

Nafion[®]/(SiO₂, ORMOSIL, and Dimethylsiloxane) Hybrids Via *In Situ* Sol–Gel Reactions: Characterization of Fundamental Properties

Q. DENG, R. B. MOORE, K. A. MAURITZ

Department of Polymer Science, University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, MS 39406-0076, USA

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ABSTRACT: Nafion[®]/SiO₂, Nafion[®]/[**OR**ganically **MO**dified **SIL**icate (ORMOSIL)] and Nafion[®]/dimethylsiloxane hybrids were created *via in situ* sol–gel reactions for tetraethoxysilane, diethoxydimethylsilane, and their mixtures. Differential scanning calorimetry studies showed a broad endotherm for unfilled Nafion[®]-H⁺ at $T_{\alpha} \approx 215^{\circ}\text{C}$ that shifts upward for the Q : D = 1 : 0 (mol : mol) [Q = Si(O_{1/2})₄, D = (O_{1/2})₂Si(CH₃)₂] hybrid, then shifts downward with decreasing Q : D. This endotherm likely arises from release of H₂O molecules bound to ≡Si–OH groups and condensation reactions among silanol groups. The decrease in T_{α} is rationalized in terms of an increasing fraction of flexible D units that disrupt hydrophilic Q structures. T_m shifts to lower temperatures with decreasing Q : D, and it is suggested that main chains are restricted by side chains embedded in silicon oxide nanoparticles, but D unit insertion causes side chains to be anchored less strongly. Thermal gravimetric analysis indicates that the first mass loss step for Nafion[®]-H⁺ shifts to higher temperatures as D : Q increases; an increase in D unit fraction inhibits Q unit degradation by evolved HF. A dynamic mechanical transition at T_{α} may arise from side chain motions, and the increase in T_{α} in passing from unfilled Nafion[®]-H⁺ to the 1 : 0 hybrid is due to side chain immobilization by their entrapment in silicon oxide domains. The progression 0 : 1 → 1 : 2 → 1 : 1 → 2 : 1 generates increasing mechanical tensile strength and decreasing ductility; strength enhancement might be due to entanglements between ORMOSIL and pure silicon oxide phases and side chains. Liquid sorption experiments quantified the affinity of these hybrids for solvents of varying polarity. A dielectric relaxation for the 0 : 1 hybrid at about 1.5 kHz might be related to side chain mobility. A weaker relaxation in the range 10⁴–10⁵ Hz exists for the 0 : 1 and 1 : 1 hybrids and Nafion[®]-H⁺, but not for the 1 : 0 hybrid that exhibits the behavior $\varepsilon'' \sim f^{-n}$ over a broad frequency (f) range, suggestive of intercluster proton hopping. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 747–763, 1998

Key words: Nafion[®]; silicon oxide; ORMOSIL; sol-gel reactions; properties

INTRODUCTION

In previous work, we exploited the nanophase-separated morphology of Nafion[®] ionomer mem-

branes as a morphological template for *in situ* sol–gel reactions of the monomers tetraethoxysilane [TEOS = Si(OC₂H₅)₄], diethoxydimethylsilane [DEDMS = (CH₃)₂Si(OC₂H₅)₂], and TEOS-DEDMS mixtures to create Nafion[®]/SiO₂, Nafion[®]/dimethylsiloxane, and Nafion[®]/[**OR**ganically **MO**dified **SIL**icate (ORMOSIL)] hybrid materials. Nafion[®] is a perfluorosulfonate ionomer whose general morphology consists of 3–5 nm-in-size clusters of —SO₃[−]X (X = H⁺ or cation)-ended perfluoroalkylether side chains.¹ These po-

Correspondence to: K. A. Mauritz.

