Mechanical Performance of Polyiosoprene Copolymer Anion Exchange Membranes by Varying Crosslinking Methods

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Anion exchange membranes (AEM) are polymer electrolytes that facilitate ion transport in alkaline fuel cells and electrochemical devices. Fabrication of mechanically durable AEMs with high ionic conductivity is a challenge. Here, a copolymer of isoprene and vinylbenzyl trimethylammonium and a terpolymer of isoprene, vinylbenzyl trimethylammonium and styrene were crosslinked by various methods, and properties, including conductivity and mechanical strength, were investigated at dry and saturated conditions. Polymer chemistry and degree of crosslinking significantly influenced conductivity, swelling, and mechanical properties. The terpolymer had a higher proportion of vinylbenzyl trimethylammonium units increasing the ion exchange capacity (IEC), but membranes could still be rendered insoluble by crosslinking. The higher IEC of the terpolymer resulted in higher chloride conductivity, 20–75 mS/cm at 50°C and 95%RH, compared to 4–17 mS/cm for the copolymer at the same conditions. At dry conditions films were stiff, having Young's moduli between 100–740 MPa, but hydration caused severe softening, reducing moduli by 1–2 orders of magnitude. The severe softening effect of hydration was confirmed by dynamic mechanical analysis. The AEMs studied did not have adequate mechanical durability at hydrated conditions, additional work is needed to determine polymer chemistries and crosslinking methods that will produce robust AEMs for long-term use in fuel cells and electrochemical devices.

Fuel cells are attractive energy conversion devices that utilize hydrogen to produce electrical energy for stationary and transportation applications, with the by-product being water.[1,2] Electrolyzers utilize a similar principle to produce hydrogen from water using electrical energy. Fuel cells and electrolyzers both utilize a polymer electrolyte membrane to separate the catalyst layers and efficiently transport ions, while limiting crossover of other species.[1,3] Proton exchange membranes (PEM), specifically perfluorosulfonic acid polymers such as Nafion, have been utilized almost exclusively for current fuel cells, owing to their high proton conductivity and suitable chemical and mechanical stability.[4,5] While PEM fuel cells have been widely researched and developed over the last few decades, anion exchange membrane (AEM) fuel cells offer potential advantages over PEMs.[6–10] The alkali nature of an AEM fuel cell allows redox reactions with non-platinum catalysts and improves oxygen reduction kinetics.[6,9,10] On going research seeks to develop robust, well performing AEMs for use in fuel cells, electrolyzers, and other electrochemical devices.

Anion exchange membranes must have a high ionic conductivity and be chemically and mechanically stable over the life-time of the fuel cell.[6,9,10] Chemical stability is a concern in AEMs as hydroxide ions present in the membrane have the potential to degrade the polymer backbone and cation functionalities.[6,11,12] Hydroxide transport is inherently slower than proton transport, to compensate the concentration of ion groups is often increased in AEMs. Increasing cation concentration in the polymer can significantly increase water uptake, causing dimensional swelling of the membrane and loss of mechanical integrity.[9] The membrane must be mechanically robust over a range of temperature and humidity conditions experienced in a working fuel cell.[13,14] At high hydrations the membrane swells with water, but at lower hydrations, drying causes contraction of the membrane and produces significant hygrothermal stresses.[13,15,16] During repeated humidity cycles these hygrothermal stresses can cause pinholes and cracks in the membrane, which contribute to the eventual failure of the membrane. A membrane must be elastic enough to accommodate for swelling and contraction due to humidity changes, and strong enough to withstand the associated hygrothermal stresses.[17] A successful AEM must combine high conductivity and mechanical

durability, making simultaneous study of these two aspects critical for new AEM development.

One method to improve mechanical performance and durability of AEMs and reduce swelling is by crosslinking of polymer chains.[18,19] Crosslinking can be applied to the inert portions of the polymer backbone or at the cation sites, and can be performed in solution or after the polymer is cast into a solid film. Crosslinking of noroborene monomers has produced high conductivity AEMs with good mechanical performance and limited swelling.[20,21] Crosslinking utilizing diamines to produce dication functionalities between polymer chains has also been demonstrated for AEMs.[22–25] More exotic cations, such as quaternary phosphoniums, can also be used as a crosslinker and have been shown to dramatically reduce membrane swelling.[26] Direct polymerization of quaternary ammonium cyclooctenes during membrane casting was used to produced mechanically stable crosslinked membranes with good ionic conductivity.[27] Crosslinking is a tunable method that can be applied to AEMs to improve mechanical stability and reduce swelling, while maintaining ionic conductivity.

In this study two polyisoprene copolymers were crosslinked and evaluated in terms conductivity and mechanical performance at a range of hydrations. A random copolymer of isoprene and vinylbenzyl trimethylammonium chloride (PI-ran-PVBTMA) and a terpolymer of isoprene, vinylbenzyl trimethylammonium chloride, and styrene (PI-ran-PVBTMA-ran-PS) were prepared. The ion exchange capacity of these polymers can be adjusted by the respective ratio of the monomers used. Conductivity of the two polymers were measured and correlated to extent of crosslinking and mechanical properties. Extensional properties of the membranes were measured with an extensional rheometer platform to simulate a tensile tester with small membrane samples. A tensile geometry allowed dynamic mechanical analysis with small-amplitude oscillatory strain experiments to evaluate moduli changes over a range of temperatures. Temperature and humidity were controlled during mechanical testing to determine the effect of hydration on membrane performance.

