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An experimental investigation of humidity and temperature effects on the mechanical properties of perfluorosulfonic acid membrane

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are expected to become a prominent technology in a variety of power generation applications, including stationary, portable, and automotive applications. Their potentially high energy density, high efficiency and clean operations offer attractive advantages over traditional methods of power generation [1,2].

The central function in a PEMFC is performed by the polymer electrolyte membrane. In use, the polymer electrolyte membrane serves to conduct protons from the anode electrode to the cathode electrode, while acting as an electronic insulator and a gas barrier to prevent mixing of oxygen and hydrogen (Fig. 1). Any discontinuity of the membrane will compromise the function of the fuel cell. A typical automotive duty cycle imposes rapid changes in the current density and voltage of the fuel cell, as well as rapid changes in the cell temperature, pressure and relative humidity. The polymer electrolyte membrane, gas diffusion layers and graphite plates will all experience expansion and contraction as a function of temperature and moisture. The different thermal expansion and swelling coefficients of these various materials introduce hygro-thermal stresses as the system is cycled, potentially leading to deterioration and eventual malfunction of the fuel cell [3–5]. A rational approach to developing an improved lifetime for PEMFC membranes necessitates that the failure mechanisms be clearly understood and life prediction models be developed so that new designs can be introduced. A critical step toward this understanding is to fully characterize the membrane's mechanical behavior under in situ operating environments. This work focuses on such characterization.

Several publications have reported the importance of the membranes mechanical properties on operational life [3–9]. Membrane failures in the membrane electrode assembly (MEA) have been precipitated solely by cycling between wet and dry operating conditions without electric potential or reactive gases [3]. These failures can appear as pinholes in the membrane or delamination between polymer membrane and gas diffusion layers [6,7]. Several analytical studies [4,5,8] have shown how hygro-thermal stresses might play an important role in these failures. Thus, it is important to characterize the hydro-mechanical properties of the constituents.

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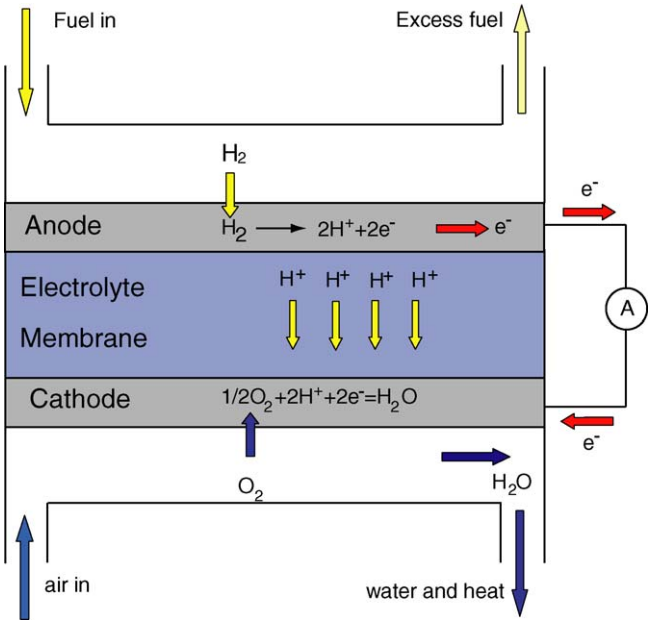

Fig. 1. Schematic of a proton exchange membrane fuel cell.

PEMFCs operate at temperatures ranging from ambient to 100 °C and a variety of humidification levels. The membranes absorb up to 50 wt.% water and experience significant volumetric swelling. Upon moisture absorption, the strength of the membrane drops dramatically due to the plasticization of the ionomer [10]. Although effects of temperature and humidity on the strength of PFSA membrane have been reported [11,12], to the knowledge of the authors, only conditions at ambient humidity or in liquid water are published in the open literature. Intermediate humidity and the coupled effects of temperature and humidity have yet to be studied.

State-of-the-art PEMFCs, such as Nafion® membranes[1] and GORE-SELECT® membranes,[2] utilize perfluorosulfonic acid polymers. In this paper, influences of temperature and humidity on the mechanical properties of Nafion®112 are systematically studied. The properties studied are the Young's modulus, proportional limit stress, break stress and the elongation at break. The in-plane swelling behavior of the membrane at different temperatures and humidity is also investigated.

2. Experimental

2.1. Preparation of membrane samples

The perfluorosulfonic acid membrane, Nafion®112 was used in all of the experiments. Nafion®112 has the following physical properties: a nominal equivalent weight of 1100 g/mol of sulfonic group and a thickness of two thousandths of an inch (52 μm). Prior to use, the membrane was pre-treated by boiling, for one hour each, in 3% hydrogen peroxide, 0.5 M sulfuric acid and deionized water (DI). Between each step, the membrane was rinsed with DI water. The pre-treatment was conducted to obtain a common material state for all samples. After pre-treatment, the membrane was dried at room temperature for 24 h, and then cut along both the machine and transverse directions into rectangular specimens with length of 100 mm and width of 10 mm.

