Elastic Modulus of Poly(ethylene-co-acrylic acid) Copolymers and Ionomers: Effects of Temperature and Relative Humidity

Kathryn Alexis Laney
May 2010

Advisor: Professor Jay B. Benziger

Submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Engineering

Department of Chemical Engineering
Program in Sustainable Energy
Princeton University

This paper represents my own work in accordance with University regulations

I authorize Princeton University to lend this thesis to other institutions or individuals for the purpose of scholarly research

Kathryn Alexis Laney

I further authorize Princeton University to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research

Kathryn Alexis Laney

– To my family, who have supported me throughout it all

All praise, honor and glory belong to my Lord and Savior who has sustained me throughout all of my journeys, including this thesis. I would like to thank all the members of the Benziger group for their guidance and support. I often found myself frustrated and their insight proved invaluable. I would like to acknowledge the McIntosh Senior Thesis funds for their generous support of this work. Lastly, I would like to thank my family and friends. Without their daily infusion of encouragement and love, I know I would not have been able to finish. Thanks!

Abstract

The persulfonate ionomer Nafion is the preeminent membrane used in polymer electrolyte membrane fuel cell applications. Despite the extensive characterization of this polymer, there is still significant uncertainty concerning the interdependence of polymer morphology, mechanical behavior and environmental conditions. In order to better understand the mechanical and transport properties of ionomers such as Nafion, the fundamental interactions between the hydrophobic and hydrophilic domains within such polymers needs to be clarified.

In this work, the amphiphilic copolymer poly(ethylene-co-acrylic acid) PEAA is examined. Using a tensile testing apparatus that carefully controls both temperature and relative humidity, it is possible to ascertain the effect of environmental conditions on the elastic modulus of PEAA. In the acid form, the copolymer modulus monotonically decreases with increasing temperature. However, there is no modulus dependence on relative humidity. By neutralizing the acid group with a sodium cation, significant plasticization effects are observed. The difference in behavior of the acid and salt form of the polymer is attributed to differences in electrostatic interactions. The energy associated with the solvation of the acrylic acid unit is insufficient to overcome the energy required to swell the polymer. This balance between the energy of solvation and swelling corresponds well with trends experienced in Nafion. The behavior of the copolymer sample highlights the importance of the strength of the electrostatic interactions on polymer morphology and mechanical behavior.

Table of Contents

List of Tables

List of Figures

Introduction

Nafion is the preeminent membrane used in polymer electrolyte membrane fuel cell applications. This polymer is composed of a tetrafluoroethylene backbone with perfluoroalkyl ether grafts that are terminated in sulfonic acid groups. [1, 2] The interaction between the hydrophobic backbone and the hydrophilic pendant groups gives Nafion its unique characteristics. Though the polymer has undergone extensive characterization, there is no scientific consensus linking the polymer's structure to its mechanical and transport behavior. Multiple studies conducted by the Benziger group emphasize the influence of environmental conditions, such as temperature and water activity, on the polymer's properties. [2-4] By carefully controlling environmental conditions, these studies have begun to illuminate how temperature and relative humidity combine to influence the microstructural development of Nafion. The examination of other amphiphilic copolymer systems is needed to further elucidate the fundamental interactions between environmental conditions, polymer morphology and mechanical behavior.

The present work examines how the elastic modulus of simple poly(ethylene-co-acrylic acid) (PEAA) copolymers and ionomers changes with respect to temperature and water activity. The elastic modulus, a material's response to small strains, is considered one of the most basic mechanical properties. Furthermore, it has been shown that the modulus affects equilibrium swelling and the absorption of water in Nafion and other ionomer systems.[4] Hence, it serves as a good starting point for understanding how the dynamics of microphase separation within poly(ethylene-co-acrylic acid) respond to environmental conditions. By increasing the knowledge of the physics governing microstructure phase dynamics, it will be possible to better predict and control the performance of such amphiphilic polymers in their end-use applications.

Background

Poly(ethylene-co-acrylic acid) [PEAA] is a carboxylated ethylene copolymer. Primarily produced under the trade names of Nucrel, Surlyn and Primacor, it is synthesized via the high pressure, free radical copolymerization of ethylene and acrylic acid. [5-7] This process results in a highly branched polymer with random placement of the constituent monomers along the backbone. The branched structure of low density polyethylene has been well documented.[8] NMR studies have been used to verify that the hydrogen opposing the acrylic acid group is also subject to backbiting during polymerization, lending itself to branching as well.[6, 9] The structure of the repeating unit of this random copolymer is depicted in Figure 1 below.

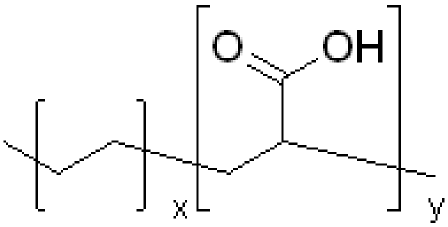


Figure 1: Basic structure of poly(ethylene-co-acrylic acid) polymer

The properties of PEAA copolymers depend strongly on the constituent monomers, ethylene and acrylic acid. Ethylene is a common monomer found in many olefinic polymers. Furthermore, its ordered, symmetric structure allows it to crystallize under appropriate conditions. Composed of only carbon and hydrogen, polyethylene is hydrophobic in nature. While acrylic acid also has a backbone of carbon and hydrogen, the pendant carboxylic acid group enables this polymer to interact with water. However, its pKa value of 4.25 indicates that the acid is relatively weak and only dissociates modestly. Thus while a driving force for separation exists between the ethylene and acrylic acid segments, it is relatively small.

Typically the fraction of acrylic acid present in PEAA is less than thirty weight percent. Depending on the amount of acid units present, substantial changes can be induced in the polymer's mechanical, transport, and thermal behavior.[6, 7, 10]

Effect of Comonomer Content

The incorporation of a comonomer such as acrylic acid into polyethylene has been known to reduce its crystallinity. [6, 8] Although the acrylic acid units are relatively small, they cannot be incorporated into the regular structure of the crystallite regions.[11] They are forced out of the crystal packing and aggregate in the amorphous matrix surrounding the crystals. All other things being held constant, reduction in crystallinity should result in a reduction in the stiffness of the material. Crystalline regions are dense areas where applied stress is distributed over a large number of polymer strands.[8] Therefore, they are much stiffer than rubbery amorphous regions.

However, dynamic mechanical analysis studies conducted at room temperature by Wakabayashi et al. on ethylene methacrylic acid copolymers indicated that increasing the copolymer acid content resulted in an increase in the elastic modulus at all weight percents > 6%. [6] Such behavior was attributed to changes in the amorphous phase glass transition temperature. The acid homopolymer has a higher glass transition temperature than the polyethylene homopolymer. Using the Fox equation to relate the composition to the mixture properties, it is expected that the incorporation of small amounts of acid will raise the T_g of the resulting copolymer above that of the ethylene homopolymer. When the T_g is raised sufficiently above room temperature, the amorphous region is still in the vitrified state during modulus testing at room conditions, which increases stiffness.

Earlier studies by Otocka and Kwei emphasized that the incorporation of acrylic acid increased the T_g beyond what could be expected using the traditional Fox equation.[11] They concluded that the existence of acrylic acid dimers provides effective crosslinks which further reduce the mobility of neighboring chains. These "crosslinks" are secondary interactions between polymer chains due to hydrogen bonding. Using FTIR studies, Otocka demonstrated that there are relatively few monomeric or free carboxyl groups at temperatures below 50°C, suggesting that all acid groups are dimerized within the sample at room temperature. Figure 2 depicts an ethylene-acrylic acid dimer. The fact that the bonding equilibrium was undeterred by the melting of the crystalline phase confirmed that these interactions occur solely within the amorphous region.

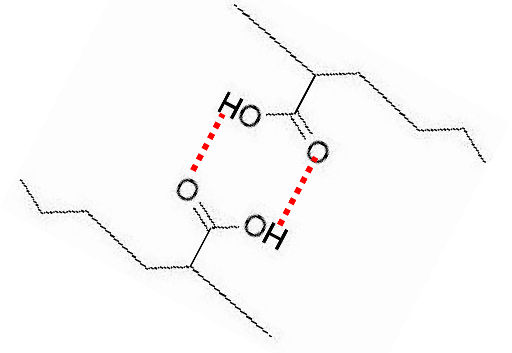


Figure 2: Dimer interaction in PEAA The carboxylic acid groups in PEAA form dimers at temperatures below 50°C. These interactions effectively link two chains together via hydrogen bonds.

Effect of Neutralization

Neutralization is a process in which the acidic proton is exchanged with a metal cation resulting in the formation of a salt. Originally, the term ionomer was reserved for amphiphilic copolymers containing acid functional groups that had been neutralized.[5, 7] Currently the term is used to describe any polymer that behaves in an ionic fashion in a humidified environment. Nafion, for example, is often referred to as an ionomer regardless of whether the polymer is in the acid or salt form (proton or metal cation respectively). This is due to the fact that the sulfonic acid ionizes in the presence of water. On the other hand, poly(ethylene-co-acrylic acid) has a pKa of 4.25 making it a weak acid. It only behaves in an ionic fashion when neutralized. Therefore, the term ionomer is used exclusively in reference to the neutralized form of PEAA whereas copolymer is used to refer to the acid form.

The necessity of the distinction arises from the difference in the strength of bonding. Ionic bonds are much stronger than hydrogen bonds; thus the ionic aggregates have a greater effect on the mechanical properties of amphiphilic copolymer systems.[5, 7] The influence of the respective intermolecular bonds on the mobility of neighboring chains clearly displays the difference in bond strength. Fourier Transform Infrared (FTIR) studies of PEAA copolymers have shown that hydrogen bonds alter the packing of crystalline polyethylene region causing a shift from stable orthorhombic to the distorted monoclinic structures.[12] This distortion decreases the regularity of the crystalline region, lowering its melting point and decreasing its stability. In low acrylic acid content samples, the primary crystallites are estimated to be on the order of 10 nm thick.[10, 15, 16] As the content of acrylic acid increases, the lamellar structures decrease in lateral extent. However, the same concentration of ionic bonds can depress the formation of crystals all together.[13, 14]

Despite the fact that the crystalline phase has an elastic modulus nearly three orders of magnitude higher than the amorphous phase, neutralization has been shown to stiffen the overall sample. [11] Similar to the previous discussion of copolymer samples, the stiffening effect has been attributed to the increase in the amorphous phase glass transition temperature. However, the observed increase is larger because the ionic bonds hinder chain mobility to a greater extent.