Experimental

The polyisoprene-ran-poly(vinylbenzyl trimethylammonium) copolymer was synthesized as previously reported[28,29] with an ion exchange capacity (IEC) of 1.5 mmol/g (Figure 1). The IEC of 1.5 mmol/g was chosen because conductivity plateaued, above this point conductivity no longer increased with increasing IEC, due to

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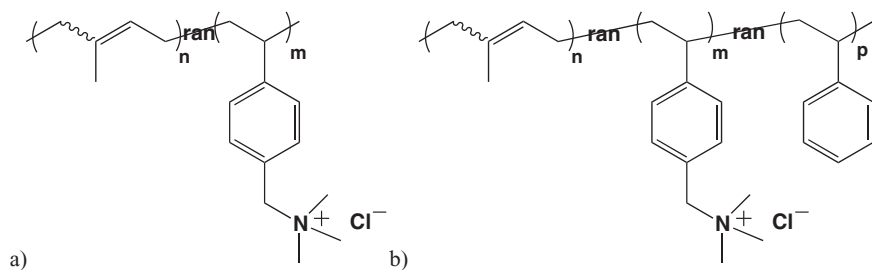[z]E-mail: mliberat@mines.edu

Figure 1. Chemistry of the a) copolymer and b) terpolymer prior to crosslinking.

excessive water uptake.[29] The terpolymer was synthesized by a similar procedure: isoprene (24 ml, 240 mmol), 4-vinylbenzyl chloride (9 ml, 63.9 mmol) and styrene (1.85 ml, 16.1 mmol) were transferred into a 50 ml Schlenk flask. 61.6 mg (0.159 mmol) SG1 BlockBuilder catalyst was added. The flask was immersed in an ice bath, and the contents of the flask were purged with nitrogen for 30 minutes. Reaction was initiated by immersing the reaction flask into an oil bath at 125°C. After 18 hours the reaction was quenched. Polymer was recovered by precipitating in excess methanol. Subsequent quaternization with trimethylamine (TMA) results in a terpolymer with an IEC of 2.3 mmol/g. The feed ratio of 4-vinylbenzyl chloride was higher for the terpolymer, resulting in a higher IEC compared to the copolymer, but membranes could still be rendered insoluble when crosslinked. Comparatively, a copolymer with an IEC of 2.3 mmol/g would require a minimum thermal crosslinking time of 12 hours, below this the membranes remained soluble in water.[29]

Film preparation and crosslinking.— Thermal crosslinking takes advantage of unsaturations on the hydrocarbon backbone to crosslink the polymer without additional crosslinking agents.[29] Polymers were dissolved in ethanol at 22 wt%. The polymers were mixed at room temperature for 4 h, sonicated at 30°C for 1.5 h, and again stirred at room temperature for 1 h. The solution was poured on a Teflon substrate and a doctor blade with a 500-micron gap height traversed over the solution at 20 mm/s using an automatic film applicator (MTI Corporation's MSK-AFA-III, Richmond, CA). The films were allowed to dry overnight at a room temperature in a fume hood. To induce crosslinking, the films were placed in an oven at 145°C for a duration of 3 or 24 hours. After removal from the oven, the films were allowed to cool, removed from the Teflon substrate, and placed in water at room temperature to allow for dimensional swelling. The films were removed from the water after 1 h and allowed to dry at room temperature. Films were stored under dry conditions for further testing.

The photocrosslinked (UV) films had a photoinitiator and crosslinking agent added to the casting solution. The photoinitiator, 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Sigma Aldrich), was added to ethanol at 1.5 wt%. The polymer was dissolved in the ethanol/initiator solution at the same concentration as the thermally crosslinked films (22 wt%). The solution was mixed in the dark, at room temperature for 4 hours and sonicated at 30°C for 1.5 h. After sonication the crosslinking agent, 1,10 decanedithiol (Alfa Aesar), was added to the polymer solution and mixed for 1 h at room temperature, avoiding light exposure. The dithiol crosslinking agent was added in a 3:1 ratio to the number of 1,2 and 3,4 addition double bonds on the polyisoprene, as determined by ^{1}H NMR. The 1,2 and 3,4 addition double bonds are susceptible to chemical crosslinking with the dithiol (Figure 2).[30] Addition of the photoinitiator and dithiol crosslinker lowers the polymer IEC because inert mass is added to the film. The copolymer IEC was reduced to 0.9 mmol/g and the terpolymer was reduced to 1.5 mmol/g. The polymer solution was cast using the automatic film applicator at the same conditions described for the thermally crosslinked films. After casting, the films were covered to prevent light exposure and allowed to dry at room temperature in a fume hood. The dry film was crosslinked by exposure to UV light using a F300 Series Fusion UV curing system with a P300MT power supply. The film was passed through the curing system four times at a speed of 76 mm/s with a power of 118 W/cm. After UV crosslinking the films were removed from the Teflon substrate, submerged in water for 1 h, and allowed to dry before subsequent testing.

Crosslinking was confirmed by soaking membranes in water for 24 h at room temperature without any dissolution or break-up of the film. Dried films returned to their initial dimensions prior to soaking in water. Films that did not undergo crosslinking dissolved in water.