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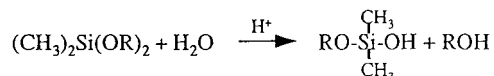
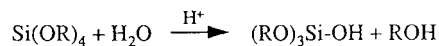
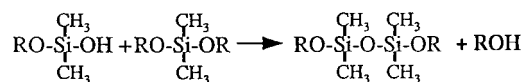
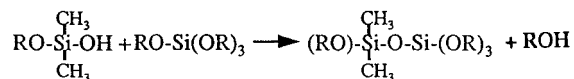
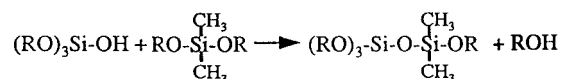
HYDROLYSIS**CONDENSATION****CO-CONDENSATION**

Figure 1 Coupled, acid-catalyzed sol-gel reactions occurring within TEOS + DEDMS + H₂O mixtures. The following exchange reaction is also possible: Si(OEt) + MeOH → Si(OMe) + EtOH, because MeOH was the carrier solvent that also swells the perfluoro-sulfonic acid membrane.

lar clusters are dispersed throughout a semicrystalline tetrafluoroethylene matrix. Hydrolyzed alkoxy- and/or alkylalkoxysilane molecules migrate to the clusters that serve as reactors in which their hydrolysis is catalyzed by pendant -SO₃H groups and the sol-gel reaction initiates in these domains.^{2,3} The coupled, acid-catalyzed hydrolysis-condensation reactions that took place in these experiments are depicted in Figure 1. Our so-called “template hypothesis”—namely that quasicrystalline order extending over the array of polar clusters directs the condensation polymerization of sorbed alkoxides and dictates the ultimate morphology of the dried gel phase—was reinforced by our small-angle X-ray scattering (SAXS) studies of these hybrid membranes.^{2,4} These SAXS studies established that the original morphology of unfilled Nafion® persists even after its invasion by the sol-gel-derived phase, but that chemical compositional variance was affected within clus-

ters *via* tailored *in situ* sol-gel reactions. These hybrids can indeed be classified as “nanocomposites” based on the fact that compositional heterogeneity exists on the scale of ~ 5 nm.

Molecular structure was characterized within silicon oxide, dimethylsiloxane, and ORMOSIL nanophases using Fourier transform infrared (FTIR) and ²⁹Si solid-state nuclear magnetic resonance (NMR) spectroscopies.^{3,5} *In situ* ORMOSIL composition, comprised of Q = Si(O_{0.5})₄ and D = (O_{0.5})₂Si(CH₂)₃ units, can be tailored by manipulating the composition of external TEOS-DEDMS monomer source solutions. A significant outcome of our NMR studies was that external DEDMS : TEOS (mol mol⁻¹) was equal to internal Q : D. Statistical cocondensation between TEOS and DEDMS monomers, rather than formation of D or Q blocks, takes place. As DEDMS comonomer feed concentration increases, ORMOSIL nanostructures, illustrated in a rather general way in Figure 2, are understandably more hydrophobic and more flexible. This fact is reflected in the properties of these hybrid materials, as will be seen.

We used pyrene as a photophysical probe to interrogate structural polarity within (1) Nafion®/SiO₂ and (2) Nafion®/ORMOSIL hybrids,⁶ and the results of these studies are as follows. The interior of the silicon oxide phase in (1) has the most polar environment. Polar/nonpolar interphase regions in (1) are next in order of decreasing polarity. The interior of the ORMOSIL phase in (2) displays the lowest polarity, reflecting the presence of CH₃ groups, and the interphase ranks somewhat higher in polarity. Nanostructural polarity determined from fluorescence emission and water uptake correlate well.

These preceding studies were aimed at elucidating the molecular and nanoscale structures of these hybrids. The goal of the work reported herein was to establish the important thermal [*via* differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA)], mechanical tensile, dielectric relaxation, and solvent affinity properties of these heterogeneous materials and to relate these properties to the underlying microstructures that were determined in our earlier investigations.

