

Improved Mechanical Strength of Partially Sulfonated Polystyrene-poly(dimethylsiloxane) Block Copolymer Proton Exchange Membranes by Nanoscale Sequestration of Thermally Crosslinked Silicone

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Introduction

As a vital component for the electric power sources based on proton exchange membrane fuel cell (PEMFC), the membrane materials represented by Nafion™, have been of great interest for polymer scientists since late 80's.¹ Nafion has prevailed as the PEM material in majority of PEMFC applications due to its superior ionic conductivity, processibility and chemical, mechanical stability.¹ Particularly targeting PEM applications in direct methanol fuel cell (DMFC) which is regarded as the most powerful fuel cell for portable devices such as cellular phone and laptop computer, there have been efforts to find alternative PEM materials to Nafion showing lower methanol crossover and better water management.²⁻⁶ Among the successful reports, the partially sulfonated polystyrene (sPS) has drawn researchers' attention since it showed promising properties toward DMFC application. sPS has been widely diversified.⁷ Especially, sPS-containing block copolymers are state of the art PEM materials which exhibit excellent physical and chemical properties originating from microphase separation between constituent blocks. To satisfy essential requirements of DMFC such as low methanol permeability and processibility, the

block copolymers consisting of sPS and rubbery diene block have been developed.⁸⁻¹⁰ In those types of PEM, there exist nanostructures of hydrophilic sPS domain through which protons can be conducted and hydrophobic rubbery phase which provides mechanical flexibility to the membrane. However, diene rubbers contain unsaturated carbons which can be easily degraded under harsh environment of fuel cell such as strong acidity and high operating temperature. In order to improve such chemical weak point of diene-based rubbery block, we have recently developed a block copolymer (BCP) PEM containing poly(dimethylsiloxane) (PDMS) as rubbery block within the partially sulfonated PS matrix.¹¹ Through DMFC performance test at the air-breathing semi-passive configuration, it was confirmed that sPS-*b*-PDMS membrane could be successfully employed for DMFC membrane electrode assembly (MEA) without any modification on the interface between the membrane and the electrode. Although the solution-cast sPS-*b*-PDMS PEMs retained a good film quality as a similarly cast Nafion membrane, there was no rigorous discussion on their mechanical strength in the previous report. In this study, we focus our attention on the improvement of mechanical strength of sPS-*b*-PDMS PEMs to test the feasibility of the membrane from the practical view point.

Experimental

Sulfonation of PS-*b*-PDMS. PS-*b*-PDMS was sulfonated following the same procedures as reported in our previous work.¹¹ As a precursor of PDMS containing block copolymer PEM, a PS-*b*-PDMS (Molar mass 159,000, 70 wt% PS, Polymer Sources Inc.) was used. In a nitrogen atmosphere, 2 g of PS-*b*-PDMS was refluxed in dichloroethane where 0.8 g of freshly prepared acetyl sulfate was added. After 3 h of reflux at 60 °C, small amount of 2-propanol was added to terminate the reaction, and the solvent was removed from the mixture by evaporation. The product was collected by filtration, washed with water and methanol, and finally dried in a vacuum oven at 60 °C. The degree of sulfonation in PS block was characterized by ¹H NMR to reveal that about 31 mol% of PS was sulfonated.

Preparation of sPS-*b*-PDMS/Sylgard-184 Casting Solution. Crosslinkable PDMS precursor used in this study was Sylgard 184™ (Dow Corning) which is composed of two parts. The mixture is known to undergo platinum-catalyzed hydrosilation between vinyl terminated PDMS oligomer (184A) and hydrosilyl PDMS crosslinker (184B). Sylgard PDMS thermally cures to form a crosslinked rubber which is tough and flexible. 1 g of 184A and 0.1 g of 184B were dissolved in 20 g of tetrahydrofuran (Aldrich). Apart from this, 1 g of previously synthesized sPS-*b*-PDMS was dissolved in THF. Aliquots of each solution were mixed at the

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volume ratios of 1: 0, 9:1, and 19:1 respectively.

Membrane Casting and Thermal Curing. The casting solutions were placed on a glass dish and left to stand at 20 °C for 4 h under a nitrogen stream (0.1 L/min) to form uniform films. Each film on the glass dish was transferred to an oven maintained at 70 °C where the formed film was heated for 12 h to induce a crosslinking reaction between 184A and 184B. The cast and cured films on the dish were immersed in deionized (DI) water for an hour to give free-standing PEMs.