Conductivity.— Conductivity was measured by electrochemical impedance spectroscopy using a four-electrode in-plane conductivity cell. Impedance spectra were obtained over a frequency range of 1 to 10^6 Hz using a multi-channel potentiostat (BioLogic VMP3). A TestEquity sample chamber controlled temperature and humidity during data acquisition. Membrane resistance was defined as the low frequency intercept of the Nyquist impedance plot and conductivity
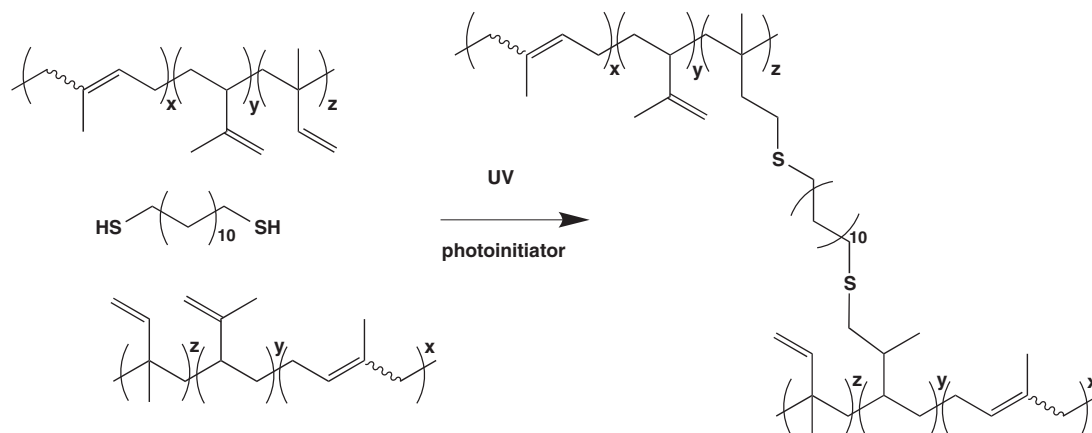

Figure 2. Crosslinking chemistry of polyisoprene with dithiol for UV crosslinking. The 1,2 (z) and 3,4 (y) addition units are susceptible to radical-mediated thiol-ene reactions.[30] Reaction of both thiols produces crosslinks between chains.

was calculated based on equation 1.

$$\sigma = \frac{l}{R \cdot t \cdot w} \quad [1]$$

Where R is the membrane resistance, l is the length between electrodes, and t and w are the thickness and width of the membrane sample, respectively. Reported conductivity data are the average of at least three separate membrane samples and multiple impedance spectra at each steady-state temperature; error bars are one standard deviation.

Water uptake.— Water uptake was measured gravimetrically after soaking in liquid water for 24 h compared to samples dried under vacuum overnight at 50°C. Samples were weighed three times and averaged. Wet samples were removed from liquid water, blotted dry, and quickly weighed to prevent drying. Water uptake was calculated based on equation 2.

$$WU = \frac{m_w - m_0}{m_0} \times 100 \quad [2]$$

Where m_w is the mass of the water soaked samples and m_0 is the dry mass of the sample.

Membrane swelling.— Dimensional swelling of the membrane was determined by measuring film dimensions in dry and wet states. Membrane samples were dried overnight in a vacuum oven at 50°C. In-plane dimensions were measured using a Marathon electronic digital caliper (0–150 mm, with 0.01 mm accuracy) and thickness measurements were made using a Marathon electronic digital micrometer (0–25 mm, with 0.002 mm accuracy). Membrane samples were placed in water at room temperature for 24 h to take up water. Samples were removed from water, blotted to remove surface water, and quickly measured to prevent drying. Percent swelling was calculated with respect to in-plane and through-plane dimensions.

Extensional testing.— A Sentmanat extension rheometer (SER) (Xpansion Instruments) fixture on an ARES G2 rheometer (TA Instruments) was utilized for extensional testing. The SER fixture typically measures elongation viscosity of polymers in their melt state, but has also been shown to measure tensile properties of solid polymer films.[31–33] The SER fixture has two counter-rotating drums that suspend the film. The drums rotate, stretching the film to its failure point, while the stress applied to the film is measured by the rheometer. The stress vs. strain curve is used to calculate Young's modulus, elongation, and ultimate strength. The Young's modulus is defined as the slope of the stress vs. strain curve in the elastic deformation regime at low strains, and is a measure of the film elasticity. Elongation and

strength are defined by the strain and stress, respectively, at the film's failure point. Reported values (Young's modulus, strength, and elongation) were the average of at least five samples and corresponding error is one standard deviation.

A custom-built sample chamber was utilized to control temperature and humidity simultaneously.[33] An aluminum sample chamber with electrical heaters was used to control sample temperature. Two mass flow controllers (10,000 SCCM, MKS 1179A) supplied wet and dry gas flows to the sample chamber. The wet gas line passed through a humidity bottle (FCT, Inc.) with 10 m of Nafion tubing that saturated the gas stream with water. The gas was delivered to the sample chamber through heated lines to prevent condensation. Extensional tests were performed at 30°C and 60°C at dry and saturated conditions.