EXPERIMENTAL**Materials**

Perfluorosulfonate membranes (1100 equivalent weight, 5 mil thick) in the K⁺ form (Nafion® 115)

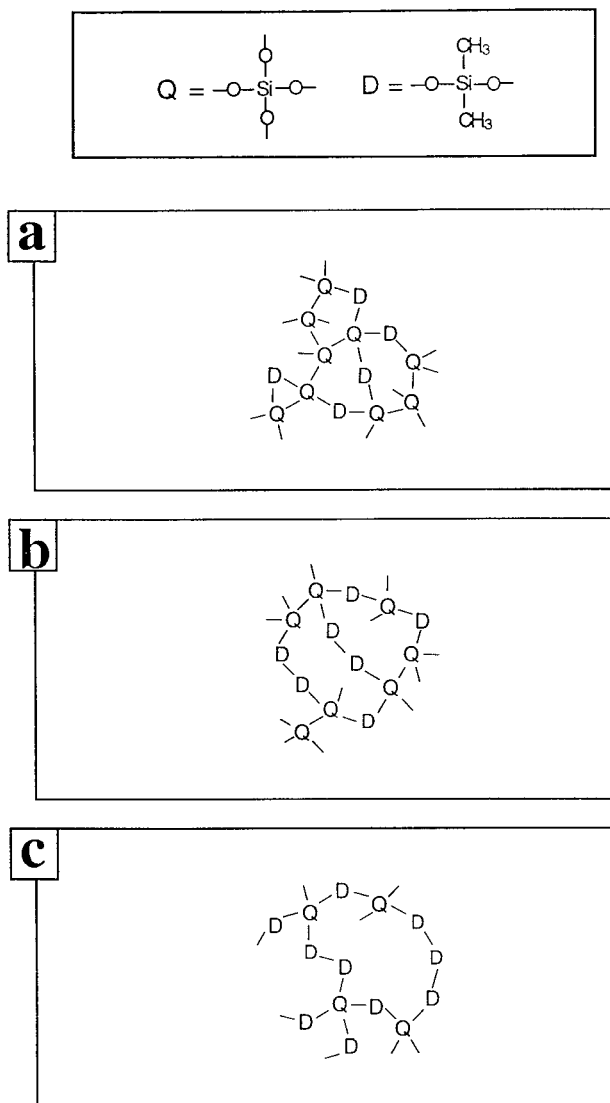


Figure 2 Rough depictions of ORMOSIL nanophase structures consisting of cocondensed Q and D units of decreasing Q : D ratio from (a) to (c). In an actual network, incompletely coordinated Q units will contain —OH groups.

were supplied by the E. I. DuPont Company (Wilmington, DE). TEOS, DEDMS, and methanol (MeOH) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received. All water used was distilled/deionized.

Formulation of Nafion®/ORMOSIL Hybrids

Complete details of nanocomposite membrane formulation were presented in a number of earlier reports and are truncated here in the interest of brevity.^{3–6} All samples were taken from the same respective batches used for our prior FTIR, ²⁹Si

solid-state NMR, SAXS, and pyrene fluorescence probe investigations of these materials so that a correlation of structure–property information would be meaningful. The following is but a review of the important aspects of sample preparation.