Mechanical Test of PEMs. Tensile stress of membranes was measured versus uniaxial strain using a universal tensile test machine (UTM, Tinius Olsen) as reported in our previous paper.¹² The strip of each membrane was prepared in a size of 5 mm×30 mm. The distance between two grips of UTM was fixed at 10 mm and the drawing speed of grips was set at 50 mm/min. % strain was calculated by the increment in the distance divided by the original distance (10 mm), and the toughness was calculated by integrating area below stress-strain curve.

Surface Morphology of PEM. Surface morphology of the reinforced membrane was characterized with atomic force microscopy (AFM, Asylum). The thin film of sPS-*b*-PDMS blended with 5 wt% Sylgard-184 was prepared on the pre-cleaned glass substrates, and subsequently cured following the same procedures as mentioned above. After thermal curing, the film was subjected to the tapping mode AFM measurement to give the images of surface topology and morphology at the same time.

Proton Conductivity Measurement. The proton conductivity of the membranes was measured by 4-point probe method using an ac impedance analyzer (Solartron 1260, UK). The proton conductivity (σ) was calculated by $\sigma = L / (A \times R)$, where L and A are the distance between the two inner Pt-probes and the cross-sectional area of the membrane, respectively.

Water Uptake Measurement. Water uptake of the membrane was measured by comparing the weight of a wet membrane and a dried membrane. Each membrane was soaked in DI water for 24 h at room temperature. After removing water on the surface, the wet film was quickly weighed, and the membrane was vacuum-dried for 24 h at room temperature. The final dried weight of the membrane was measured, and water uptake ($(W_{\text{wet}} - W_{\text{dried}}) / W_{\text{dried}}$) was calculated.

Methanol Permeability Measurement. For measuring the methanol permeability of the membranes, we used a custom-made cell which consists of two identical compartments of 35 mL volume (V_A and V_B) separated by the membrane of interest. The exposed area of the membrane to the compartments was 10 cm². A and B compartments initially contained 3 M methanol solution and the DI water, respectively. The increase of methanol concentration at the DI water compartment (C_A) due to the methanol permeation was

measured using a digital refractometer (Atago, RX-9000a, Japan).

Results and Discussion

The main idea is to reinforce PDMS microdomains by physical blending of thermally crosslinkable PDMS oligomers with sPS-*b*-PDMS and subsequent thermal curing of those oligomers.^{13,14} When the sPS-*b*-PDMS is slowly cast from the polymer solution to form a membrane, hydrophilic sPS blocks tend to be microphase separated with hydrophobic PDMS blocks. A unique membrane morphology has been revealed from the structural analyses in the previous report.¹¹ Here, we aimed for an improvement of sPS-*b*-PDMS PEM in mechanical strength by incorporating thermally crosslinkable PDMS precursor within PDMS microdomains. Mechanical reinforcement in nanometer scale is expected to improve membrane properties such as processibility of MEA fabrication and further blocking of methanol crossover during DMFC operation. As illustrated in Figure 1, hydrophobic PDMS microdomains should be distributed within sPS major phase. If the crosslinkable, yet oligomeric PDMSs are mixed with sPS-*b*-PDMS in the casting solution, they will preferentially be localized within PDMS microdomains as the solvent dries out due to a thermodynamic driving force.

Since the main chain chemical structures of both vinyl-terminated oligomer and hydrosilyl crosslinker are PDMS, they tend to be sequestered into PDMS microdomains of BCP together. Subsequent thermal curing would crosslink the oligomeric PDMSs within the microdomain, and consequently enhance mechanical strength of the entire membrane. In order to confirm such scenario, 5 and 10 wt% of crosslinkable PDMS (Sylgard 184) precursors with respect to total polymer amount were premixed with sPS-*b*-PDMS in THF followed by membrane casting at room temperature and thermal curing. Each membrane was delaminated from the casting dish by soaking in DI water, and the moisture content was measured by comparing the membrane weight before and after drying. As additional PDMS (Sylgard 184) amount increased, the moisture content was decreased as expected.