Dynamic mechanical analysis.— The ARES G2 rheometer was used to perform DMA testing using a film/fiber rectangular tension geometry. The rectangular tension geometry has two screw-down clamps that hold the sample in tension while a small-amplitude oscillatory strain is applied to the film. DMA tests were performed under dry or saturated conditions while ramping temperature from 30°C to 70°C at 0.5°C/min. Samples were approximately 6 mm (W) by 25 mm (L), but were loaded at a starting gap height of 10 mm. A oscillatory strain of 0.1% was applied at a frequency of 1 Hz. The axial force on the samples was set to be at least 20% greater than the oscillatory strain force applied to the film, with a minimum value of 0.008 N. Under hydrated conditions the films were extremely soft and maintaining tension on the sample resulted in significant sample elongation as temperature was ramped. Films were loaded at ambient conditions, for saturated humidity tests the samples were allowed to equilibrate and take up water at 30°C and 90% relative humidity for 1 h prior to the start of the test. For dry tests the samples were allowed to equilibrate at 30°C and <10%RH for 10 min prior to the start of the test. DMA tests were repeated at least twice at each condition to confirm a consistent moduli response; tests were limited due to sample availability.

Results

Duration and method of crosslinking had a significant impact on film conductivity, water sorption, and mechanical performance. Increased crosslinking reduced water uptake and improved mechanical properties, but lowered ionic conductivity. Polymer chemistry and ion concentration also influenced membrane performance.

Conductivity.— In-plane conductivities of the copolymer and terpolymer films were measured as a function of temperature (50–90°C) at a constant relative humidity of 95% (Figure 3). Overall, the terpolymer had higher conductivity, ranging from 20–76 mS/cm at 50°C,
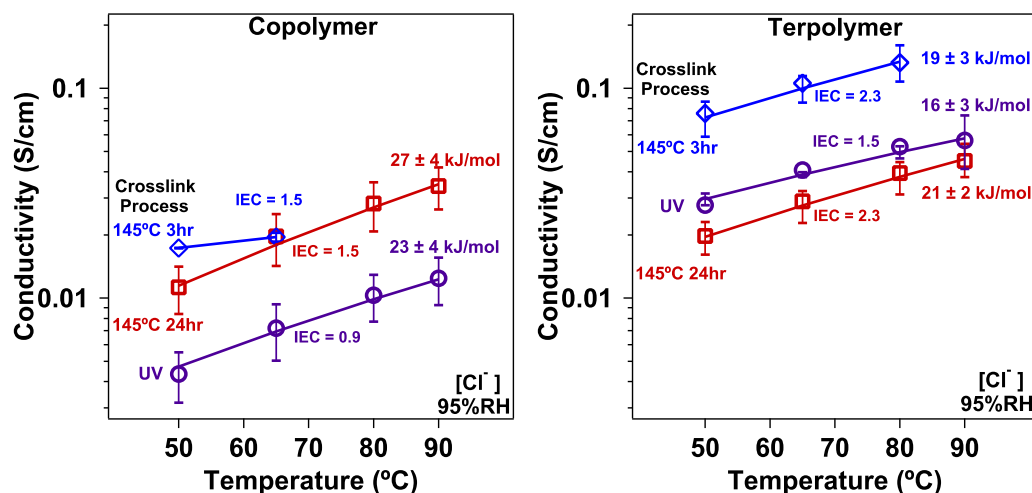

Figure 3. Conductivity of the copolymer and terpolymer films crosslinked either thermally at 145°C for 3 or 24 hrs, or UV crosslinked
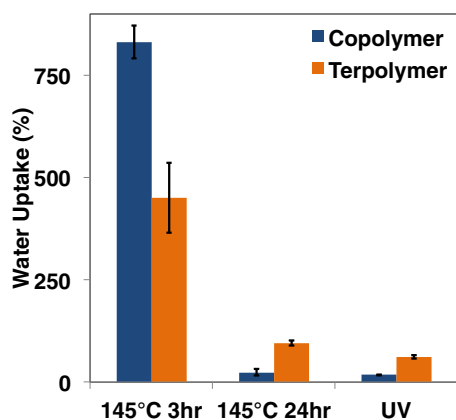
Figure 4. Water uptake of the copolymer and terpolymer as a function of crosslinking method.

compared to the copolymer, 4–17 mS/cm, as a result of the terpolymer's higher IEC. Crosslinking method and extent of crosslinking had a significant influence on membrane conductivity. The UV crosslinked films have lower IECs than the thermally crosslink films, due to the addition of the inert crosslinking agent. The reduced IEC results in lower conductivity for the UV crosslinked films. For example, the UV crosslinked copolymer film had 35% lower conductivity compared to the thermally crosslinked copolymer films. The UV crosslinked terpolymer has lower conductivity than the 3 hr thermally crosslinked film, but slightly higher conductivity compared to the 24 hr thermally crosslinked film. The short duration (3 hr) thermally crosslinked films had the highest conductivity in both the copolymer and terpolymer systems, due to the lower degree of crosslinking and higher swelling that allows better ion mobility. The 3 hr thermally crosslinked films could only be measured at lower temperatures. At higher temperatures the 3 hr thermally crosslinked membranes softened to the point that they would flow out of the conductivity cell during testing, this softening effect due to hydration was investigated further by mechanical testing. The 3 hr thermally crosslinked terpolymer film had measurable conductivity up to 80°C, while the copolymer was immeasurable after 65°C. The terpolymer has better film integrity at higher temperatures under hydrated conditions, despite the fact that the terpolymer has a higher IEC. The addition of glassy polystyrene to the polymer matrix improves film integrity allowing the higher IEC terpolymer to remain a solid film at higher temperatures when hydrated.