First, all unfilled membrane samples were initialized to a standard dry —SO₃H form before the *in situ* sol–gel reaction to maximize sample reproducibility. The polymer-attached —SO₃H groups conveniently serve to catalyze the sol–gel reactions. All initialized samples were swollen in stirred solutions of 5 : 1 (v/v) MeOH : H₂O at 22°C for 24 h in covered glass jars. MeOH serves two purposes: (1) to swell the membranes to facilitate water permeation and subsequent permeation of TEOS and DEDMS, and (2) to act as a cosolvent for these three species. Premixed TEOS/DEDMS/MeOH solutions, such that H₂O : TEOS = 4 : 1 and H₂O : DEDMS = 2 : 1 (mol mol^{−1}), were then introduced into the jars (subsequently stoppered) while maintaining stirring. TEOS : DEDMS (mol mol^{−1}) was systematically adjusted over the sequence 1 : 0, 2 : 1, 1 : 1, 1 : 2, and 0 : 1 to vary network former (Q)/modifier (D) composition over the entire range. As described previously, our ²⁹Si solid-state NMR studies of the same hybrids indicated that the resultant *in situ* Q : D ratio is essentially the same as that in the external source solution.⁵ After 9 min, the membranes were removed from these solutions. The time between addition of TEOS–DEDMS and removal of a given membrane from solution is referred to as “permeation time.” Upon removal, the membranes were quickly soaked in MeOH for 1–2 s to wash away reactants adhering to the surface to eliminate the precipitation of ORMOSIL layers on these surfaces. Finally, samples were surface-blotted and dried at 100°C under vacuum for 48 h to remove trapped volatiles and promote further condensation of SiOH groups within the *in situ* ORMOSIL network. In each case, percent weight uptake was determined relative to that of the initial unfilled, dry H⁺ form weight. For this series of samples, the weight uptakes were quite the same, at around 10%. Figure 3 is a rough depiction of the sequence of steps in Nafion®/ORMOSIL hybrid membrane formulation.

Property Characterization

DSC

DSC scans were obtained using a Perkin–Elmer DSC 7 with samples under nitrogen. “Dry” sam-

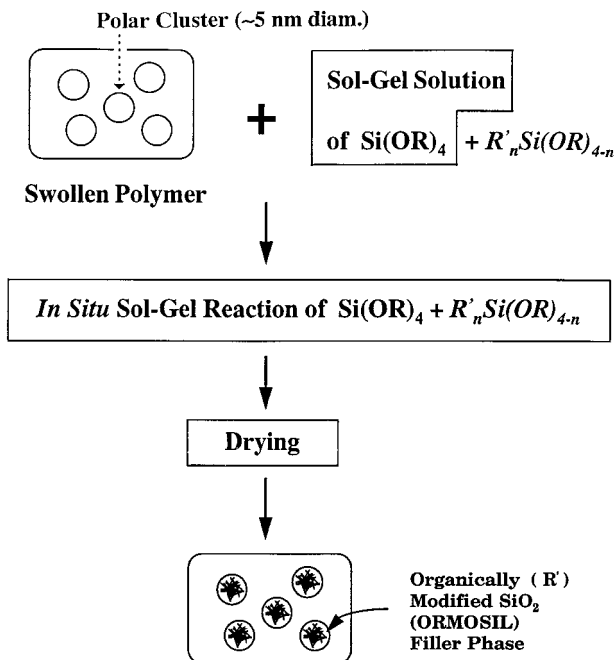


Figure 3 General diagram illustrating the formulation of [perfluoro-organic]/ORMOSIL hybrid materials via the sol-gel reaction of TEOS and DEDMS within the nanoscopic polar clusters of Nafion[®] membranes.

ples were first heated from 22 to 120°C at 20°C min⁻¹. The samples were held at 120°C for 15 min to further remove volatiles, after which cooling to 22°C at 10°C min⁻¹ occurred. The reported thermograms were obtained when the samples were finally heated from 22 to 300°C at a rate of 20°C min⁻¹.

Thermogravimetric Analysis (TGA)

TGA experiments were conducted using a Du Pont 9900 Thermal Analysis System (951 TGA). TGA thermograms were obtained on heating from room temperature to 140°C at the rate of 20°C min⁻¹, with the exception that an isothermal hold was placed at 120°C for 20 min to remove volatiles. Samples were then heated continuously to 650°C at 10°C min⁻¹. In all steps, the experiments were performed with ~ 20 mg samples under nitrogen introduced at ~ 50 mL min⁻¹.