2.2. Experimental apparatus

Tensile tests were conducted with an MTS Alliance™ RT/5 material testing system with an ESPEC custom-designed environmental chamber (Fig. 2A). The chamber can operate in conditions from –70 to 170 °C and relative humidity between 30% and 95%. Besides the sensors installed in the chamber to control the temperature (copper/copper–nickel type 'T' thermocouple) and humidity (Rotronic H290 humidity transmitter) of the chamber, an additional Testo 645 humidity sensor was positioned close to the specimen in order to measure the temperature and humidity as close to the specimen as possible.

2.3. Testing procedures

Membrane properties were measured at 16 temperature and humidity combinations, i.e., at four different temperatures (25, 45, 65, 85 °C) and four different relative humidities (30%, 50%, 70%, 90%) each. Five specimens were tested at each temperature and humidity combination. For each specimen, the thickness and width were taken as the average of three measurements distributed over the sample. The specimen was aligned with the extension rod by a pair of vise-action grips (Fig. 2B), and the gauge length was adjusted to 50 mm as determined by the grip separation.

To achieve the desired environmental conditions in the chamber the temperature was increased to the set point and allowed to stabilize, where after the humidity was slowly increased to the desired RH-set point. During this process, the length of the specimen changes due to the thermal and swelling expansions of the membrane. Before testing, the crosshead was manually adjusted until the initial load applied to the specimen was brought back to zero, eliminating the slack caused by thermal and swelling expansions. Thus, the gauge length of the specimen was now the original length plus the displacement of the crosshead. The recorded value of the crosshead change is taken as a measure of the dimensional change of the membrane due to a change in temperature and humidity. For all tests, the strain rate was 0.2 mm/mm per minute.

3. Results and discussions

3.1. Stress–strain curves at different temperature and humidity

Fig. 3 shows typical results for the engineering stress–strain curves of Nafion®112 along the transverse direction at the fixed relative humidity of 50% for a range of temperatures (the stress–strain curves along machine direction are similar to transverse direction). As the temperature decreases, the curves monotonically shift upward corresponding to increasing tensile

[1] Nafion® is a registered trademark of E.I. DuPont De Nemours & Co.
[2] GORE-SELECT® is a registered trademark of W.L. Gore & Associates, Inc.