The ionic groups also induce a microphase separation between the hydrophilic and hydrophobic domains in the ethylene acrylic acid ionomers. This separation is caused by electrostatic interactions between the charged ions embedded in a low dielectric constant, polyethylene matrix. [10, 14, 17, 18] Small angle x-ray scattering studies, along with electron microscopy, have shown that the ion rich domains in poly(ethylene-co-acrylic acid) sodium ionomers self assemble into aggregates.[13, 15, 19] Taubert et al. used scanning transmission electron microscopy to define three distinct regions in sodium neutralized ethylene methacrylic acid ionomers: featureless regions, small aggregates ~2nm-15nm in size, and large clusters ~20nm-160nm.[19] Such differences in the aggregate size could not be distinguished in SAX imaging which showed one uniform peak for the isotropic collection of aggregates.[18] No such aggregates have been observed in the acrylic acid copolymer samples suggesting that the hydrogen bond dimer interactions shown in Figure 2 are the primary intermolecular attractive force.

Thermal Transitions

Thermal transitions of ethylene acrylic acid and similar polymers have been extensively studied. Using differential scanning calorimetry and dynamic mechanical thermal analysis, the melting temperature of primary crystallites has been determined and corroborated by numerous studies. [6, 10, 11, 13, 14] For 5 weight percent PEAA copolymers, the primary melting temperature is ~100°C. Increasing the acid content to 20 wt% decreases the peak melting temperature to ~75-80°C.

Transitions occurring below this primary crystallite melting temperature are more controversial, however. A low temperature endotherm near ~45°C has been observed by DSC and DMTA. Wakabayashi et al. attributed this second relaxation to the melting of "secondary crystallites" that form during storage at room temperature.[10, 16] They posit that these secondary crystallites are composed of polymer chain segments that were unable to pack into the primary crystal structure during initial crystallization. In other studies, this endotherm near 45°C has been attributed to the dissociation of hydrogen bonds. In FTIR spectrometric studies, bands for free carboxyl groups are initially observed ~50°C.[11,12, 20]

In partially neutralized samples, the thermal analysis also shows a transition in the 45-50°C range. The transition is attributed to an increase in T_g caused by the ionic/acid clusters.[14, 21] As the degree of neutralization increases, the carboxylic/ionic functional groups begin to phase separate. Lacking these mobility hindering linkages, the T_g of the ion-free amorphous phase is lowered and approaches that of the polyethylene homopolymer. However, a separate transition temperature associated with breaking apart the ionic clusters arises. Saturated with the strong salt-salt and salt-acid linkages, this transition temperature is much higher than the original copolymer T_g. The fact that the T_g of samples fully neutralized with Na^+ only increased modestly above those that were 30% neutralized suggests that unneutralized acid groups tend to associate with the ionic aggregates.[6, 22] Khanna's work showed that for sodium neutralized PEAA with 7 mol% acrylic acid, the upper T_g was ~ 40°C.[21]

Water Sorption

Studies performed by Kutsumizu on the sorption dynamics of ethylene methacrylic acid sodium neutralized ionomers revealed that when relative humidity approaches 30% a solution sorption isotherm is observed.[23] They suggested that at this level of humidity water molecules are incorporated into the inside of the clusters. For relative humidity < 30%, a Langmuir isotherm is present suggesting that any water present is simply adsorbed on the outside of the ionic clusters. FTIR imaging done in that study concluded that three water molecules are needed to hydrate one ion pair. Their x-ray scattering work suggested that the number of ionic clusters and the number of ionic multiplets per cluster seemed unchanged with hydration. Furthermore, it showed that individual ion pairs hardly dissociate in the presence of water.

Experimental Section

Materials

Poly(ethylene-co-acrylic acid) copolymers with 5 and 20 weight percent acrylic acid content (PEAA-5H and PEAA-20H, respectively) used in this study were obtained from Sigma Aldrich. The acid content was determined by the manufacturer via titration as per the ASTM D2708 standard. Table 1 lists the physical properties of the respective samples as well as thermal transitions as determined in previous studies. Tetrahydrofuran with BHT stabilizer and xylene solvents were obtained from Fischer Scientific and used as received. The 1M sodium hydroxide and 1M sulfuric acid solutions used to wash samples were prepared from standard stock solutions.

Table 1: Physical properties of poly(ethylene-co-acrylic acid) copolymer

Sample	Mol % Acrylic Acid	Equivalent Weight (g/mol AA)	Crystalline Volume Fraction (25°C)	T_g (°C)	T_i (°C)*	T_m (°C)
PEAA-5H	2.0	1441	0.37	4[a], 12[b]	<39[d]	108
PEAA-20H	8.9	360	0.14	1[c], 24[a]	40[d]	77[a], 85[c]

* T_i = intermediate transition temperature as observed via previous imaging and calorimetric studies
a Wakabayashi [11] b Otocka [6] c Nuño-Lucas [20]
d Based off of approximations from similar weight percent, polyethylene methacrylic acid copolymers and ionomers in a Wakabayashi study

Film Preparation

Films of PEAA-5H were prepared by dissolving polymer pellets in xylene (5v/v%) at 80°C for 45 minutes with intermittent agitation. Samples were immediately cast in a Petri dish at 80°C in an oven with dry nitrogen flow. Solvent removal was allowed to occur for at least 12 hours under aforementioned conditions before films were removed from dish with razor blade. Samples were vacuumed dry at a temperature of 80°C. Solvent removal was considered complete when sample weight change was no longer appreciable (< 0.0004 g/hr). A more detailed explanation of the solvent casting procedure is provided in the Appendix: Casting.

PEAA-20H samples were prepared with a similar solvent casting procedure. Polymer pellets were dissolved in tetrahydrofuran at room temperature with continuous agitation. Solution was immediately cast in ~55°C oven with dry nitrogen flow. Solvent was evaporated for at least 12 hours under aforementioned conditions before films were removed from dish with razor blade. In order to ensure complete solvent removal, films were placed in vacuum oven at room temperature until sample weight change was no longer appreciable.

Figure 3 depicts the poly(ethylene-co-acrylic acid) films resulting from the respective casting procedures. Both PEAA-5H and PEAA-20H films were macroscopically uniform. The translucent appearance of the PEAA-5H films is likely indicative of its modest degree of crystallinity. The crystalline regions have a different refractive index than the amorphous region causing light to scatter. [8] On the other hand, PEAA-20H is transparent. This suggests that the polymer has very small crystallites and/or a significantly lower degree of crystallinity.

Resulting films were on average 0.006" thick after complete removal of solvent. However, the uneven nature of the dish bottom resulted in variations in the film thickness.[a]

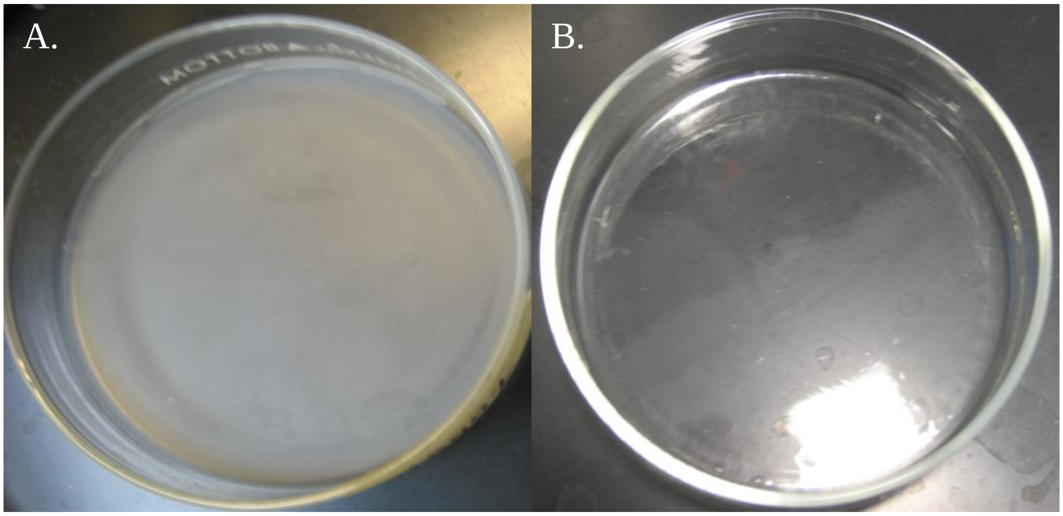


Figure 3: Photographs of prepared PEAA films in the petri dish molds A) The translucency of PEAA-5 is indicative of its modest degree of crystallinty B) The transparency of PEAA-20 indicates its reduced crystalline volume fraction. Due to the sample's optical properties, environmental elements (i.e. overhead lighting, shadows and scratches in benchtop) can be seen on film surface.

Following casting, both copolymer samples were cleaned and treated. Due to the relatively low melting point of the polyethylene crystallites, the standard procedure of boiling films in solution[2, 3] had to be slightly modified in order to prevent sample deformation. All solution temperatures were reduced to ~55°C, and the samples were heated for twice the standard time in order to compensate for the reduction. The cleaning procedure for the films was as follows: heat for 2 hours in hydrogen peroxide at 55°C, heat for 2 hours in deionized water at 55°C, heat for 2 hours in 1M sulfuric acid at 55°C, rinse twice for 2 hours in deionized water at 55°C. Ionomer (Na^+ neutralized) samples were prepared by rinsing the original copolymer in 1M NaOH as opposed to sulfuric acid in the third step listed above. When neutralizing other amphiphilic copolymers such as Nafion, the use of a simple aqueous salt solution has proved adequate. However, due to the weak nature of acrylic acid

---

[a] See Appendix: Casting for further discussion

group, it was necessary to use a strong base in order to exchange cations in PEAA. The resulting films were then placed between filter paper and dried on the laboratory bench under the weight of several books. Upon drying to ambient conditions, the samples were cut into strips approximately ¼" wide using a template and a razor blade.