DMA

DMA was performed using a Seiko Instruments SDM5600 Viscoelasticity Analysis System with the DMS 210 Tension Module. Samples were subjected to a 1-Hz (mainly) cyclic tensile deformation, as temperature was ramped from 30 to 300°C at a heating rate of 2°C min⁻¹.

Mechanical Tensile Analysis

Tensile stress *versus* strain evaluations were performed at 22°C using an MTS 810 Universal Test Machine operating at a strain rate of 0.2 mm s⁻¹. Each tensile sample was tested three times to provide assurance of good data reproducibility.

Solvent Uptake Studies

Unfilled Nafion[®]-H⁺, Nafion[®]/SiO₂, and Nafion[®]/ORMOSIL samples were dried at 100°C under vacuum for 24 h, then weighed to determine their initial weights. These dried samples were then immersed in either deionized water, MeOH, or isobutanol (*i*-BuOH) solvents, which decrease in polarity in this order, for 40 hr at 22°C. After this time, they were surface-blotted and rapidly transferred to a balance to determine their final weight. Weight uptake showed very good reproducibility.

Dielectric Relaxation Studies

Mauritz and Stefanithis⁷ earlier reported a similar dielectric relaxation study of Nafion[®] membranes that contained sol-gel-derived silicon oxide phases.⁷ Here, in similar fashion, dry films of unfilled Nafion[®]-H⁺ and the 1 : 0, 1 : 1, and 0 : 1 hybrids were placed between and in good contact with gold parallel plate electrodes. All experiments were performed at 22°C as a function of the frequency (f), over the range of 100 Hz–13 MHz, of an applied low-amplitude sinusoidal signal, using a Hewlett-Packard 4192A LF impedance analyzer. Electrical impedance (Z^*) data was converted to the real and imaginary components of the complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$ ($i = \sqrt{-1}$), knowing the film thickness and surface area as discussed in an earlier report.⁸

RESULTS AND DISCUSSION

As described previously, the dry weight uptakes for all of the hybrids are approximately the same. This is significant in the sense that filler content is largely eliminated as a variable that might account for property differences among the different materials. Furthermore, ~ 10% weight uptake corresponds to a condition wherein incorporated nanoparticles exist in single isolation rather than being contiguous over appreciable distances, as discussed earlier.⁹

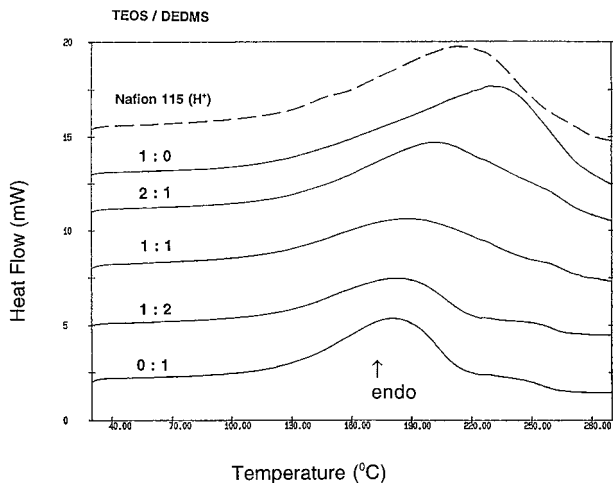


Figure 4 DSC thermograms for unfilled Nafion®-H⁺ and hybrids having indicated Q : D molar ratios.

DSC Analysis

Figure 4 shows the DSC thermograms for the series of hybrids, including that for the unfilled Nafion®-H⁺ control. Pure Nafion®-H⁺ exhibits a broad endothermic transition with onset at $\sim 135^\circ\text{C}$ and peak $\sim 215^\circ\text{C}$. This peak significantly shifts upward, relative to unfilled Nafion®, for the pure silicon oxide-filled (1 : 0) sample to $\sim 235^\circ\text{C}$. Thereafter, the peak progressively shifts to lower temperatures with decreasing Q : D.