Water uptake.— Water uptake was dependent on polymer chemistry and crosslinking method (Figure 4). A low degree of crosslinking (3 hr thermal) resulted in significant water uptake by the film, 830% and 450% for the copolymer and terpolymer, respectively. Increasing the degree of crosslinking (24 h thermal and UV) reduces the water

uptake. Water uptake for the copolymer was reduced to 24% for the 24 h thermally crosslinked and 18% for the UV crosslinked films. The terpolymer films had higher water compared to the copolymer, 96% for the 24 h thermally crosslinked and 62% for the UV crosslinked. The copolymer has a higher percent of isoprene (87 mol%) compared to the terpolymer (71%), so more crosslinkable units are present in the copolymer. The large number of crosslinkable units, along with a high degree of crosslinking in the 24 hr thermally and UV crosslinked copolymer films prevents significant water uptake. The lower number of crosslinkable units in the terpolymer, along with its higher IEC, causes water uptake to be higher, even when degree of crosslinking is high (24 hr thermal and UV crosslinked). While water uptake is critical to maintain ion conduction, excess water uptake causes significant membrane swelling and can weaken the film to the point of mechanical integrity loss.

Membrane swelling.— The extent of crosslinking impacted initial dimensional swelling, when the cast films were removed from the casting substrate, soaked in water for 1 h, and subsequently dried. The films crosslinked for a short duration (3 hr) had larger dimensional swelling and did not fully contract back when drying. This resulted in the 3 hr crosslinked films being significantly thinner (20–30 microns) compared to the 24 hr crosslinked films (60–70 microns) and UV crosslinked films (90–110 microns).

Dimensional swelling between dry and hydrated states can impact mechanical integrity of the membrane and assembly during operation. Dimensional swelling was influenced by polymer chemistry and crosslinking, and directly related to measured water uptake (Figure 5). The 3 hr thermally crosslinked copolymer film had the highest degree of swelling at 118% in the in-plane direction, through-plane swelling was much lower at 16%. The other copolymer films (24-hr thermally and UV crosslinked) had significantly lower dimensional swelling, 12–15% in-plane and 5–6% through-plane. Compared to the copolymer, the terpolymer had a higher degree of swelling (excluding the high in-plane swelling of the 3 hr thermally crosslinked copolymer). The terpolymer had similar in-plane swelling for all films, 44% and 54% for the 3 hr and 24 hr thermally crosslinked respectively, and slightly less for the UV crosslinked at 34%. Through-plane swelling was highest for the 3-hr thermally crosslinked terpolymer film at 58% and this was the only film to have a higher through-plane swelling than in-plane swelling. Through-plane swelling was 30% lower compared to in-plane for the 24 hr thermally crosslinked terpolymer and 76% lower for the UV crosslinked terpolymer. Limiting dimensional swelling is important to prevent membrane degradation and assembly damage when a fuel cell undergoes humidity changes, and crosslinking is one technique to successfully reduce dimensional swelling.

Extensional tests.— Extensional tests were performed at 30°C and 60°C under dry and hydrated conditions. Films were extremely stiff at dry conditions and underwent severe softening when hydrated (Figure 6) causing films to become extremely weak. Under dry
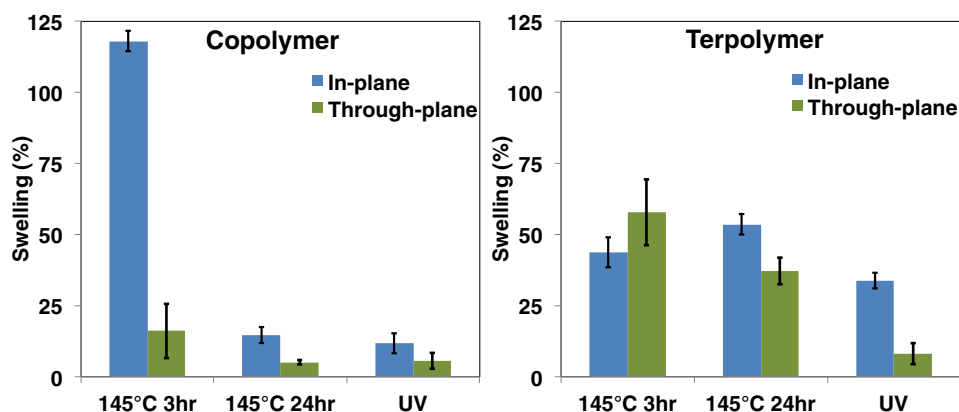