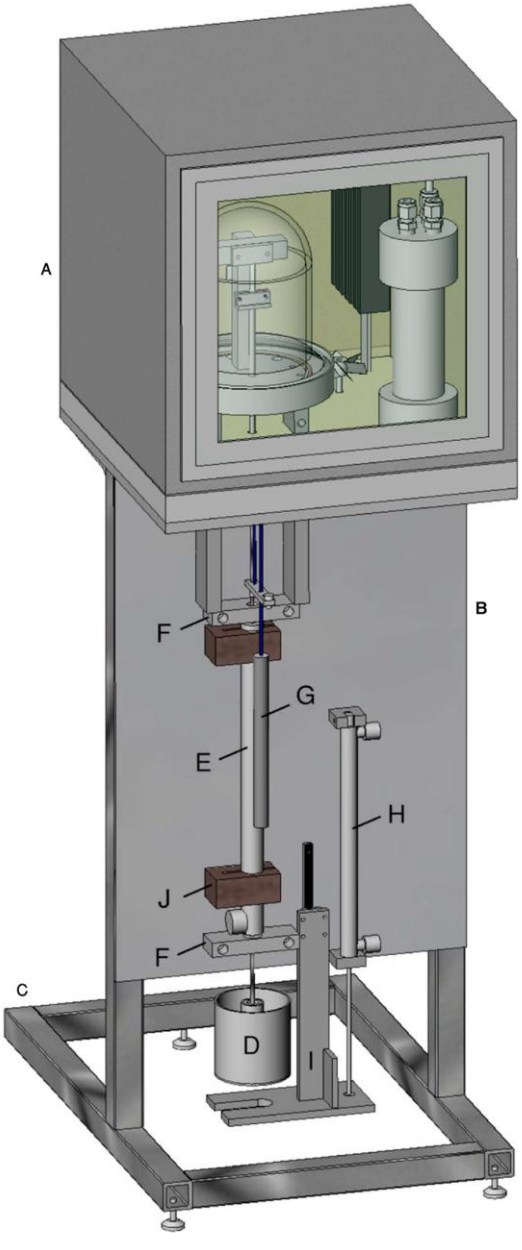


Figure 4: Schematic of tensile testing apparatus. The environmental chamber (A above) allows for the simultaneous controlling of temperature and relative humidity during viscoelastic testing. Source: Majsztrik [24]

Experimental Apparatus

While commercial instruments exist that enable the mechanical characterization of materials over a broad range of temperatures, relatively few are available that also control relative humidity. An instrument for environmental control of temperature and relative humidity during viscoelastic mechanical testing was designed specifically for this purpose by Paul Majsztrik. Figure 4 shows the schematic for said instrument.[24] A sample approximately 1 inch in length is mounted in a stationary upper and variable lower clamp. Stress is applied uniaxially by hanging a mass from a rod connected to the lower clamp. The strain caused by the imposed stress is measured by a linear variable displacement transducer (LVDT). The LVDT is a transformer that measures changes in voltage due to the movement of the LVDT core. The change in voltage can be used to ascertain the sample length (within ± 0.0003 in). However, direct contact is not made with the sample. Guides and universal joints are used to ensure proper alignment of the rod and mass. A sliding stage, mounted on a guide rail, is used to apply and remove the mass from the sample.

The controlled environmental chamber consists of an insulated box with viewing window and an inner chamber (Pyrex vessel) that directly encloses the sample. A finned heater, fan and PID temperature controller are used to create an isothermal environment around the inner chamber.[b] Humidity is established in the inner chamber by flowing dry N_2 gas and humidified N_2 gas from a bubbler into the chamber in the desired ratio. A dual humidity and temperature sensor (Sensirion, SHT75) is used to measure the environmental conditions within the inner chamber. A Labview program records the length of the sample as well as the temperature and relative humidity of the inner chamber in real time. Data are acquired every second for the first 20 minutes and once every minute after that.

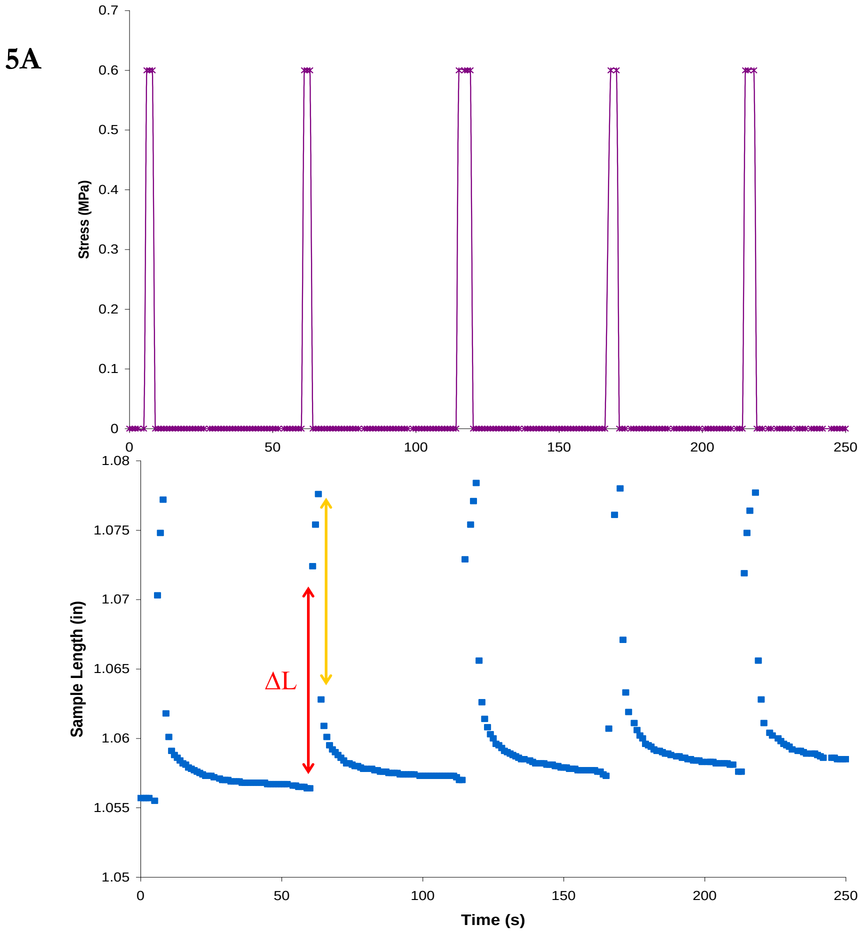
Instantaneous Elastic Modulus

The elastic response of the PEAA films was measured as a function of water activity at various temperatures. At a given temperature, measurements were started with a film that had been dried in-situ. Water activity was increased incrementally by using a mixture of dry N_2 feed and a humidified N_2 feed passed through a bubbler. By varying the ratio of these feeds, relative humidity ranging from 0 to 95% was achieved. The length of the film was monitored during the equilibration with the surrounding vapor. Films were considered to be in equilibrium when the sample length changed < 0.004 in/hr.

---

[b] Due to the offset of the PID controller, the observed temperature of the chamber was frequently 1-2°C below the set point value. Throughout this work the setpoint value will be cited.

With the film in equilibrium with its environment, a mass was lowered to apply a constant stress and removed after ~2-3 seconds. After approximately 1 minute of unstressed state, the mass was reapplied to the sample. The stress was cycled on and off five times for every temperature and water activity. Figure 5 shows a representative diagram for this procedure.



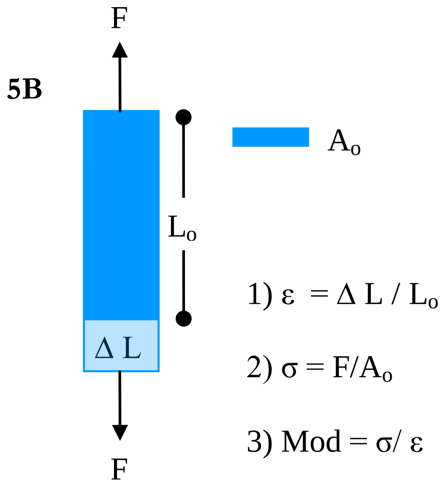


Figure 5: Strain response to cyclic stress during elastic modulus test A) Response of PEAA-20Na at 60°C, 90% RH to 75 g applied load. Sample thickness was 0.007". The red bar indicates change in length in response to the applied load and the yellow corresponds to change in length with load removal. B) Schematic of sample dimensions used to calculate elastic modulus. Engineering measurements use the initial dimensions of the material to calculate stress and strain as opposed to the true values.

The elastic regime for most thermoplastics is observed at strains < 5%. The applied load was selected to ensure that the largest relative humidity range at a given temperature would be within this elastic response range. Strain measurements were recorded every second. The elastic modulus was defined as the engineering stress divided by the engineering strain. Table 2 lists the numerical value of the modulus measurements for the test depicted in Figure 5. Samples did not always return to their initial length after load removal as illustrated, which is indicate of viscous losses. Due to these losses, the modulus values associated with the removal of the load are always higher than those corresponding to load application. Modulus measurements listed hereafter correspond to load application unless otherwise specified.

Table 2: Modulus measurements for application and removal of load

	Load Application		Load Removal	
Cycle	Strain (in/in)	Modulus (MPa)	Strain (in/in)	Modulus (MPa)
1	0.018	33.47	0.015	41.52
2	0.017	36.53	0.014	43.20
3	0.016	37.28	0.012	49.95
4	0.015	41.52	0.014	43.49
5	0.015	40.60	0.014	42.91
Average	0.016	37.201	0.014	44.540

Results and Discussion

In-situ Drying

Prior to modulus testing, all of 20 wt% copolymer samples were dried in-situ without a load applied. Dry nitrogen was fed into the environmental chamber until 0% relative humidity was achieved. The temperature was then increased to 60°C. Samples were dried for ~3 hours (including ramp time) before the temperature of the environmental chamber was adjusted to the desired testing condition. The sample length during the drying step is depicted in Figure 6. The temperature profile within the inner is also shown for reference.