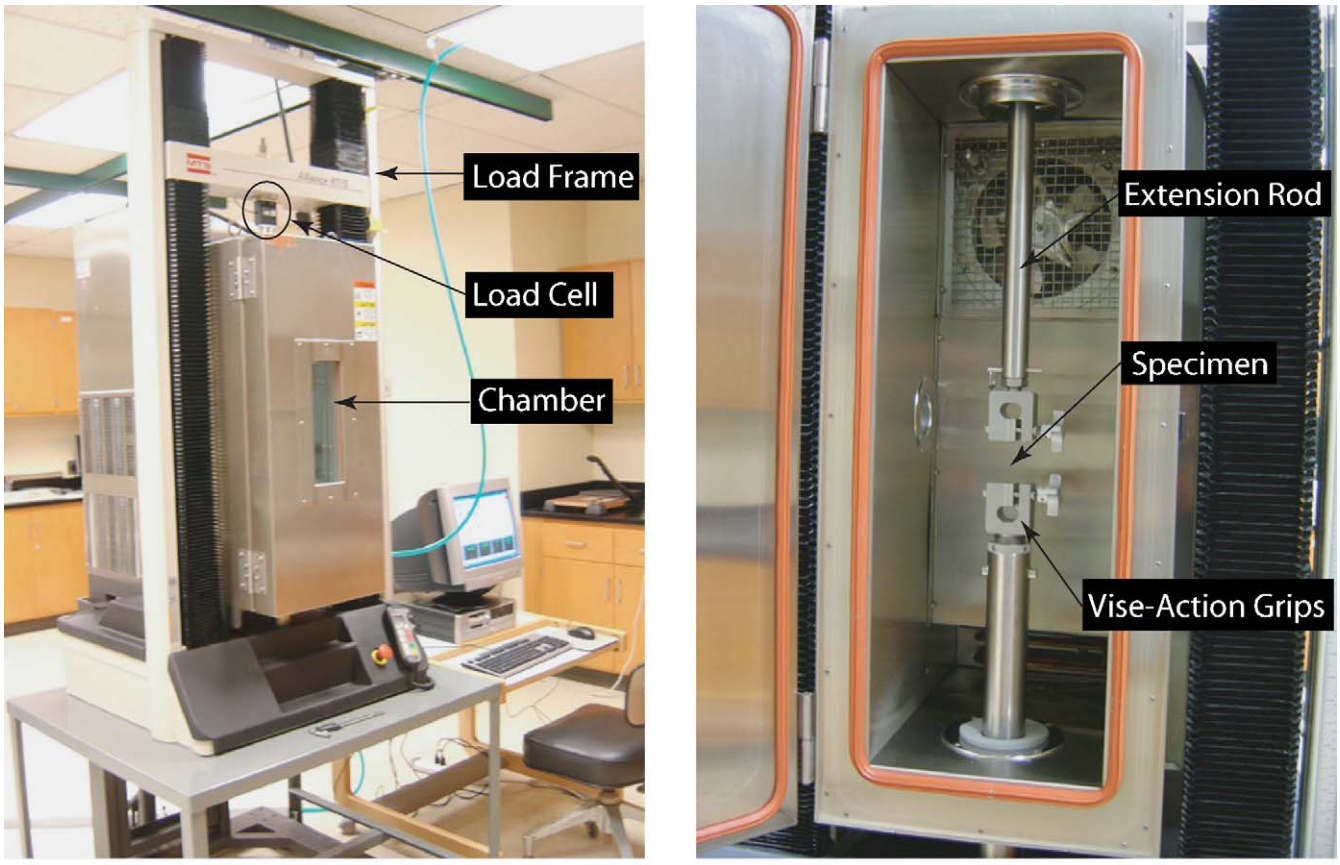

Fig. 2. (A) Experimental equipments: MTS alliance RT/5 material testing system with custom-designed environmental chamber from ESPEC Inc. (B) Tensile tests of the membrane. Specimen was aligned with the extension rod by a pair of vise-action grips.

strength. The elongation at break increases with increasing temperature. Fig. 4 shows the stress–strain curves along the transverse direction at fixed temperature 45 °C, for a range of relative humidities. At higher humidity, more water is absorbed in the hydrophilic sulfonic acid clusters, which weaken the ionic interactions and change the mechanical stability significantly. Although the tensile strength decreases as the humidity increases, it is not clear if the break stress and the elongation at break point are affected much by humidity change. Figs. 3 and 4 indicate that, in the range of values studied, temperature generally has a more significant effect on the mechanical behavior of Nafion® membrane than humidity.

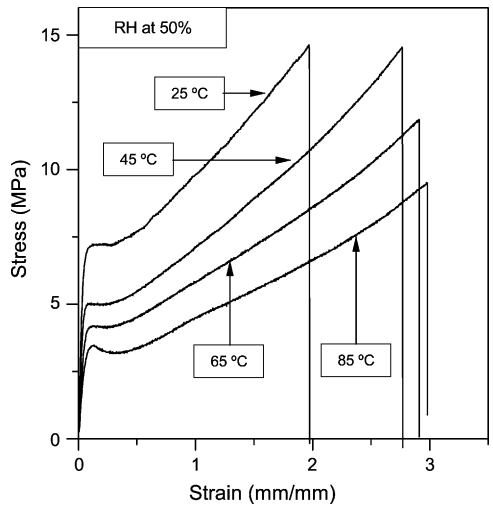

Fig. 3. Engineering stress–strain curves of tensile tests at different temperatures at 50% relative humidity (transverse direction).

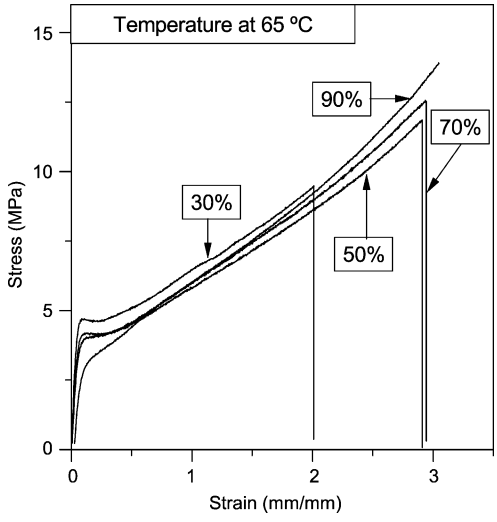

Fig. 4. Engineering stress–strain curves of tensile tests at different relative humidity at 45 °C (transverse direction).