A physical transition of this magnitude has never been reported at this temperature for unfilled Nafion® and is likely due to the release of incorporated water. Moreover, structural relaxations within the filler are not implicated owing to the fact that the unfilled form also shows this activity, although the transition is clearly modified by the filler. Integration under this peak for the unfilled H⁺ form yields an energy of 56.7 J g^{-1} . Nafion® has a heat of melting, at $\sim 250^\circ\text{C}$, of only $\sim 5.0 \text{ J g}^{-1}$, although this endotherm is not visible in the topmost curve, being overwhelmed by the broad, lower temperature peak. The melting event, which is discernible in the 2 : 1 to 0 : 1 curves, involves the disordering of chains in the crystalline tetrafluoroethylene regions. It is clear, on the basis of energy, that the major thermal event is not melting. Subtracting the energy for melting from the entire peak envelope, the true energy associated with the large peak is 51.7 J g^{-1} .

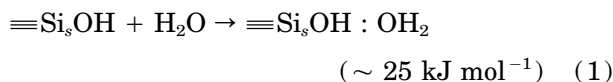
The heat of vaporization of pure water at 180°C is 36.3 kJ mol^{-1} . Using this number, as well as the initial mass of the sample, a simple calculation yields a percent weight loss of 2.5%, assuming

that all of 51.7 J g^{-1} is used to vaporize water from an incorporated liquid-like component. For this 1100 equivalent weight membrane, this corresponds to only $\sim 1.6 \text{ H}_2\text{O}$ molecules per $-\text{SO}_3\text{H}$ group. However, it will be seen in the TGA scans presented later that little mass loss, in fact, occurs in the range of this transition. To be sure, this calculation is rather simplistic due to the assumption that water exists in a liquid-like state within the polar clusters of Nafion®. Infrared (IR) spectroscopic investigations that have probed the nature of water in perfluorosulfonate ionomers indicate that this indeed is not the case at low hydration levels. Falk,¹¹ who analyzed spectra of “nearly dry” Nafion®-H⁺, suggested the presence of undissociated $-\text{SO}_3\text{H}$ groups and suggested that hydrogen-bonded dimers of these groups may exist. $-\text{SO}_3\text{H}-\text{H}_2\text{O}$ hydrogen bonds are possible at low hydration levels. Falk also points out that a large fraction of H_2O molecules must have $-\text{OH}$ groups that are not involved in hydrogen bonding, but must necessarily face the perfluorocarbon phase, especially for low water contents. Ostrowska and Narebska^{12,13} discussed the breakup of $\text{H}_2\text{O}-\text{H}_2\text{O}$ structures with progressive dehydration. The general conclusion of these mid-IR, as well as the near-IR spectroscopic studies of Barnes,¹⁴ is that the overall strength of hydrogen bonding *between H₂O molecules* within Nafion®, including the H⁺ form, is lower than that within pure water and decreases with dehydration; $\text{H}_2\text{O}-\text{H}_2\text{O}$ bonds are replaced with $-\text{SO}_3\text{H}-\text{H}_2\text{O}$ bonds.

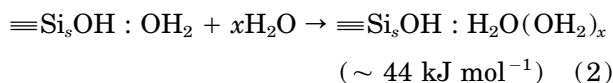
Escoubes and Pineri,¹⁵ from water sorption and calorimetric studies, determined that the energy of interaction between H_2O and the H⁺ form increases, negatively, with decreasing hydration until a water content of $\sim 2.7 \text{ mol H}_2\text{O/mol SO}_3\text{H}$ is reached; beneath this hydration level, the energy is asymptotic at about $-54 \text{ kJ (13 kcal)/mol H}_2\text{O}$. This asymptote corresponds to ionic hydration energy rather than to interactions within liquid-like water. Whereas the experiments of these investigators apply to a 1200 rather than an 1100 equivalent weight membrane, it is reasonable to assume that the hydration energy for the latter is not too different from -54 kJ mol^{-1} because ionic hydration structures are local, whereas a liquid phase for water—which might exist at water contents larger than those under consideration—would involve larger scale hydrogen-bonded structures. The fact that this interaction energy is greater than that for pure water would account for the elevated temperature (i.e., $> 100^\circ\text{C}$)

of the peak and a calculated weight loss of 1.7% rather than 2.5%.

