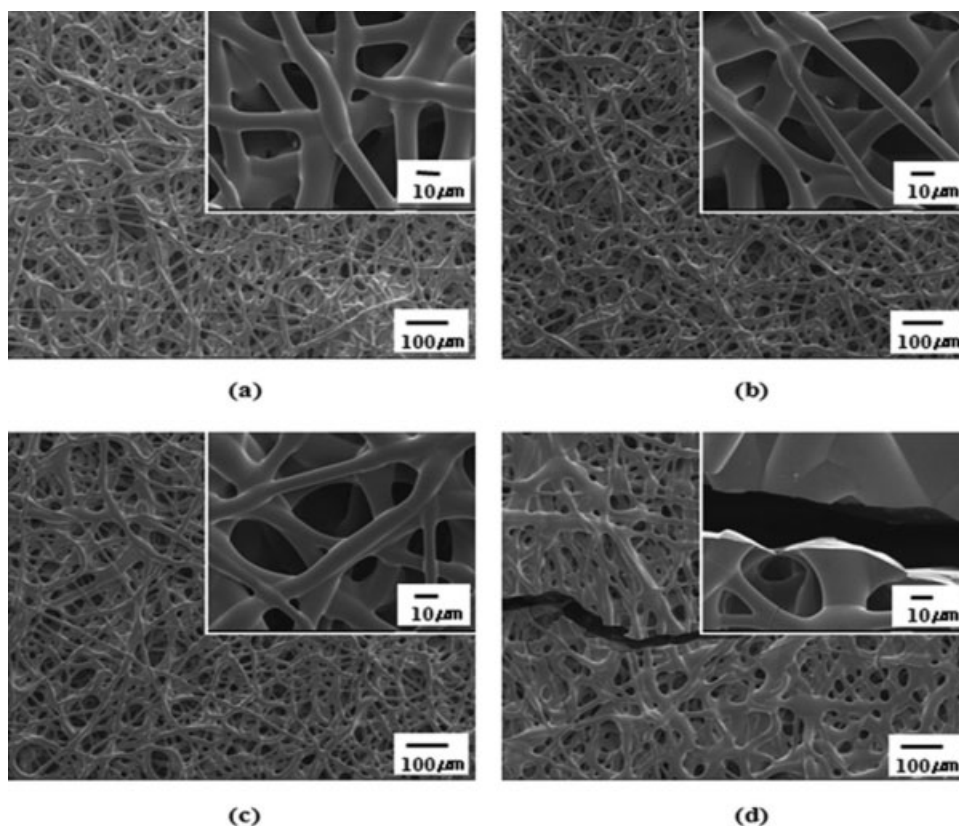
cross-linking reaction. An equilibrium swelling experiment using toluene was carried out to compare the degree of crosslinking of the as-spun and heat-treated PDMS fibers. Table I lists the equilibrium swelling ratios (ESR, %). The ESR of the as-spun PDMS fibers decreased gradually from 443 to 91% with increasing heat treatment temperature due to the higher crosslinked network structure.

Table II presents the tensile properties of the as-spun and heat-treated PDMS fibers. In general, the



**Figure 3** TGA thermograms of the as-spun and heat-treated PDMS fibers; (a) as-spun, (b) 200°C, (c) 250°C, and (d) 300°C.

tensile modulus increases with increasing cross-linking density, whereas the elongation at break decreases. All tensile properties (tensile strength, breaking elongation and modulus) of the PDMS fibers increased slightly with increasing heat treatment temperature, i.e., higher cross-linking reaction.



**Figure 4** SEM images of the PDMS fibers heat treated at different temperatures; (a) as-spun, (b) 200°C, (c) 250°C, and (d) 300°C.



**TABLE II**  
**Tensile Properties of the As-Spun and After-Treated PDMS Fibers**

	PDMS (As-Spun)	PDMS (200°C, 3 h)	PDMS (250°C, 3 h)	PDMS (300°C, 3 h)
Tensile strength (Kgf/mm <sup>2</sup> )	0.014 ± 0.002	0.017 ± 0.002	0.019 ± 0.001	–
Elongation at break (%)	93.3 ± 7.3	98.6 ± 5.6	97.8 ± 6.3	–
Modulus (Kgf/mm <sup>2</sup> )	0.019 ± 0.002	0.021 ± 0.003	0.027 ± 0.002	–

This is coincident with the results reported elsewhere<sup>6</sup> and may be explained by the increased stiffness of the heat-treated PDMS fibers due to the longer and crosslinked molecular chains. The as-spun PDMS fibers are composed of shorter molecular chains, resulting in a lower tensile strength and breaking elongation, although the mechanical strength of the electrospun fibrous mat is strongly dependent on the interfiber interaction (bonding).<sup>15,18</sup>

### CONCLUSION

Crosslinked PDMS fibers were fabricated by electrospinning in combination with a sol–gel process, followed by heat treatment. After heat treatment, the chemical and thermal properties of the PDMS fibers was examined by DSC, equilibrium swelling tests, and contact angle measurements. There was no significant change in morphology or average diameter of the as-spun PDMS fibers after heat treatment. The tensile properties of the as-spun PDMS fibers mat increased with increasing heat treatment temperature. These electrospun PDMS fibers are expected to have potential applications as thermostable fibrous membranes and inorganic/organic composite fibers for high temperature performance.

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