Figure 5. Dimensional swelling of the copolymer and terpolymer measured after soaking in water for 24 hrs compared to films vacuum dried at 50°C overnight.
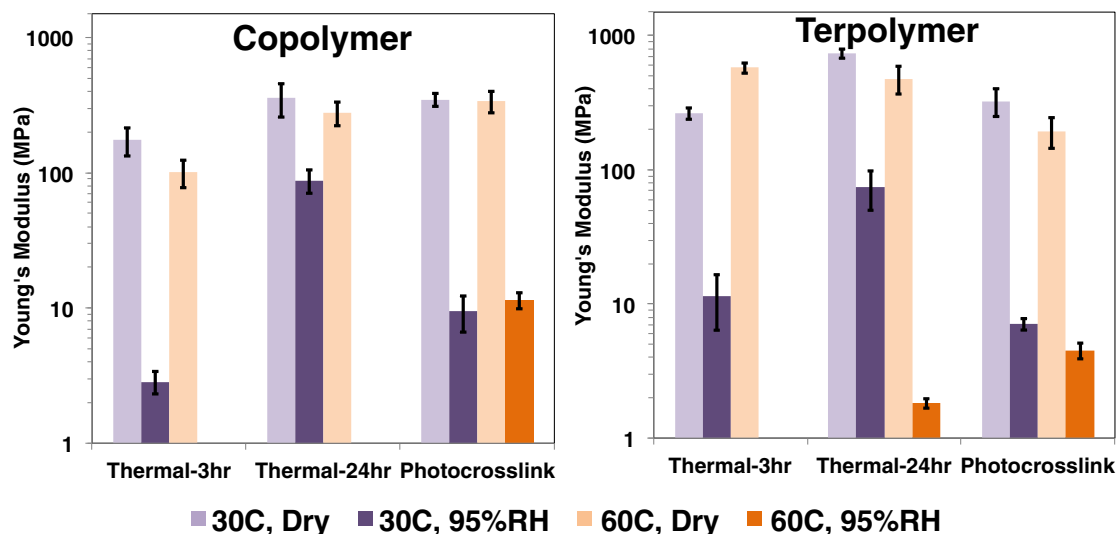
Figure 6. Young's Moduli (on a log scale) of the copolymer and terpolymer based on crosslinking technique.

conditions, all films are stiff having moduli between 100 and 740 MPa; this is comparable to moduli reported for other AEMs.[32,34–36] Generally, the terpolymer was slightly stiffer than the copolymer due to the addition of glassy polystyrene to the polymer matrix. A lower degree of crosslinking (3 hr thermal) resulted in softer films than those with a higher degree of crosslinking (24-hr thermal/UV). All films were severely softened at hydrated conditions due to the plasticizing effect of water in the film. At 30°C, the 24 hr thermally crosslinked films had the smallest decrease in moduli from dry to hydrated states, however reduction was still 76% for the copolymer and 90% for the terpolymer. The 3 hr thermally and UV crosslinked films all had at least a 95% reduction in modulus from dry to hydrated states. Humidifying the films at higher temperature, 60°C, caused several of the films to soften to the point that the measured stress was below the noise level of the instrument. Extensional properties were not measurable for the 3-hr thermally crosslinked films or the 24 hr thermally crosslinked copolymer at 60°C and saturated. The 24 hr thermally crosslinked terpolymer was measurable, suggesting that adding polystyrene to the polymer matrix improves mechanical durability when hydrated, despite the terpolymer's higher IEC. Both UV crosslinked films were measurable at the 60°C and saturated conditions, however measured

moduli were extremely low, being 11 MPa for the copolymer and 5 MPa for the terpolymer. These moduli values are low compared to working fuel cell membranes such as Nafion, which has a modulus of 114 MPa in water at 23°C.[37]

While the moduli values of the films were fairly high at dry conditions, the stress to failure was low to moderate compared to other AEMs (5–70 MPa),[12,32,38] crosslinked AEMs (2–27 MPa)[20,21,27] and PEMs (20–50 MPa)[4,37] (Figure 7). At dry conditions the thermally crosslinked copolymer films had relatively low stress to break, between 3 to 6 MPa, while the thermally crosslinked terpolymer films had slightly higher stress to break, 7 to 15 MPa. The UV crosslinked films had consistently higher stress to break, 13 to 30 MPa for the copolymer and 19 to 20 MPa for the terpolymer. At dry conditions the copolymer had a slight decrease in strength from 30°C to 60°C, while the terpolymer had little to no change with temperature, likely due to the added polystyrene that is thermally stable within this temperature range. Hydrating the films causes significant reduction in strength due to the severe softening discussed above. At 30°C film strength was reduced to between 1 MPa to 2.7 MPa, and at 60°C the maximum stress to break measured for any of the films was only 1.4 MPa. The strength of these films at hydrated conditions is
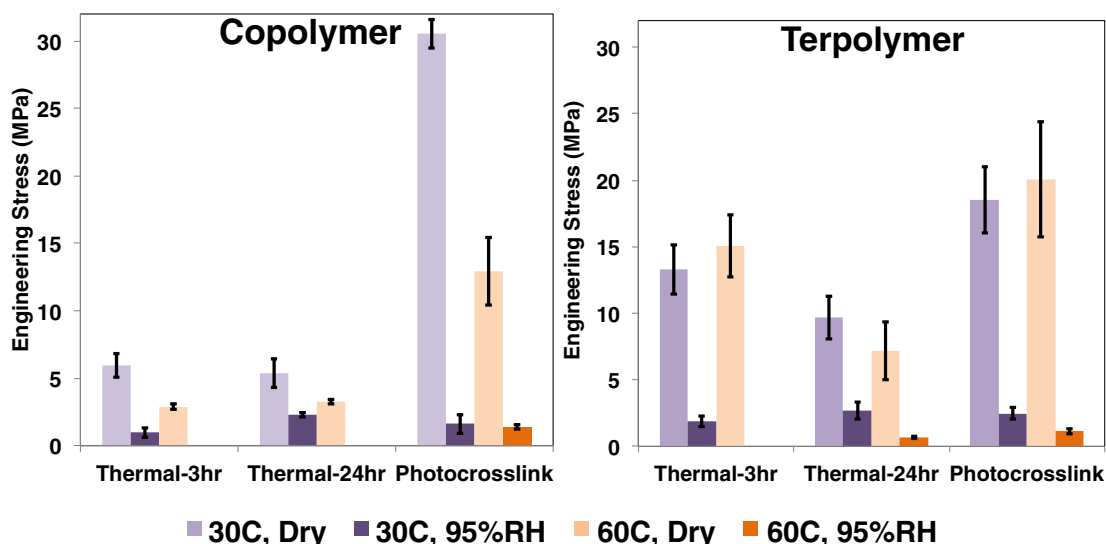