We propose that the significant upward displacement of the major peak for the silicon oxide-filled (1 : 0) sample, relative to the unfilled sample, is due to the introduction of strong hydrogen bonding sites within Nafion® in the form of $\equiv\text{Si}-\text{OH}$ groups that reside on the surfaces of silicon oxide nanoparticles. The heat of adsorption of a water molecule on an isolated (as opposed to vicinal or geminal) surface (*S*) silanol site is rather large¹⁶:



Subsequently added H_2O molecules that interact with the bound H_2O molecule have an even greater heat of adsorption¹⁶:



These energies would be somewhat different for adsorption on vicinal and geminal SiOH groups, because a single H_2O molecule might be able to hydrogen-bond to more than one group.

It is known on a qualitative level that numerous silanol groups are present in the Nafion®/ SiO_2 hybrids in this work based on IR spectroscopic studies.³ It has been established that, for silica gels, physically sorbed water (i.e., H_2O molecules bound to surface $\equiv\text{SiOH}$ groups) start to be driven off, and surface silanol groups condense, at about 170–175°C.^{17,18} These events would precede the peak in Figure 4 at $\sim 230^\circ\text{C}$ for the 1 : 0 hybrid to account for this endothermic feature. Kratochvila and coworkers¹⁹ investigated hydroxyl groups and sorbed water on silica gels using IR spectroscopy and saw that absorption bands of OH groups in silica gels (i.e., OH groups in free, liquid-like, and bound H_2O molecules, as well as in $\text{Si}-\text{OH}$ groups), in the 3000–4000 cm^{-1} region, are broad and cannot be resolved. This is in harmony with our spectral observations with regard to Nafion®/ SiO_2 hybrids, but their near-IR studies were able to discriminate between these groups to some degree. Ying and Benziger²⁰ investigated the structural evolution of silica gels to the denser glass state upon heating using FTIR photoacoustic spectroscopy and were able to resolve these OH groups. Heating the gels to 200°C and then annealing at this temperature is sufficient to diminish $\text{Si}-\text{OH}$ groups, create more $\text{Si}-$

$-\text{O}-\text{Si}$ bridges, and drive off H_2O that issues from condensation reactions, as well as physically adsorbed water and increase the relative number of free (i.e., isolated) SiOH groups. These studies demonstrated that water is adsorbed in the gel by hydrogen-bonding with free silanol groups. If the silica gels in these studies are sufficiently similar to the silicon oxide phases dispersed throughout Nafion® membranes, then the large, broad DSC peak for the 1 : 0 hybrid can be understood in terms of water release by these mechanisms. Moreover, a general view of the altered (condensed) structure of the gel after this dehydration is possible.

Assuming that the large peak arises mainly from the release of H_2O molecules that were bound to surface $\equiv\text{Si}-\text{OH}$ groups, as well as to condensation reactions among these groups, the progressive shift of this peak to lower temperatures in proceeding from the 1 : 0 to 0 : 1 hybrid is easily rationalized. Our pyrene photophysical probe studies of these systems indicated that the environments posed by the nanoscopic filler phase do in fact become less polar with decreasing $Q : D$.⁶ Moreover, we have established that the relative water uptake of these hybrids decreases in this compositional order. As the D content increases, surface $\equiv\text{Si}-\text{OH}$ groups are replaced by hydrophobic $-\text{Si}(\text{CH}_3)_2$ groups, thereby reducing the number of sites for H_2O molecule attachment.