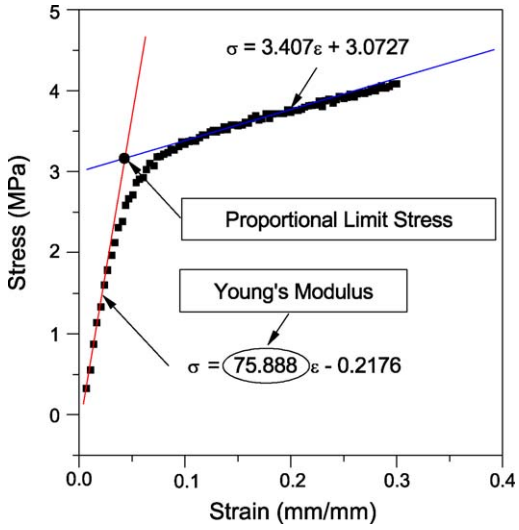

Fig. 5. Definition of proportional limit stress and Young's modulus.

Based on these monotonic engineering stress–strain curves of tensile tests (Figs. 3 and 4), it is not possible to identify the onset of yielding. Instead, a "proportional limit" stress is defined in this paper to describe the onset of non-linearity. To determine the proportional limit stress, the tangents to the regions on either side of the "bend" are extended until they intersect, as indicated in Fig. 5. This point is defined as the proportional limit stress. Young's modulus is taken as the linear regression of the initial linear part of stress–strain curve.

3.2. Effects of temperature and humidity on the mechanical properties of the membrane

The Young's modulus, proportional limit stress, break stress and break strain are determined from each engineering stress–strain curve and the average value for each of these parameters is evaluated at each temperature–humidity combination. These average values are plotted in Figs. 6–13 to show each parameter as a function of either temperature or relative humidity. Properties in both the transverse and the machine directions have been investigated.

The effects of temperature and humidity on the Young's modulus on both the machine and transverse directions are shown in Figs. 6 and 7, respectively. The results indicate that higher temperature and relative humidity lead to lower Young's modulus. Since water has a very low glass transition temperature T_g (estimated value at −130 °C) [11], it acts as a very good plasticizer even in small quantities. In the presence of water, the interference between water and the chain-to-chain secondary bonding reduces the intermolecular forces. As a result, chains acquire greater mobility and the free volume increases, leading to a decrease in the glass transition temperature and the strength [13]. Although the glass transition temperatures of perflurosulfonic acid membranes such as Nafion® are usually between 100 and 150 °C [14], with increasing temperature, the amorphous domain (with higher strength) decreases, leading to lower Young's modulus and proportional limit stress. From

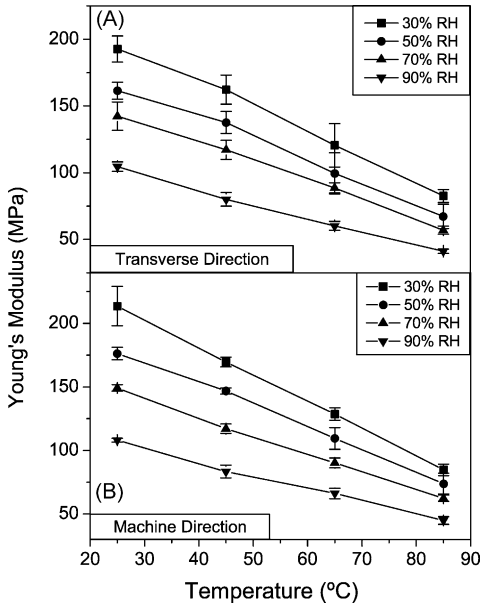

Fig. 6. Young's modulus as a function of temperature at various relative humidities: (A) transverse direction and (B) machine direction.

Figs. 8 and 9, we see that the proportional limit stress of Nafion® membrane decreases as the temperature and humidity increase.

Although relative humidity apparently affects Young's modulus and the proportional stress, no obvious effects can be seen for break stress and break strain (Figs. 10 and 11). However, higher temperature does tend to cause to lower break stress and may lead to higher break strain, at least in the machine direction (Figs. 12 and 13).

Fracture surface morphologies of two extreme cases are shown in Figs. 14 and 15 (temperature at 25 °C and humidity at 30% (T25-RH30), and temperature at 85 °C and humidity at 90%

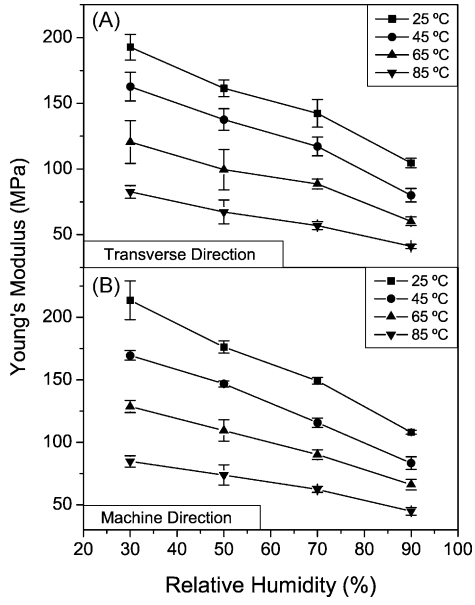

Fig. 7. Young's modulus as a function of humidity at various temperatures: (A) transverse direction and (B) machine direction.