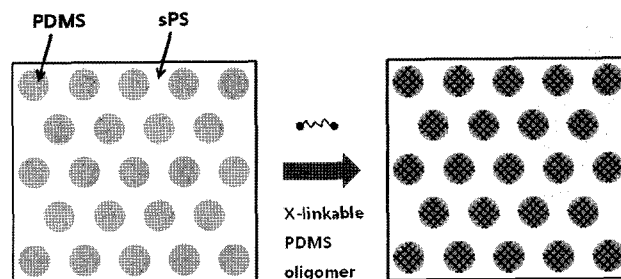


Figure 1. Schematic representation of sequestration of crosslinkable PDMS oligomers within sPS-*b*-PDMS PEM.

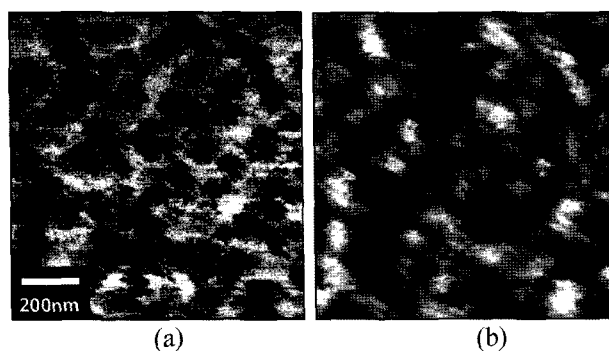


Figure 2. Tapping mode AFM image of the sample 2 (sPS-*b*-PDMS with 5 wt% Sylgard 184) (a) phase image showing dark PDMS microdomains within white sPS domains (b) height image showing the root-mean-square-roughness of 0.4 nm.

Figure 2 shows the surface morphology of the membrane with 5 wt% Sylgard 184 analyzed by tapping-mode AFM. There was no trace of macrophase separation which could have deteriorated membrane property. From the AFM phase image, rubbery PDMS microdomains having the size of several tens of nanometer were found as dark dot-like morphology. In the phase mode of AFM which relies on the contrast of hardness of the surface morphology, rubbery PDMS domains appear darker than sPS domain at low humidity condition. Since PDMS is minor phase in BCP even with added Sylgard PDMS, brighter sPS matrix were found to occupy a majority of membrane surface. Although the surface of the membrane was very even (root-mean-square roughness of 0.38 nm) as revealed from the height image, an interesting feature was that the regions where the rubbery microdomains (darker region in Figure 2(a)) are concentrated were generally bulged out of the surface which might be attributed to a volume contraction during PDMS curing. Other samples with higher content of Sylgard 184 were also analyzed by AFM, but the surfaces of those samples were so rough that the image quality was poor. Within our observation, the sample 3 with 10 wt% Sylgard always showed opaqueness in the film which tells us macrophase segregation of Sylgard-184 upon curing.

In Figure 3, tensile stresses of the dried membranes were plotted versus axial strain. No membrane showed yield point. Compared to the elongation behavior of Nafion 115

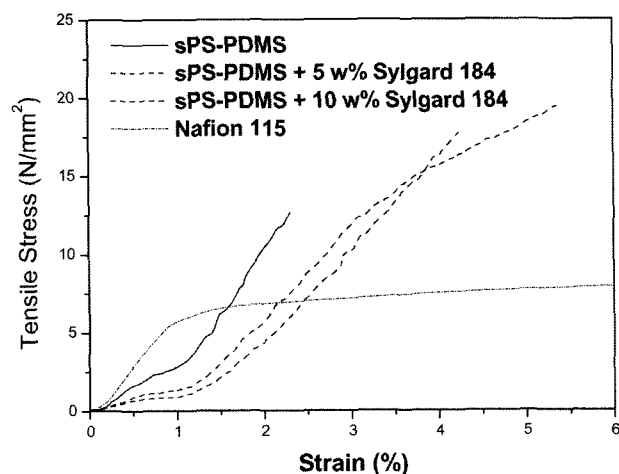


Figure 3. Stress-Strain curves of Nafion 115 and three sPS-*b*-PDMS membranes with different Sylgard 184 contents.