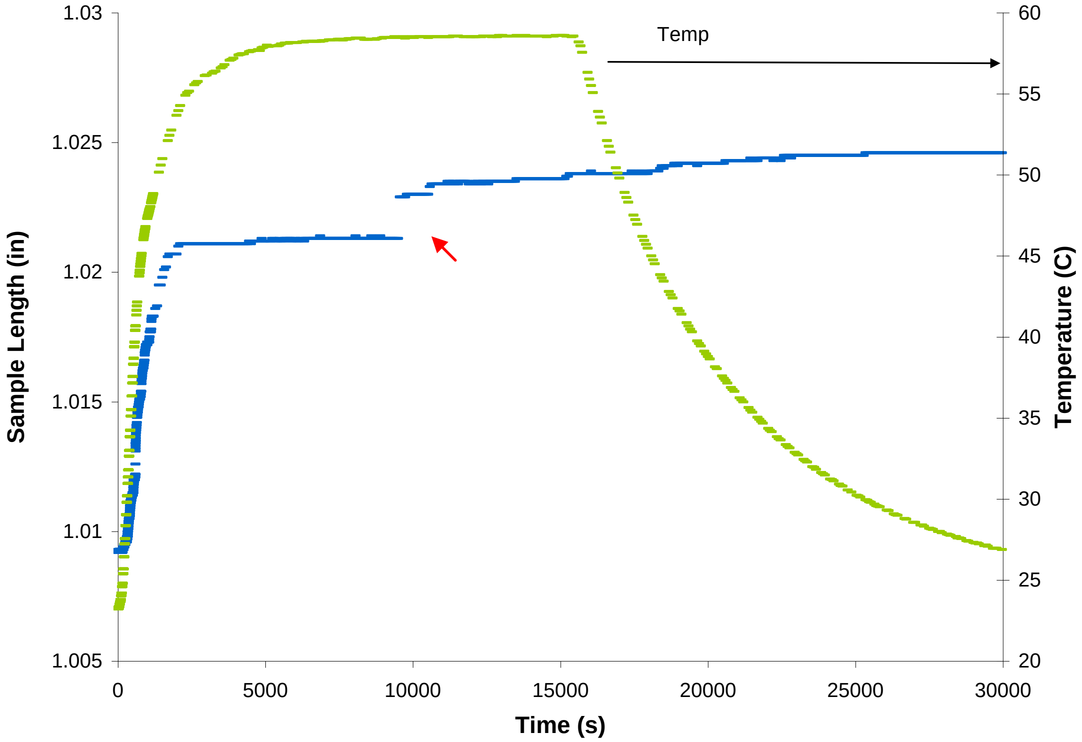


Figure 6: Length of PEAA-20H sample during in-situ drying All samples dried in-situ at 60°C, 0% relative humidity without an applied load. Red arrow highlights the occurrence of the instantaneous jump possibly due to sample necking.

The length of the sample immediately increases as the temperature rises in the chamber. When the temperature approaches its set point value, the rapid change in length slows and ceases approximately 2000s into the drying procedure. During this initial rise, the sample strains ~1.2% of its original length. The sample length remains constant for nearly 7200s and appears to be in equilibrium. However, an abrupt change occurs at ~10000s (indicated by red arrow in Figure 6). In less than one minute, the sample length increases by 0.002”, which increases the observed strain by 15% almost instantaneously. Approximately 40% of the PEAA-20H samples showed similar discontinuities in sample length change during the in-situ drying procedure. The samples appeared to be in equilibrium before these events and achieved slightly higher steady state values almost immediately thereafter.

It is unknown what causes these sudden increases in sample length, but a likely explanation is necking. Necking is a yield behavior in polymers that results from shearing or slipping of polymer segments past one another.[25] The copolymer microstructure can be roughly divided into three domains: a crystalline lamellar region, an amorphous region containing functional groups and a functional group-free amorphous region. It is often assumed that 60°C is sufficiently below the primary crystalline melting point that primary crystallites are still largely intact.[10] Furthermore, 60°C is substantially above all reported glass transition temperatures; hence, the amorphous region should be fully relaxed. If one assumes the existence of secondary crystallites, all such units should also be melted at the in-situ drying temperature.[10] Thus at 60°C, the polymer morphology can be reduced to crystalline lamellae connected by a relaxed amorphous region with randomly distributed acrylic acid dimers.

Given this depiction, the resulting phenomenon is likely a result of chain slipping within the amorphous region. At room temperature, intermolecular hydrogen bonds are strong enough to serve as effective crosslinks between chains. These links prevent large scale chain slipping from occurring. However, as the temperature increases, there is enough thermal energy available to disrupt the hydrogen bonds holding dimers together. Free hydroxyl groups (indicating the dissociation of acid dimers) have been observed in infrared studies of PEAA copolymers at ~50°C.[11,12] The dissociation of acid dimers reduces the intermolecular chain interactions enabling shearing to occur. It should be noted that actual macroscopic necking was never observed in the polymer samples during the drying procedure. Examination of samples with polarized lenses after testing revealed that several specimens had small regions of chain alignment close to the clamp positions.

PEAA-20Na ionomer samples were dried under the same in-situ drying conditions. Figure 7 depicts the change in length of an ionomer sample during the drying procedure. As with the copolymer sample, the length increases as the temperature is ramped to its set point value. However, no instantaneous jumps in the sample length are observed once equilibrium is reached. Interestingly, ionomer samples retract upon cooling as shown by the reduction in sample length after times greater than 10000s. Such behavior was not observed in PEAA-20H samples.

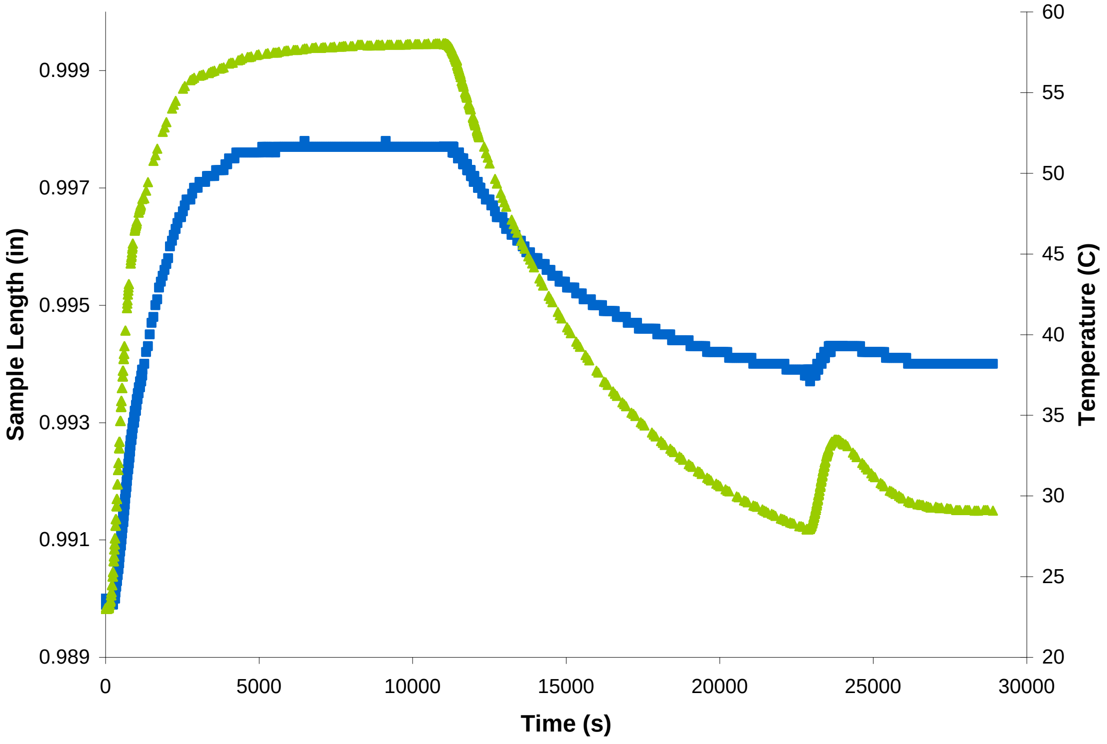


Figure 7: Length of PEAA-20Na sample during in-situ drying All samples were dried in-situ at 60°C, 0% relative humidity with no applied load. Ionomer samples experienced a "reversible" thermal expansion not observed in parent copolymer equilibration.

In the copolymer sample, the amorphous phase was fully relaxed at 60°C. However, this is not necessarily the case for the ionomer. As aforementioned, the neutralization of the copolymer species results in the segregation of the amorphous domain into amorphous polyethylene regions and ionic aggregates (containing both salt and unneutralized acid groups). The aggregates essentially serve as nodes due to the strong bonding interactions. As the temperature is increased, thermal energy enables the amorphous region surrounding the clusters to uncoil and reptate. However, the presence of the clusters preserves some of the material's memory. When the temperature is reduced, the chains retract in a somewhat elastic fashion. Dynamic mechanical analysis conducted by Khanna et al. identified 40°C as the upper transition temperature for the ionic aggregates in a partially neutralized 7 mol% ethylene acrylic acid ionomer.[21]

Due to the differences in weight percent of functional groups, degree of neutralization and molecular weight of samples used, the transition temperature of the 20 wt% polymer studied herein is likely higher. As such, a large fraction of ionic clusters may be intact at the 60°C drying temperature. The fact that reducing the temperature to initial conditions does not result in the sample returning to its original length indicates that 1) some of the clusters may be disrupted and 2) the interactions are not completely elastic in nature.

Swelling Dynamics

After drying at 60°C, the temperature of the environmental chamber is changed to the desired testing temperature. The rise in temperature that occurs at ~22500s in Figure 7 depicts such a change in set point. Samples were allowed to stabilize at the testing temperature before humidity was increased. Typical equilibration times for water uptake were 60-240 minutes. Figure 8 shows the swelling curves obtained for the 20 wt%

copolymer and ionomer samples at 23°C, 10 and 90% RH. It is clear that with the exception of the Na^+ neutralized ionomer at high relative humidity, polymers swelled negligible amounts during the equilibration period. Previous studies performed on Nafion assumed that when the change in sample length was < 0.004 in/hr (strain rate less than ~0.025/hr) the samples were sufficiently equilibrated.[3] Under this assumption, one hour is ample time for equilibration for many of the copolymer samples studied herein. Nevertheless, samples were generally allowed at least 90 minutes to equilibrate even if the change in length was negligible.