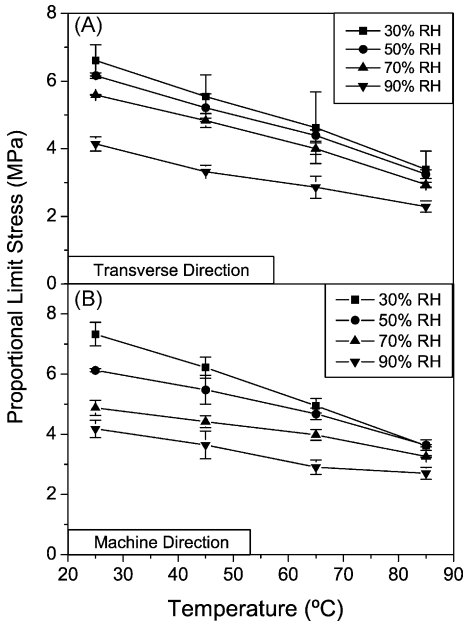

Fig. 8. Proportional limit stress as a function temperature at various relative humidities: (A) transverse direction and (B) machine direction.

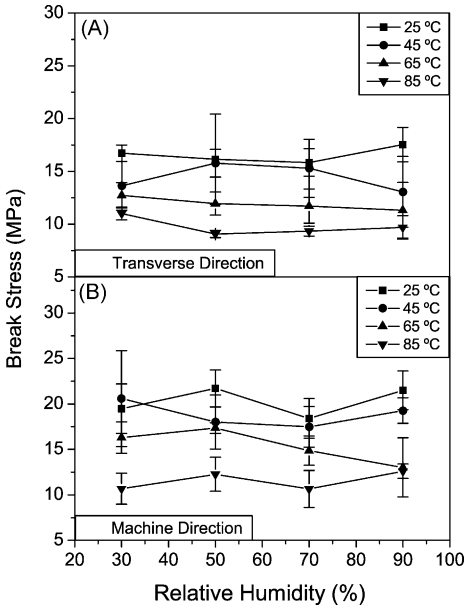

Fig. 10. Break stress as a function of humidity at various temperatures: (A) transverse direction and (B) machine direction.

(T85-RH90)). Both show a typical ductile polymer tensile fracture surface [15], however, at higher magnification (Fig. 15), the fracture surface of the membrane tested at 25 °C and 30% RH shows smaller "cavities" and corresponding "pull-outs", thus indicating a less ductile behavior than for the membrane tested at 85 °C and 90%.

The mechanical property changes with respect to temperature and humidity, in the transverse direction are similar to those on the machine direction. However, at the same temperature and humidity, the Young's modulus, proportional stress and break stress on the machine direction are all slightly larger than those on the transverse direction. The break strain in the machine direction, however, is smaller than that in the transverse direction.

3.3. Swelling behaviors of the membrane at different temperatures

Dimensional changes with relative humidity at different temperatures along the transverse and machine directions are shown

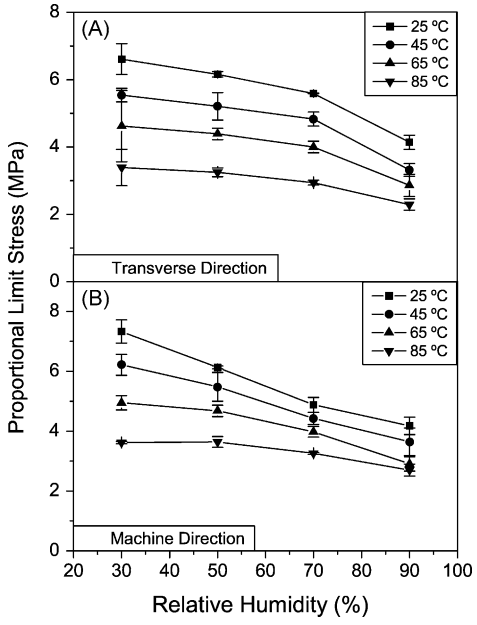

Fig. 9. Proportional limit stress as a function of humidity at various temperatures: (A) transverse direction and (B) machine direction.