which is quite rubber-like (usually axial strain > 100%), our BCP membranes were observed to show only a little elongation. However, tensile strengths (tensile stress at the fracture point) of all BCP membranes were much higher than that of Nafion as shown in Table I. It was clear that the reinforced sPS-*b*-PDMS membranes exhibit enhanced tensile strength compared to the membrane without Sylgard 184. The original BCP membrane showed only 2% deformation before fracture while the membranes with 5 wt%, 10 wt% Sylgard 184 showed 4.3% and 5.4% of strain respectively. Tensile strength and toughness of the membranes are summarized in Table I. Tensile strengths increased (41% and 53% respectively) by incorporation of PDMS reinforcing agent, and the toughness increased as well. In general, one should consider the processibility which is affected by mechanical properties of the membrane. If the membrane is brittle or stiff, there will be problems in manufacturing MEA which usually accompanies hot-pressing process. The membrane might be cracked or form a bad adhesion between electrodes and membrane in MEA during the hot-pressing step. Such MEA failures can be minimized if the mechanical properties such as tensile strength or toughness are improved. By nanometer-scale incorporation of Sylgard PDMS, we have achieved improvements in both values of mechanical strengths.

Table I Physical Properties of the Membranes

Samples	Content of Sylgard 184 (wt%)	Membrane Thickness (μm)	Moisture Content (wt%)	Tensile Strength (N/mm^2)	Toughness (kJ/m^2)	Methanol Crossover ($10^{-7}\text{cm}^2/\text{s}$)	Proton Conductance (S/cm^2)
Sample 1	0	27	8.4	12.6	1.1	2.39	5.3
Sample 2	5.0	37	6.8	17.8	2.8	2.06	5.5
Sample 3	10	56	5.7	19.4	5.1	3.60	5.9
Nafion 115	0	150	27	12.1	209	26	6.0

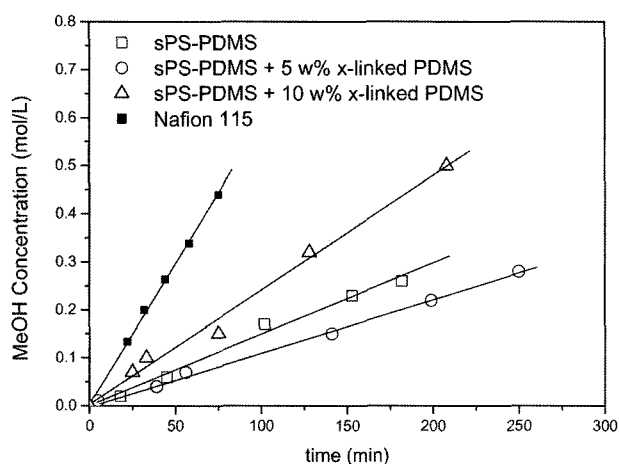


Figure 4. Methanol crossover plots for different membranes.

In order to test a usefulness of the reinforced sPS-*b*-PDMS as a PEM material for DMFC, methanol crossover and proton conductance were measured for each membrane. The calculated values are summarized in Table I. Figure 4 shows the change of methanol concentration permeated through each membrane with time. As expected, the BCP membrane containing 5 wt% Sylgard 184 was found to exhibit approximately 20% reduction in methanol crossover compared to that of a sPS-*b*-PDMS membrane without Sylgard. In addition, proton conductance of the sample 2 and 3 were comparable to the original membrane and even to Nafion 115 as shown in Table I. Those results reflect that the sequestered Sylgard PDMS does not hamper proton conduction path in sPS microdomains.

Despite high content of Sylgard PDMS (>10 wt%) resulted in a phase separation from the major component of BCP, incorporation of small amount of crosslinkable PDMS and subsequent thermal curing indeed exhibited a mechanical reinforcement of the BCP membrane as revealed by an improved uniaxial tensile strength and a reduced methanol crossover. An intriguing feature of such reinforcement is that the proton conductance was even increased probably due to a more efficient formation of proton conduction path by crosslinking of PDMS microdomains which enhanced hydrophobicity and mechanical strength.

The strategy used in this study should be applicable to other types of BCP ionomer systems in which mechanical reinforcement is required to ensure long term stability of the devices.

Conclusions

To improve the mechanical property of sPS-*b*-PDMS proton conducting membrane for DMFC application, crosslinkable PDMS oligomer has been incorporated within the BCP ionomer. Premixing different amount of Sylgard 184 PDMS

in the ionomer solution, and subsequent membrane casting and thermal curing revealed that the composite membrane containing 5 wt% of Sylgard 184 showed enhanced properties in the uniaxial tensile strength, toughness, methanol permeability, and even in the proton conductance. This results show that the PDMS oligomers were successfully sequestered within PDMS block of sPS-*b*-PDMS during casting procedure, and safely crosslinked without deterioration of the membrane microphase structure.

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