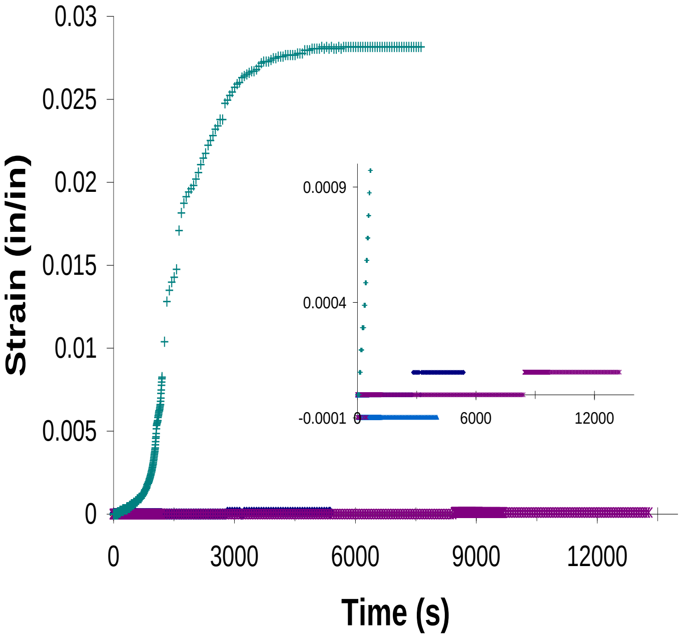


Figure 8: Equilibrium swelling curve for PEAA-20H and PEAA-20Na samples at 23°C, 10%RH and 90%RH
●- H^+ 10% RH. ●- H^+ 90% RH. ●- Na^+ 10%RH ●- Na^+ 90%RH. The only sample to show appreciable swelling is the PEAA-20Na at 90% relative humidity. The inset is provided to show that any change in length in the other three samples is miniscule. No load was applied during sample equilibration.

It is possible that swelling dynamics are enhanced at time scales >> 3600-7200s. However, no experiments were done to examine these long time equilibration ranges. The behavior of the copolymer samples in other moist environments suggests that the change will be small. Copolymer membranes did not swell appreciably even when immersed for several hours in heated aqueous solutions during the aforementioned cleaning procedure. Crude absorption studies on the parent copolymers were performed in order to get a sense of the rate of water uptake. Films were immersed in water and weighed periodically to observe change in mass. Excess water clinging to polymer surface upon removal from water bath was gently wiped away prior to mass measurements. Table 3 lists the results. Sample weight did not change appreciably for either PEAA-5H or PEAA-20H during this testing. It should be noted that the polymer specimens used for the tests were samples that had been precut for use in tensile testing experiments and had starting weights on the order of 10 mg. Therefore, given the precision of the scale, the listed changes are within the instrument's margin of error. Nevertheless, the results do show that even after extended periods of time the amount of water absorbed is < 1% of the sample's original weight.

Table 3: Preliminary water sorption studies of copolymer samples

Cumulative Immersion Time (hr)	Average % Wt Change PEAA-5H	Average % Wt Change PEAA-20H
0	0.00	0.00
12.5	0.06	0.06
26.5	0.00	0.41
39	0.37	0.59
119.5	0.18	0.65

The ionomer samples on the other hand have a much greater affinity for water sorption. Figure 9 shows the linear expansion of the PEAA-20Na$^+$ ionomer as a function of relative humidity at various temperatures. In this plot, the linear expansion at X% RH is defined as the strain incurred in going from the equilibrium sample length at 0% RH to the equilibrium length at X% RH.

$$Expansion = \frac{\sum_{0\%}^{x\%} L(X\%)_{equil} - L(X\%)_{initial}}{L(0\%)_{equil}}$$

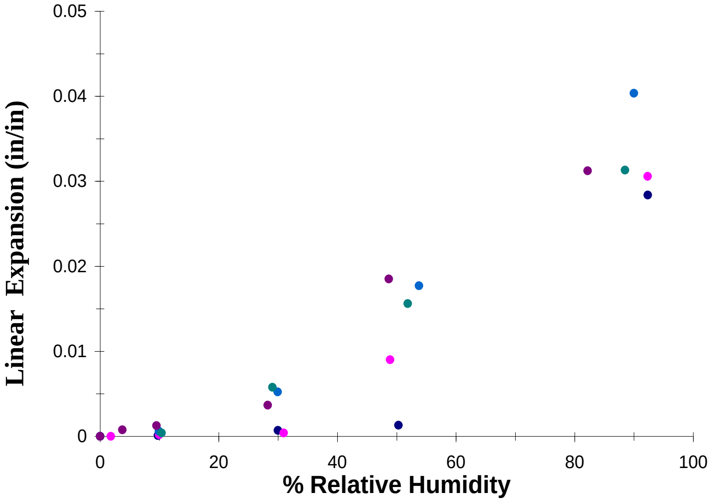


Figure 9: Linear Expansion of PEAA-20Na$^+$
●-23°C ●-40°C ●-50°C ●-60°C ●-72°C
The expansion of the 20 wt% ionomer is strongly influenced by relative humidity

The response to humidity follows the same general trend at all temperatures suggesting that water absorption is the dominant swelling mechanism. However, the graphs do not collapse completely. At low relative humidity (0-10%) all of the curves show negligible expansion. At 30%, the upper temperatures (T > 40°C) begin to expand at a faster rate. This differential is further magnified at 50% RH where the linear strain at 40°C rapidly increases. In going from 50→90%, the linear expansion at 23°C increases by over an order of magnitude. Thus by 90%, the linear expansion at all temperatures is roughly comparable.

The temperature dependent expansion behavior could be the result of inadequate equilibration times. Studies performed on Nafion showed that time > 100000s may be needed for complete equilibrium to be reached. Long time equilibration of the lower temperature runs should be conducted in the future in order to examine this possibility.

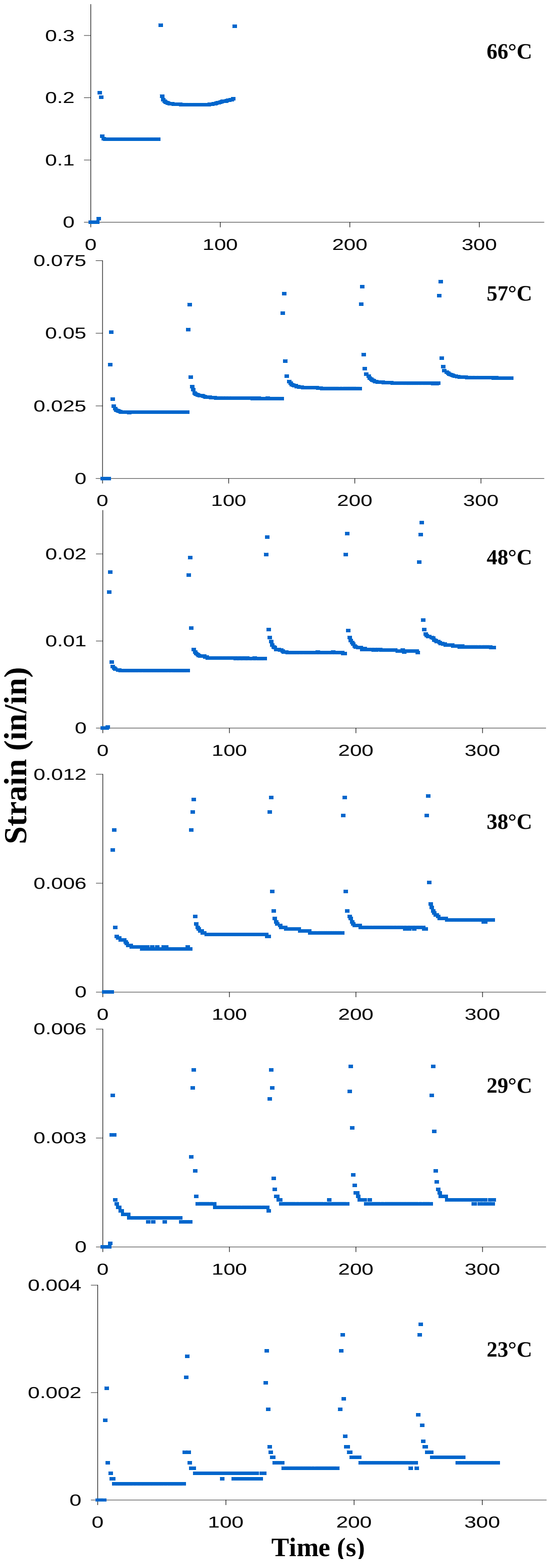


Figure 10: Strain response of PEAA-20H from 23-66°C, 0%RH As the temperature is increased, the elastic strain increases as well as the amount of viscous losses. Load applied for all Temp = 25 g. Sample cross sectional area = 0.96 mm^2

Elastic Modulus

After equilibration at the respective environmental conditions, the elastic modulus was tested with the cyclical stressing method detailed previously. In order to strictly examine temperature induced changes, a series of dry elastic modulus measurements were made. A single sample was dried in-situ, and modulus testing was commenced at 23°C, 0%RH. The set point temperature was then raised, and the sample was allowed to equilibrate before new modulus testing began. In this way, a series of consecutive modulus tests from 23°C→60°C was conducted. Figure 10 shows the strain response curves obtained from this procedure.

All curves in Figure 10 were generated using a 25g load. The curves clearly indicate that as the temperature increases, the polymer's strain response to applied stress increases (that is, its stiffness is reduced). The response to the applied load remained within the small strain regime for all temperatures examined with the exception of the 66°C run. During the 66°C modulus test, the sample strained nearly 30% of its original length far exceeding the elastic small strain range. After the third stress cycle, the sample failed to respond to the removal of the applied load and rapidly crept to failure. It is possible that reducing the test load may enable additional measurements to be made at elevated temperature ranges. However, at temperatures above 70°C, the polyethylene crystals begin to melt. The melting of these crystals significantly decreases the stiffness of the PEAA-20H resulting in the mechanical failure of the sample even under negligible loads.[c]

The viscous losses incurred during testing are also evident from the fact that the sample length does not return to its original length with the removal of stress. As the temperature is increased from 23°C to 66°C, the losses increase several orders of magnitude (~0.0001 in/in at 23°C → >0.1 in/in at 66°C). This behavior is observed in many thermoplastic polymers. Thermal energy increases the polymer chain motion making it easier for the polymer to disentangle. The losses experienced in these samples were relatively small and may have been recovered with additional relaxation time. Extensive creep response studies need to be conducted in order to further examine the time-dependent relaxation behavior of the polymer with respect to environmental conditions.