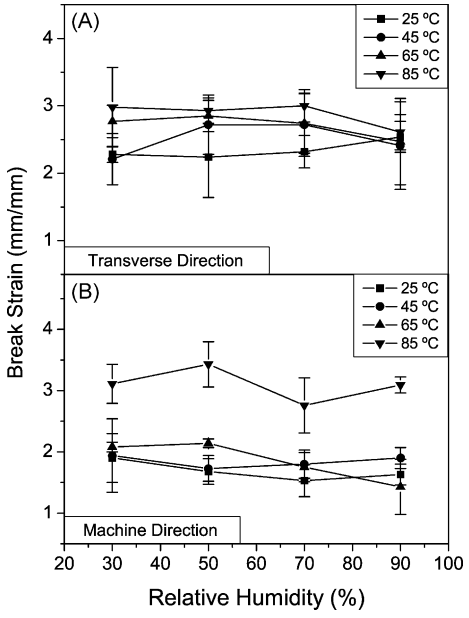

Fig. 11. Break strain as a function humidity at various temperatures: (A) transverse direction and (B) machine direction.

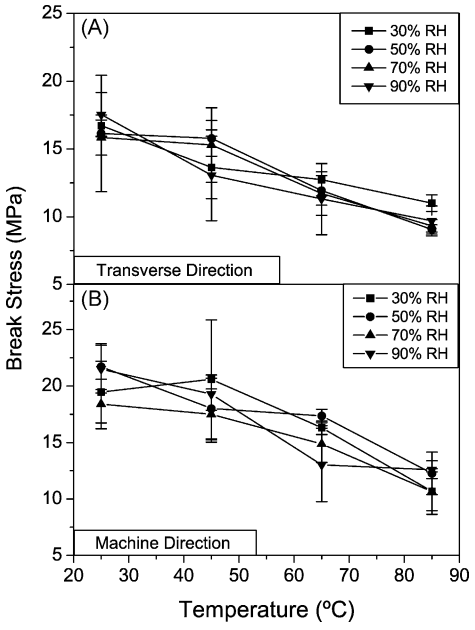

Fig. 12. Break stress as a function temperature at various relative humidities: (A) transverse direction and (B) machine direction.

in Fig. 16. With increasing humidity, the swelling coefficient (the derivative of the curve) increases; the swelling coefficient at higher relative humidity, above 70%, increases dramatically compared with the intermediate humidity range. It is clear from Fig. 16 that the swelling coefficients at higher temperatures are larger than that at lower temperatures. At the same temperature and humidity, the dimensional change percentage along the transverse direction is larger than that along the machine direction, although the trends are similar.

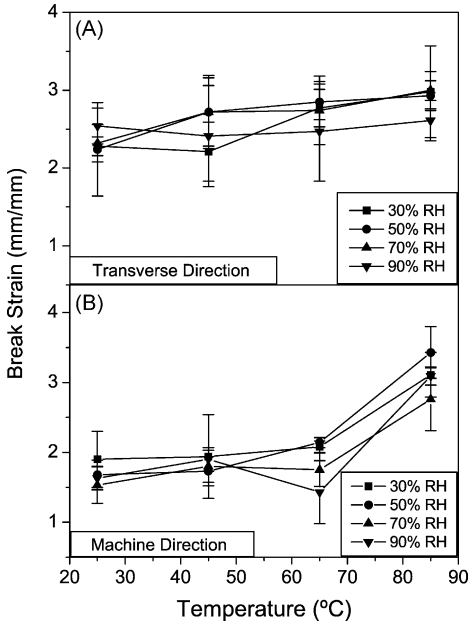

Fig. 13. Break stain as a function temperature at various relative humidities: (A) transverse direction and (B) machine direction.

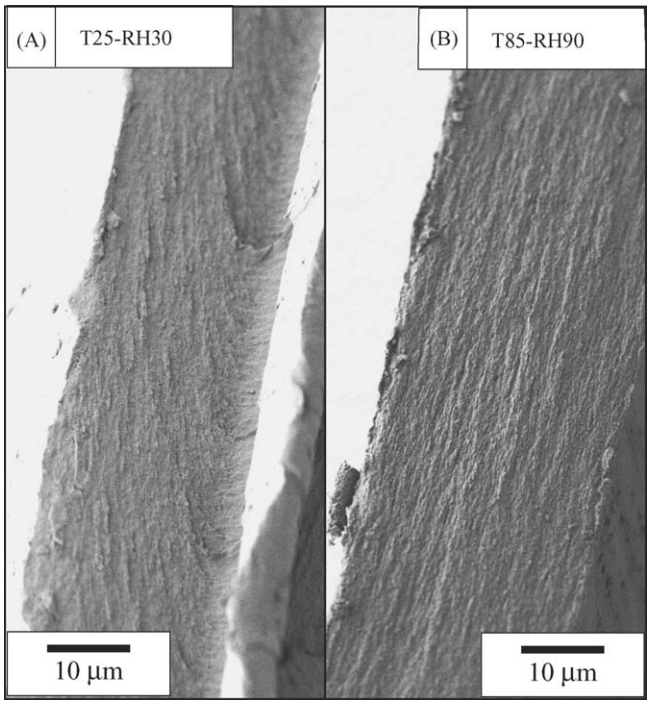

Fig. 14. SEM images at low magnification of the fracture surface of the membrane at: (A) temperature 25 °C and relative humidity 30%; (B) temperature 85 °C and relative humidity 90%.