Figure 7. Engineering stress of the copolymer and terpolymer based on crosslinking technique.
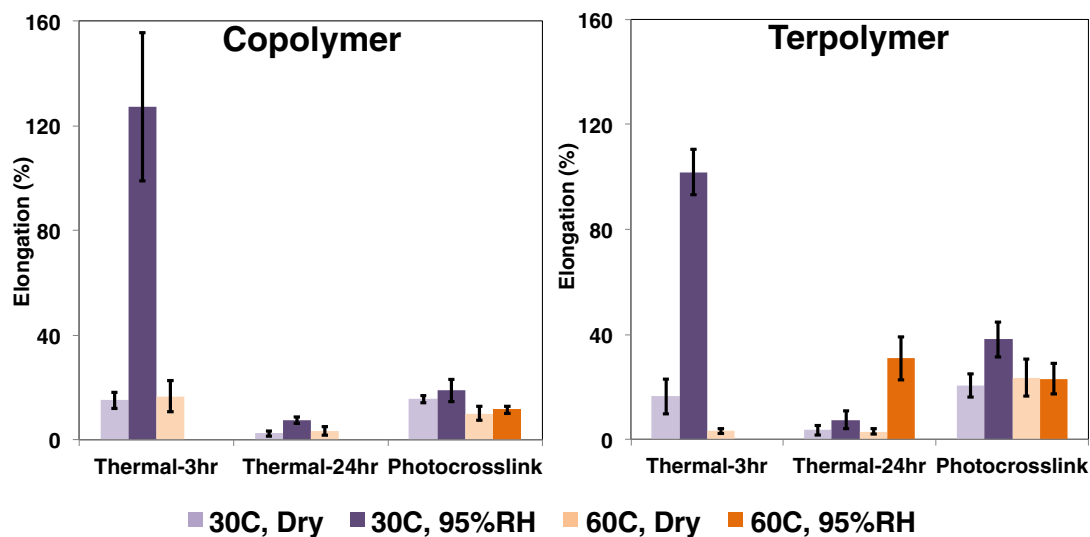
Figure 8. Elongation of the copolymer and terpolymer based on crosslinking technique.

insufficient and the extreme differences in mechanical properties between dry and hydrated states could cause membrane degradation and assembly failure.

Adequate film elongation is important to accommodate dimensional changes with swelling (Figure 8). At dry conditions the films have low elongation, and elongation decreases with crosslinking duration. The 3 hr thermally crosslinked films have dry elongations about 15%, except for the terpolymer at 60°C, while the 24 hr thermally crosslinked films have lower elongations between 2% to 3%. The UV crosslinked films have slightly higher dry elongations between 10% to 23%. The low degree of crosslinking in the 3 hr thermally crosslinked films causes elongation to increase dramatically when hydrated, up to 130% and 100% for the copolymer and terpolymer, respectively, at 30°C. Alternatively, the higher degree of crosslinking for the 24 hr thermally crosslinked films results in relatively small increase in elongation, up to 7% for both the copolymer and terpolymer at 30°C. Elongation of the UV crosslinked films is much more consistent across different temperature and hydration conditions, the copolymer film ranges from 10% to 19% while the terpolymer ranges from 21% to 31%. The narrow range of elongations of the UV crosslinked films suggests that UV crosslinking provides greater mechanical stability compared to the thermal crosslinking.

Extensional tests revealed dramatic differences in the mechanical properties of the crosslinked polymer films from dry to hydrated states. The films were relatively stiff at dry conditions, particularly as the degree of crosslinking was increased by increasing crosslinking duration. While stiff, the films had relatively low strength and elongation at dry conditions. Hydrating the films caused severe softening and weakening of the films, to the point that at higher temperature some films were immeasurable and were deemed to have lost film integrity. Overall, the UV crosslinked films had better, more consistent, mechanical properties over the range of temperatures and hydrations tested. Ultimately, while crosslinking increased film stiffness, these films are too weak when hydrated for use in an electrochemical device. The extreme disparity between dry and hydrated mechanical properties, and the fact that some films were immeasurable at high hydrations, warranted further study by dynamic measurements of mechanical behavior.