---

[c] See Appendix: Melting for further examination of creep failure at elevated temperatures

Figure 11 depicts the elastic modulus measurements derived from the trials shown in Figure 10. In going from room temperature to 40°C, the modulus decreases over 70%. From 40°C to 60°C, the modulus continues to decrease but the temperature dependence is reduced. This leads to a change in slope of the modulus versus temperature curve is observed. This change suggests a transition within the polymer microstructure. The observed behavior may be attributed to any one or a combination of the following mechanisms: the relaxation of amorphous regions, the disruption of functional group clusters, the melting of secondary crystallites or some combination there within. As discussed earlier, several thermal transitions have been identified in this temperature range making it difficult to conclusively ascribe a cause to the observed transition.

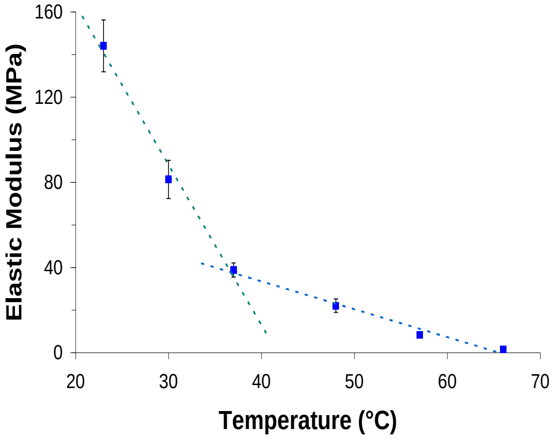


Figure 11: Instantaneous elastic response of PEAA-20H from 23-66°C at 0% RH Modulus measurements for the strain responses depicted in Figure 10. Two nearly linear regions in the elastic modulus are observed suggesting the occurrence of a morphological transition.

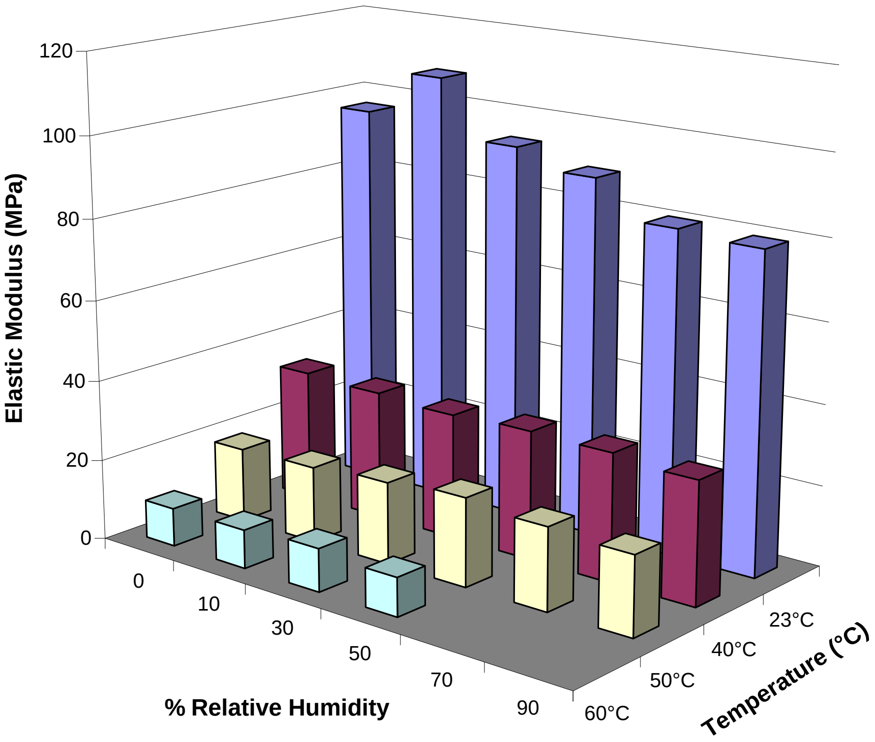


Figure 12: Elastic Modulus of PEAA-20H as a function of relative humidity and temperature. 23°C modulus testing was performed with 25 g load. All others used 14.5 g load. Average cross-sectional area of the four samples was 1.03 mm2 ± 0.1. Data points are missing for 60°C, 70% and 90% RH because samples mechanically failed under these test conditions.

The effect of water on the mechanical behavior of the PEAA-20H sample was also examined. Figure 12 shows the elastic modulus of the copolymer as a function of temperature and water activity. Following the modulus as a function of water activity at a constant temperature, it is clear that plasticization is negligible. The profile at 23°C appears to show some plasticizing effect with the modulus decreasing from 96 MPa under dry conditions to 79 MPa at 90% RH. However, this is within the ± 10% margin of error as determined by multiple modulus tests and is not believed to be significant. In contrast, a monotonic reduction in stiffness is always observed by increasing the temperature at a given relative humidity. The fact that water has a negligible effect on the elastic modulus of the copolymer sample highlights how the weak electrostatic nature of the acrylic acid group affects the morphological behavior of the polymer.

The modulus measurements of PEAA-20H at 60°C and relative humidity > 50% were unattainable due to sample failure. As mentioned previously, the melting of the crystalline region results in a significant decrease in the polymer's mechanical stability. It seems that prolonged exposure to temperatures slightly below the peak melting point could also results in creep failure of the PEAA-20H sample. Because the response to relative humidity is tested sequentially, by the time modulus testing for 60°C, 70% RH begins, the sample has been in a high temperature environment for > 25,000s. The decreased effectiveness of the hydrogen bonds at elevated temperatures has already been discussed. If the crystalline structure also begins to weaken, the mechanical integrity of the specimen is greatly compromised. The application of the load is enough to elicit viscous creep. Similar to the 66°C, 0% RH strain response curve shown in Figure 10, 70% RH samples at 60°C failed to respond to the removal of stress during the modulus test and crept until failure. The mechanical failure of samples during 70% RH testing prevented the examination of sample properties at 90% RH.

The elastic response to environmental conditions of the 20 wt% poly(ethylene-co-acrylic acid) Na^+ ionomer was much more dynamic. Figure 13 shows the elastic modulus of PEAA-20Na as a function of temperature and relative humidity. Following the modulus as a function of humidity at a constant temperature reveals the significant plasticization effects of water. By increasing the relative humidity from 0% to 90% at room temperature, a 10 fold reduction in the modulus is observed. Similar trends occur at all temperatures examined. Interestingly, the plasticizing nature of water only manifests itself at relative humidity $\geq$ 30%. Below this value, the elastic modulus seems to be independent of humidity.

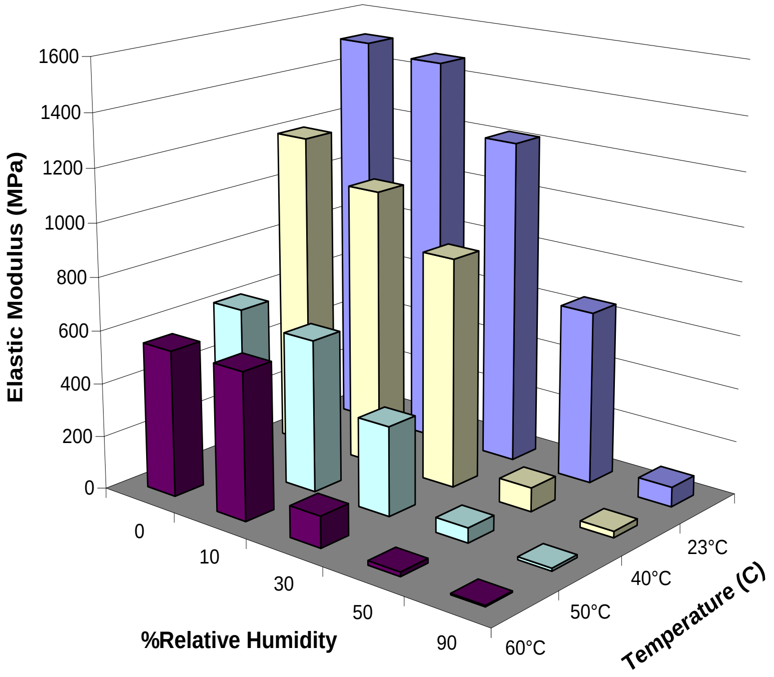


Figure 13: Elastic modulus of PEAA-20Na as a function of temperature and relative humidity All modulus tests performed with 75 g load. Average cross-sectional area of the four samples used was 0.89mm^2 ± 0.1. The linear expansion information depicted in Figure 8 corresponds to the equilibrium swelling observed in these samples. The strain response of the dry 23°C and 40°C was very close to the machine's margin of error; therefore, the numerical values may be artificially high. Nevertheless, the trends are still applicable

In order for water to be accommodated within the hydrophilic ionic domains, the polymer must swell. The reduction in the elastic modulus as the relative humidity increases indicates that this swelling results in the reduction of the polymer stiffness. At moderate temperatures, the ionic clusters can be modeled as crosslinks in the amorphous matrix. Bonds between polymer chains are disrupted as water swells the cluster. Therefore, solvation effectively decreases the crosslink density resulting in greater chain mobility and a decrease in stiffness.

The temperature dependence of the linear expansion curves may also be a result of differences in ionic cluster bonding at various temperatures. As the temperature is increased, the clusters will be thermally driven to expand. This expansion should enable water to be taken up more quickly because less energy is needed to swell the ionic domains. The fact that water has such a marked effect on the ionomer compared to its negligible influence on the copolymer suggests that the nature of the electrostatic attraction has a strong impact on the observed morphological and mechanical behavior of PEAA samples. According to estimates based off of pKa values, the free energy of solvating the sodium-carboxylate is over an order of magnitude higher than the solvation energy associated with solvation of the acid. This difference is a result of the ionic bonding in the former.