3.4. Effect of pre-treatment procedures on the membrane properties

Finally, we compare the Young's modulus at 50% RH of the as-received membrane with that of the pre-treated mem-

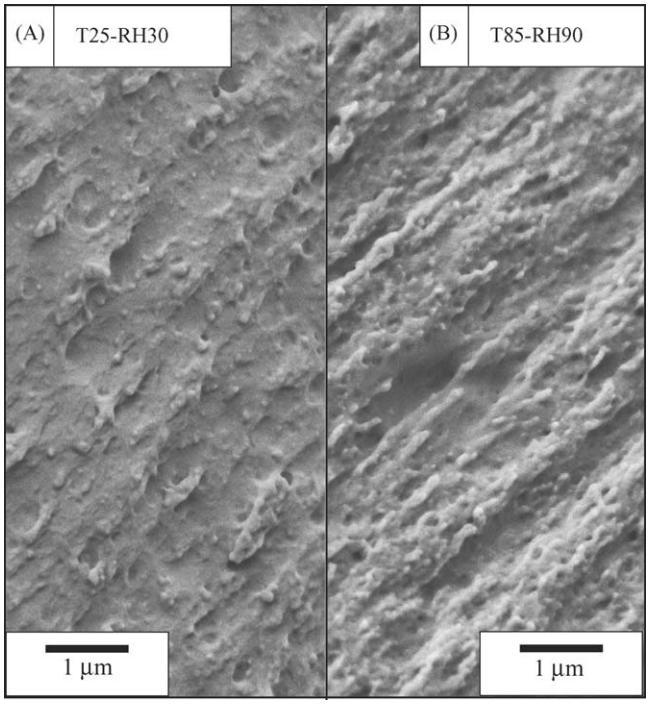

Fig. 15. SEM images at higher magnification of the fracture surface of the membrane at: (A) temperature 25 °C and relative humidity 30%; (B) temperature 85 °C and relative humidity 90%.

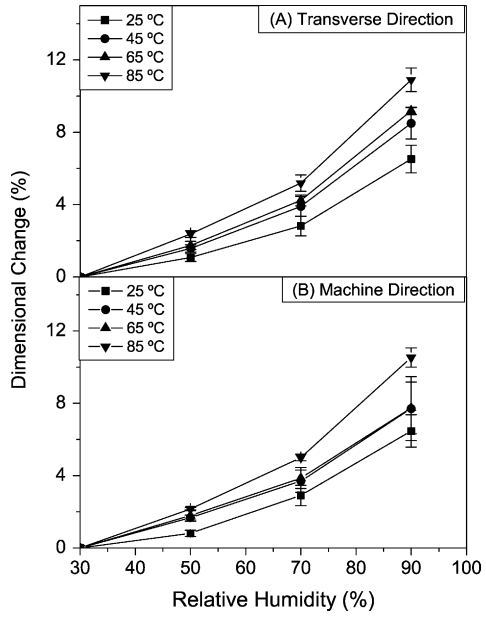

Fig. 16. Dimensional changes as a function of relative humidity at various temperatures: (A) transverse direction and (B) machine direction.

brane in Fig. 17. It is evident that the as-received membrane has higher Young's modulus than that of the pre-treated membrane. The pre-treatment procedure in this study involves boiling membrane samples in hydrogen peroxide, sulfuric acid solutions, and deionized water, as described in Section 2. According to Zawodzinski et al. [16], whereas the conductivity of Nafion® membrane is improved upon pre-treatment due to removal of low-molecular weight impurities left during processing, boiling Nafion® membrane during the pre-

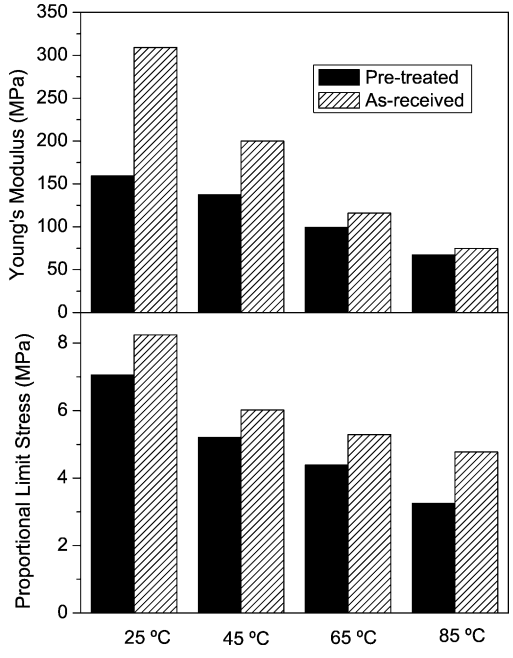

Fig. 17. Comparison of Young's modulus at 50% relative humidity between the as-received membrane and the membrane which was pre-treated.