Dynamic mechanical analysis.— Dynamic mechanical analysis observed moduli changes while ramping temperature from 30°C to 70°C at dry or saturated relative humidity conditions (Figure 9). DMA distinguished mechanical changes due to temperature compared to those due to hydration level. At dry conditions, little change in
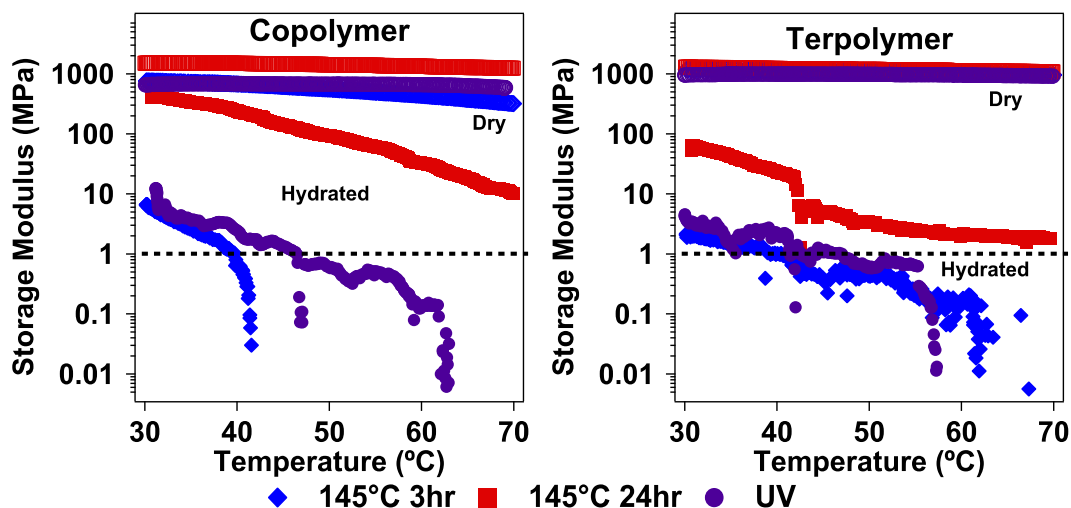

Figure 9. Storage modulus vs. temperature for the copolymer and terpolymer, solid points are at saturated relative humidity and the unfilled data points are at dry conditions. The dashed line shown is defined as minimum modulus for film integrity.

storage modulus was measured between 30°C and 70°C. The copolymer films had slightly different moduli based on crosslinking technique (750–1500 MPa at 30°C) that decreased little as temperature was ramped to 70°C. Alternatively, the terpolymer films moduli do not change with crosslinking method and are consistent over the 30°C to 70°C temperature range, having moduli around 1000 MPa for all films tested.

Compared to the narrow change in moduli with temperature at dry conditions, the response of the films at saturated conditions were significant, spanning orders of magnitude. The films had moduli one to two orders of magnitude lower than the dry films at 30°C. The 24 hr thermally crosslinked films were measurable over the entire temperature range, while the softer 3 hr thermally and UV crosslinked films became so soft as temperature increased that moduli became immeasurable. A sharp decrease in modulus, indicating severe softening, was observed for the 3 hr thermally and UV crosslinked films. While magnitude and change in moduli were consistent between tests, the temperature for the onset of modulus decrease varied slightly between runs (1–8°C), so rather than define film integrity loss by the onset of the modulus decrease we defined a modulus of minimum integrity as 1 MPa (dashed line in Figure 9). The temperature when the minimum modulus was reached, was independent of chemistry; both of the 3 hr thermally crosslinked films reached this minimum modulus at 40°C while the minimum moduli for UV crosslinked films were at 46°C for the copolymer and 47°C for the terpolymer. The modulus of the 24 hr thermally crosslinked films remained above the 1 MPa for the entire temperature range.

Overall, saturated humidity conditions lead to a sharp decrease in moduli, even to the point of being immeasurable, as temperature is increased. Conversely, a nearly constant moduli at dry conditions demonstrates the significance of membrane hydration to mechanical performance and membrane integrity. Anion exchange membranes must be mechanically stable over a large range of temperature and humidity conditions, the change in moduli by orders of magnitude from dry to saturated conditions makes these crosslinked films inadequate for a working fuel cell or electrochemical device.

Conclusions

In this work, two polyisoprene based copolymers were crosslinked by various methods to render insoluble anion exchange membranes. The terpolymer had styrene added to the polymer matrix compared to the copolymer consisting of only isoprene and vinylbenzyl trimethylammonium units. The addition of styrene to terpolymer improved membrane integrity following crosslinking, allowing the ion concentration to be increased for better ion conduction. Three crosslinking methods were investigated, thermal crosslinking at two durations (3 or 24 hrs) and UV crosslinking with a dithiol crosslinker. Reduction of IEC due to UV crosslinking led to lower conductivity. A shorter duration of thermal crosslinking increased conductivity, but films became fluid-like at higher temperatures when hydrated, causing loss of solid film integrity. The copolymer films were more resistant to swelling due to the larger number of crosslinkable isoprene units and lower IEC.

Mechanical properties of the crosslinked films were highly dependent on hydration level. Dry films were stiff with relatively low strength and elongation. Hydrated films were extremely soft and even weaker, but had higher elongation. UV crosslinked films had more consistent mechanical properties than the thermally crosslinked films, but still suffered poor mechanical integrity at hydrated conditions that would be insufficient for a fuel cell. Dynamic mechanical analysis

demonstrated the difference in mechanical properties was due to hydration not thermal transitions, i.e., the dry films were stable over the range of temperatures tested. Saturated conditions caused moduli to be reduced to the point of being immeasurable. While crosslinking rendered solution-processed films insoluble, the extreme disparity of the films' mechanical properties between dry and hydrated states is unacceptable for fuel cell operations. Additional study of polymer chemistry and crosslinking is required to achieve a narrow range of mechanical properties that can withstand dimensional swelling and hygrothermal stresses associated with humidity changes in a fuel cell or electrochemical device.

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