Figure 13 also highlights the influence of temperature on sample stiffness. By increasing the temperature at any fixed relative humidity, a monotonic reduction in elastic modulus is observed. While increasing the temperature of the dry copolymer sample from 23°C to 40°C resulted in a 70% decrease in the elastic modulus, the decrease observed in the ionomer sample is only 20%. Again, much of the difference can be attributed to the ionic bonds. As aforementioned, salt-salt, salt-acid, and unneutralized acid groups aggregate into ion rich regions that have a higher transition temperature. At 40°C, the ionic aggregates are still largely in a vitrified state, which increases the overall polymer stiffness.

Due to brittleness, the 5 weight percent copolymer samples were not dried in-situ. Figure 14 shows the elastic modulus profile for samples that were tested after drying under vacuum at 80°C until sample weight change was negligible. The behavior of the PEAA-5H polymer is very similar in characteristic to the 20 wt% copolymer. Because samples with such different acid content behave in a similar manner under the conditions examined, it suggests that the properties of acrylic acid group itself are responsible. The small amounts of energy released when water solvates acrylic acid is insufficient to swell the polymer; therefore, water cannot disrupt the intermolecular interactions and the modulus profile with respect to relative humidity remains relatively flat.

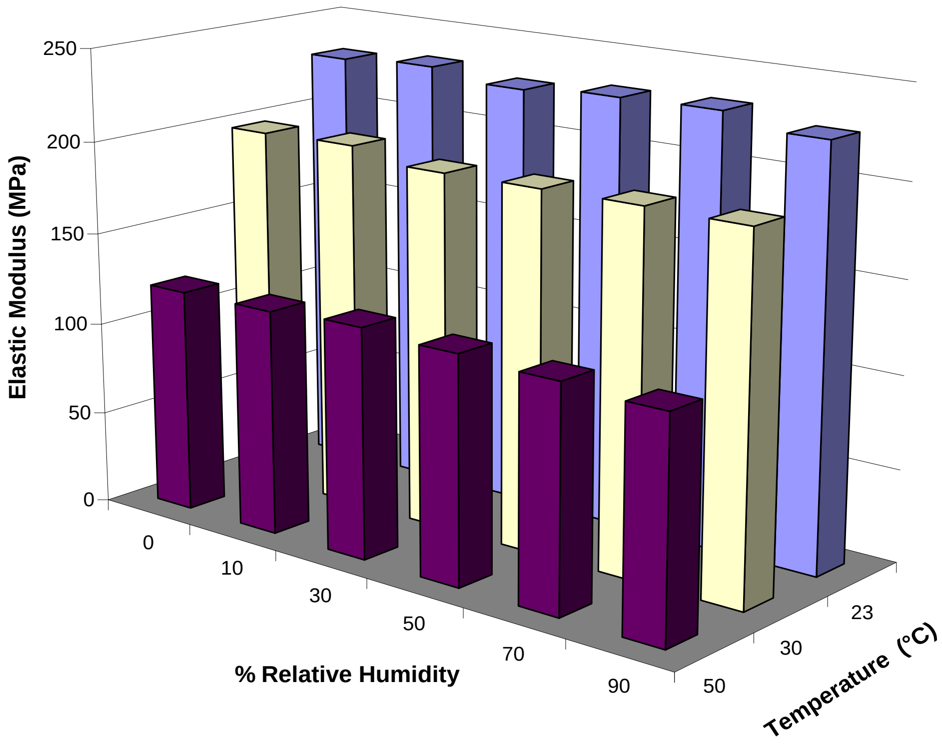


Figure 14: Elastic Modulus of PEAA-5H as a function of temperature and relative humidity. Sample thickness ~0.007". 75g applied load. Samples did not undergo the in-situ drying procedure.

As expected, increasing temperature reduces the stiffness of the PEAA-5H sample. In going from 23°C to 30°C, the elastic modulus of PEAA-20H decreased ~ 50% whereas that of the PEAA-5H sample decreased only 20%. The primary crystalline structure is largely unaltered by temperature changes significantly below the melting point of ~108°C. Therefore, if one assumes that the modulus of the 5 wt% copolymer sample is dominated by its degree of crystallinity, a dampened response to temperature changes below T_m should be expected.

Interestingly, the lower acid content copolymer has a modulus that is two times larger than PEAA-20H. These results conflict with those obtained by Wakabayashi et al. on similar copolymers.[6] In said study, a monotonic increase in the elastic modulus measured at room temperature was observed for acid contents > 6 wt%. This behavior was attributed to the increase of T_g above room temperature as the weight percent of the acid group increased. However, it is conceivable that the T_g of the 20 wt% copolymer studied herein is lower than that measured by Wakabayashi. DSC tests performed on PEAA-20H samples that were solvent cast from THF and DMSO solutions revealed that the glass transition of the cast polymer was closer to 1°C (See Table 1). [20]

If this lower T_g is stipulated, then the amorphous region should be fully relaxed for both 5 and 20 wt% samples during room temperature modulus measurements. The increased stiffness of PEAA-5H with respect to PEAA-20H would be a result of differences in crystallinity. The PEAA-5H sample has a crystalline volume fraction nearly 2.5 times that of the PEAA-20H copolymer. The increased number of hydrogen bonds within the amorphous phase is insufficient to overcome the concurrent loss of crystallinity. However, preliminary test results with PEAA-5Na suggest that the trend is reversed upon neutralization. A comparison of elastic modulus values at room temperature, 0% RH is given in Table 4 and it is apparent that the 20wt% ionomer is stiffer than the 5 wt%.

Table 4: Comparison of elastic modulus of different acid content polymers

	Neutralizing Cation	
Sample	H^+	Na^+
PEAA-5	225	325
PEAA-20	96	1509
Modulus measurements made at 23°C, dry conditions. All values are in MPa. ±10% error		

The implications of this potentially lower glass transition temperature may also shed light on the change of slope that occurs in the modulus versus temperature diagram of PEAA-20H (See Figure 11). If the glass transition temperature of the material is close to 1°C, then it is highly unlikely that the rapid decrease in going from room temperature to 40°C is due to the relaxation of the amorphous region. Secondly, the existence of secondary crystals is rather controversial; however, studies that postulate their existence emphasize the fact that the crystals only form after ageing for significant periods (~several days).[10, 16] PEAA-20H samples were dried at temperatures well above the proposed melting point for these secondary crystals, and the modulus testing commenced in a matter of hours after the sample was dried. Therefore, even if secondary crystals *were* present, they should be non-existent during the modulus measurements. This suggests that the transition is associated with the acid functional groups within the polymer sample.

Conclusion

The results presented herein reveal the effects of temperature and relative humidity on the elastic modulus of poly(ethylene-co-acrylic acid) polymers. A monotonic reduction in stiffness of 20 weight percent poly(ethylene-co-acrylic acid) occurs as the testing temperature increases. The thermal energy at elevated temperatures is sufficient to cause the dissociation of acrylic acid dimers. The interruption of these hydrogen bonds reduces the intermolecular chain interactions resulting in increased chain mobility. Furthermore, the modulus of PEAA-20H does not show any response to water activity. This lack of plasticization can be explained by the fact that the energy released during solvation of the acid groups is insufficient to swell the hydrophilic domain.

Neutralization of the copolymer sample results in drastic changes in the mechanical behavior. The strength of the ionic bond was sufficient to provide the ionomer with resistance to thermally induced changes. Furthermore, the solvation of the ionic bonds is sufficient to overcome the energy required to swell the polymers. Therefore, the ionomers showed increased plasticization as the relative humidity increased.

The behavior of the neutralized PEAA system shows similarities to Nafion. However, the modulus results of the copolymer sample demonstrate the importance of the strength of electrostatic interactions on polymer morphology and mechanical behavior.

Future Work

There are a variety of future directions that this work can take that will uncover additional information about concerning microstructure dynamics, environmental conditions and mechanical behavior. The reproducibility/reliability of these results depends on fine-tuning the casting methodology outlined herein. Replacing the petri dish with another cast that has a completely flat surface will reduce the variability in film thickness. Furthermore, microscopic and calorimetric characterization of the solvent cast films would provide useful information concerning the uniformity of prepared samples and any thermal transitions that occur as a result of solvent casting.

Furthermore, there are many interesting properties of the polymer that will only become apparent by looking at the time-dependent nature of its behavior. The next logical step for the characterization of the mechanical properties with respect to environmental conditions would be to examine the viscoelastic response of the polymer to environmental conditions. Similarly, the long term equilibration dynamics of the samples, especially at lower temperatures, are needed. Lastly, examination of poly(ethylene-co-acrylic) acid samples with different acrylic acid contents and/or neutralizing cations will yield more information concerning the interaction of the two phases.

References

1.DuPont. "DuPont Nafion Membranes and Dispersions" http://www2.dupont.com /FuelCells/en_US/products/nafion.html

2. Benziger, J., Bocarsly, A., Majsztrik, P., Satterfield, B. & Zhao, Q. Mechanical and Transport Properties of Nafion: Effects of Temperature and Water Activity. Macromolecules (Submitted 2009).

3. Majsztrik, P., Bocarsly, A. & Benziger, B. Viscoelastic response of Nafion. Effects of temperature and hydration on tensile creep. Macromolecules 41, 9849 (2008).

4. Satterfield, M. & Benziger, B. Viscoelastic properties of Nafion at elevated temperature and humidity. Journal of polymer science. Part B, Polymer physics 47, 11 (2009).

5. Tant, M., Mauritz, K. & Wilkes, G. Ionomers: Synthesis, structure, properties, and applications. (1997).

6. Wakabayashi, K. & Register, R. Micromechanical interpretation of the modulus of ethylene(meth) acrylic acid copolymers. Polymer 46, 8838 (2005).

7. Holliday, L. Ionic Polymers. , 415 (1975).

8. Rosen, S. in Fundamental Principles of Polymeric Materials (John Wiley & Sons, 1993).

9. McCord, E., Shaw, H. & Hutchinson, R. Short-chain branching structures in ethylene copolymers prepared by high-pressure free-radical polymerization: an NMR analysis. Macromolecules 30, 246 (1997).