treatment steps also promotes creation and growth of hydrated ionic clusters which leads to an increase in water content of the membrane. The rejuvenation of the membrane, along with the formation of ionic clusters, is responsible for the higher water content of pre-treated samples [16]. Comparing with as-received Nafion® membranes, pre-treated samples have lower tensile strength at the same temperature and humidity conditions.

3.5. Kruskal–Wallis tests of the experimental results

A nonparametric statistical analysis, Kruskal–Wallis test [17], has been applied to the experimental results in order to examine the significance of temperature and humidity effects on the mechanical properties of the tested material. The Kruskal–Wallis test is primarily a rank test where all the data for a given temperature or relative humidity is collected and ordered from the smallest to the largest value, regardless of the group which the data came from. An H-value can be found by applying Kruskal–Wallis equation:

$$H = \frac{12}{n(n+1)} \sum_{i=1}^{k} \frac{R_i^2}{n_i} - 3(n+1) \tag{1}$$

In which n_i ($i = 1, 2, \ldots, k$) represent the sample sizes for each of the k groups (i.e., samples) in the data. R_i is the sum of the ranks for group i. $n = \sum_{i=1}^{k} n_i$. Each of the n_i should be at least 5 for the approximation to be valid. This statistic approximates a χ^2-distribution with $k - 1$ degrees of freedom under the significance level alpha (typically set to 0.05). The corresponding χ^2-value can be found in the χ^2-distribution table [17]. In this study, the χ^2-value is 7.815. If the H-value is greater than the χ^2-value, the input being tested is significantly affecting the data. Table 1 lists the H-values of the humidity effects on the membrane properties in the transverse direction at four different temperatures. From the results, it is clear that Young's modulus and proportional limit stress of Nafion® are affected by humidity significantly, however, the break stress and break strain of the membrane are not affected much. The H-values from Kruskal–Wallis tests on the temperature effects at four different humidities are listed in Table 2. These results show that temperature change affects the Young's modulus, proportional limit stress and break stress. However, the break strain is not significantly affected under temperature change. A similar analysis on the mechanical properties in the machine direction showed that the same conclusions are valid for this set of materials.

Table 1
The Kruskal–Wallis statistical H-values for humidity at various temperatures*

Temperature (°C)	Young's modulus	Proportional limit stress	Break stress	Break strain
25	15.647	14.763	3.360	3.274
45	16.592	15.303	3.309	3.753
65	14.776	16.282	1.571	1.355
85	14.951	10.432	9.477	3.994

* A value greater 7.815 indicates statistical significance for this sample set.

Table 2
The Kruskal–Wallis statistical H-values for temperature at various humidities*

Relative humidity (%)	Young's modulus	Proportional limit stress	Break stress	Break strain
30	15.109	17.108	13.703	9.852
50	16.895	16.592	15.071	8.136
70	17.857	17.857	14.314	5.811
90	13.150	12.829	8.725	0.079

* A value greater 7.815 indicates statistical significance for this sample set.

4. Concluding remarks

The mechanical properties of perfluorosulforic acid (PFSA) membrane Nafion®112 have been investigated at different humidities and temperatures in a custom-designed environmental chamber. The results show that Young's modulus and the proportional limit stress of the membrane decrease as humidity and temperature increase. Higher temperature leads to lower break stress and higher break strain. However, humidity has little effect on the break stress and elongation at break. The dimensional changes of the membrane at different temperature and humidity are also studied. Membranes at higher temperature experience higher swelling coefficient.

Only a minor, but consistent, difference in mechanical properties was detected between the transverse and machine directions: the Young's modulus, proportional stress and break stress in the machine direction are all larger than those on the transverse direction at the same temperature and humidity. The break strain in the machine direction is smaller than that in the transverse direction. The dimensional change percentage along the transverse direction is larger than that along the machine direction, although the trends are similar.

The statistical analyses show consistent temperature and humidity effects on the membrane mechanical properties: the temperature and relative humidity significantly affect the Young's modulus and proportional limit stress. Additionally, the break stress was significantly affected by the temperature but not the humidity and the break strain was not significantly affected by either the temperature or the relative humidity.

Acknowledgements

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