10. Wakabayashi, K. & Register, R. Morphological origin of the multistep relaxation behavior in semicrystalline ethylene/methacrylic acid ionomers. Macromolecules 39, 1079 (2006).

11. Otocka, E. & Kwei, T. Properties of ethylene-acrylic acid copolymers. Macromolecules 1, 244 (1968).

12. Kang, N. The correlation between crystalline behavior of polyethylene segments and hydrogen bonds among carboxyl groups in Ethylene-Acrylic Acid copolymers. Physical chemistry chemical physics 2, 3627 (2000).

13. Kutsumizu, S., Tagawa, H., Muroga, Y. & Shinichi, Y. Small-angle X-ray scattering investigation of noncrystalline poly (ethylene-co-methacrylic acid) ionomers. Macromolecules 33, 3818 (2000).

14. Otocka, E. & Kwei, T. Properties of Ethylene-Metal Acrylate Copolymers. Macromolecules 1, 401 (1968).

15. Sauer, B. & McLean, R. AFM and X-ray studies of crystal and ionic domain morphology in poly (ethylene-co-methacrylic acid) ionomers. Macromolecules 33, 7939 (2000).

16. Loo, Y., Wakabayashi, K., Huang, Y., Register, R. & Hsiao, B. Thin crystal melting produces the low-temperature endotherm in ethylene/methacrylic acid ionomers. Polymer 46, 5118 (2005).

17. Tsujita, Y., Yasuda, M., Takei, M., Takizawa, A. & Yoshimizu, H. Structure of ionic aggregates of ionomers. 1. Variation in the structure of ionic aggregates with different acid content and degree of neutralization of ethylene and styrene ionomers. Macromolecules 34, 2220 (2001).

18. Benetatos, N. & Winey, K. Ionic aggregates in Zn-and Na-neutralized poly (ethylene-ran-methacrylic acid) blown films. Journal of polymer science.Part A, Polymer chemistry 43, 3549 (2005).

19. Taubert, A. & Winey, K. Imaging and X-ray Microanalysis of a Poly (ethylene-ran-methacrylic acid) Ionomer Melt Neutralized with Sodium. Macromolecules 35, 7419 (2002).

20. Nuño-Donlucas, S., Puig, J. & Katime, I. Hydrogen Bonding and Miscibility Behavior in Poly [ethylene-co-(acrylic acid)] and Poly (N-vinylpyrrolidone) Mixtures. Macromolecular chemistry and physics 202, 3106 (2001).

21. Khanna, Y., Wenner, W. & Krutzel, L. Amorphous phase segregation in polyethylene-based ionomers. Macromolecules 21, 268-268-270 (1988).

22. Quiram, D., Register, R. & Ryan, A. Crystallization and ionic associations in semicrystalline ionomers. Macromolecules 31, 1432 (1998).

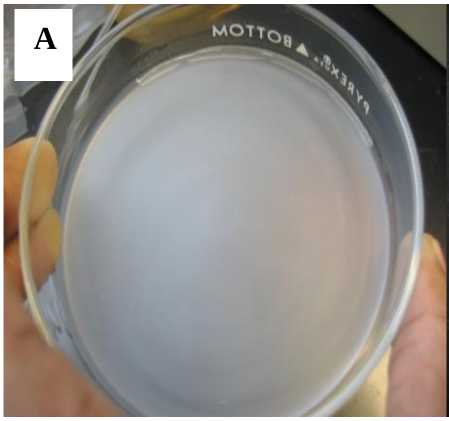
23. Kutsumizu, S. et al. Effects of water sorption on the structure and properties of ethylene ionomers. Macromolecules 25, 6829 (1992).

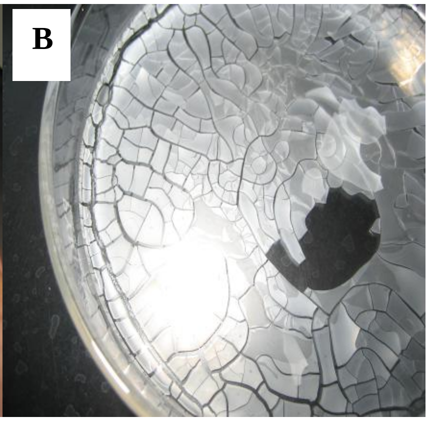
24. Majsztrik, P., Bocarsly, A. & Benziger, J. An instrument for environmental control of vapor pressure and temperature for tensile creep and other mechanical property measurements. Rev. Sci. Instrum. 78, 103904 (2007).

25. Bower, D. in An Introduction to Polymer Physics 444 (Cambridge University Press, New York, NY, 2002).

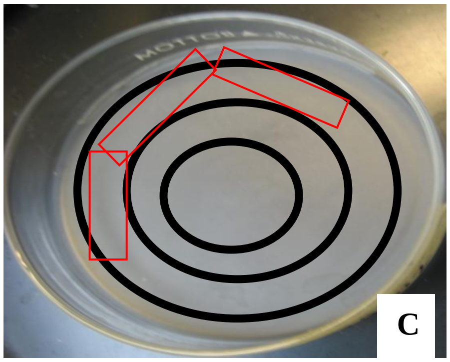
Appendix

Solvent Casting



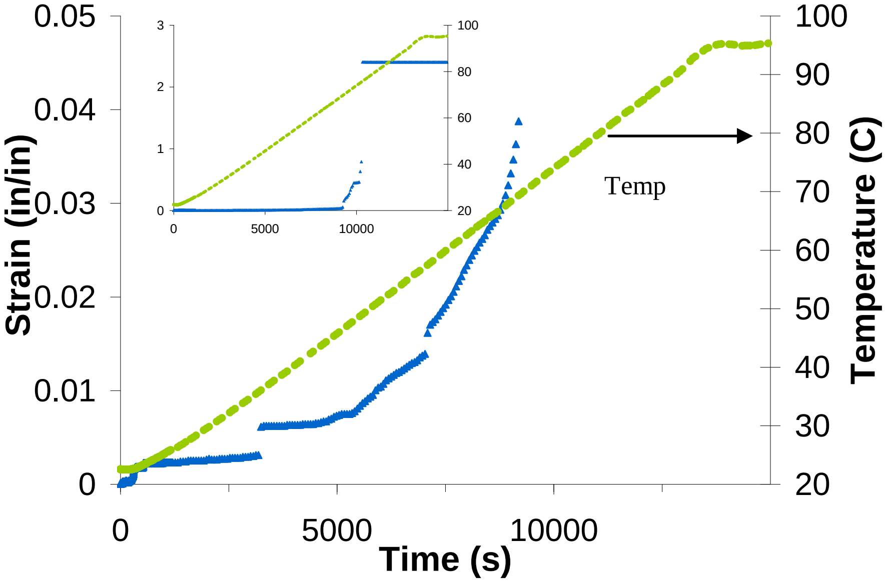


The casting methodology utilized herein was developed via a trial and error procedure. Solvent, drying temperature, drying time and solvent removal all strongly influenced the integrity of the resulting films. Figure A above shows PEAA-5 sample cast using the methodology reported herein. Figure B is a film cast using a slightly lower temperature (60°C). Though films appear macroscopically uniform an evaluation of the microscopic properties of the films may aid in film characterization.

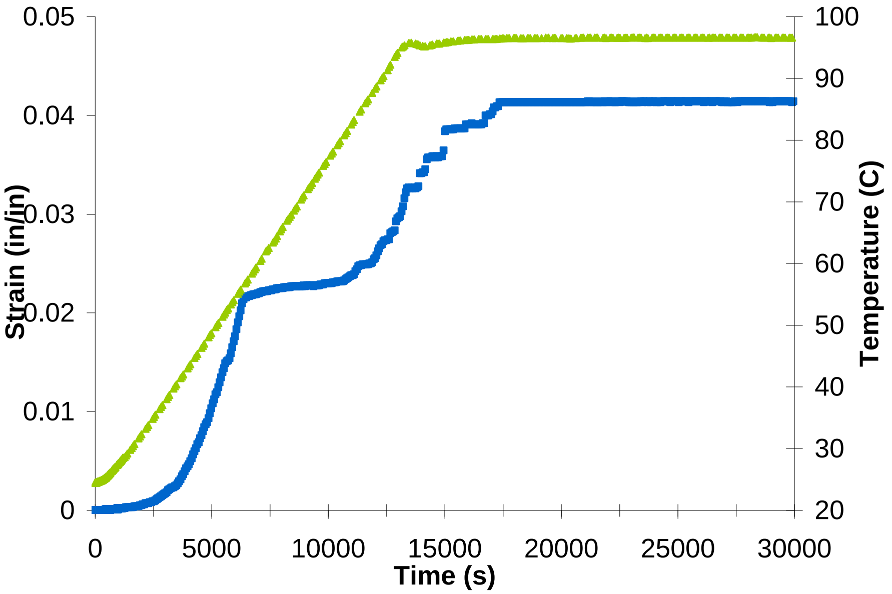


Due to the fact that the Petri dish molds were not completely flat, there was a thickness gradient in the resulting films. Samples near the center were thinner than those near the circumference. Because the samples are so thin (> 0.010”) small changes in the thickness account for large differences in applied stress. Therefore, in an attempt to keep the thickness of individual specimen relatively uniform, samples were dissected in a concentric fashion as illustrated by Figure C above.

Melting



PEAA-20H samples experienced creep induced failure at elevated temperatures. The temperature of PEAA-20H sample was slowly ramped to 95°C. However, when the sample exceeded ~70°C, it began to creep rapidly and failed shortly thereafter as depicted in the inset. No load was applied to this sample. The weight of the rod and counterbalance (~10g) were sufficient to cause creep. Upon removal from testing apparatus, it was clear that the polymer had melted onto the clamps.



The temperature of PEAA-20Na sample was slowly ramped to 95°C. The initial rapid expansion is likely due to relaxation of the amorphous regions within the ionomer sample. The second steep increase may be caused by the melting of the primary crystals. The sample did not fracture despite the fact that the crystalline melting point was surpassed highlighting the strength of the ionic electrostatic interactions.