Now, consider the higher temperature melting peak that exhibits a gradual shifting to lower temperatures with decreasing $Q : D$. Our pyrene photophysical probe studies of these materials⁶ suggested that the sulfonate groups at the ends of the long side chains become embedded in the silicon oxide phase during the sol–gel reaction for TEOS within the clusters. Given that the main chains, *via* coupling through the side chains, are tethered in silicon oxide nanoparticles in this way, their mobility is greatly hindered with the result that the temperature at which chains in crystalline arrays would become disordered increases. However, the progressive insertion of difunctional D units into silicon oxide nanostructures reduces their conformational rigidity as longer and flexible D unit statistical blocks are present, as depicted in Figure 2. As this phase becomes “softer,” the perfluoroalkylether side chains would be anchored therein to a lesser degree. In turn, it is reasonable to think that this would cause the melting peak to shift to lower temperatures with decreasing $Q : D$. This, in fact, is what is seen in Figure 4, wherein the peak is ultimately displaced downward to $\sim 185^\circ\text{C}$ for the 0 : 1 hybrid in which

dimethylsiloxane oligomers are present as suggested by our ^{29}Si solid-state NMR studies.⁵ One might also consider the possibility that dimethylsiloxane oligomers penetrate the perfluorocarbon regions and disrupt chain packing, which might account for why T_m has dropped to this extent.

It is also possible that some $-\text{SO}_3\text{H}$ groups interact with $\equiv\text{SiOH}$ groups at the surfaces of silicon oxide or ORMOSIL nanoparticles; this form of coupling would also restrict main chain mobility. However, as D content increases, surface $\equiv\text{SiOH}$ groups become replaced by $\equiv\text{SiCH}_3$ groups, thereby reducing the number of potential interactions between side chains and nanoparticles.

TGA Analysis

In addition to modification of physical thermal transitions, it is of interest to see whether Nafion®- SiO_2 , Nafion®-ORMOSIL, and Nafion®-dimethylsiloxane interphase interactions will affect the temperature of ultimate thermal degradation. Figure 5 consists of TGA thermograms of samples taken from the same batches used in the DSC experiments, including that of the unfilled Nafion®- H^+ control sample.

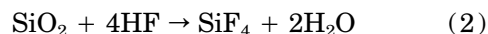
As in earlier studies of unfilled Nafion® and Nafion®/ SiO_2 hybrids,¹⁰ thermal degradation profiles that were multistage in nature were observed for all Nafion®/ORMOSIL variants. The peak in the derivative curve seen at 120°C for all samples occurs because the temperature was purposely held at this temperature for 20 min to remove water and volatiles, as described earlier; this accounts for the step decrease. The mass losses incurred up to the corresponding large peak temperatures in Figure 4 are not large, which indicates that residual volatile levels (H_2O , solvent) are not high.

The first significant mass loss event for unfilled Nafion®- H^+ occurs with an inflection temperature at $\sim 343^\circ\text{C}$. This feature monotonically shifts to higher temperatures as DEDMS : TEOS increases (i.e., from 358°C for the 1 : 0 hybrid up to 426°C for the 0 : 1 hybrid). The pure DEDMS-reacted sample exhibits the greatest stability in this sense. Owing to the fact that Nafion® is already a thermally robust material, the elevation of its degradation onset temperature by about 83°C is significant with regard to applications of these membranes in harsh environments.

Each of these Si-containing hybrids exhibit at least three significant mass loss steps, and all are more thermally stable than unfilled Nafion®- H^+ .

Future studies involving the use of the coupled FTIR/TGA technique will explore the evolution of specific reaction products that correspond to specific degradation steps, as well as the reaction between Q units and HF gas that is generated as a Nafion® degradation product. With regard to the latter issue, an increase in D unit fraction would increasingly inhibit Q unit degradation with concomitant SiF_4 evolution. These future studies will also involve a hybrid wherein a Q unit core is shielded by a D unit shell. The initial degradation event for unfilled Nafion® and Nafion®/ SiO_2 is believed to involve cleavage of the C—S bond leading to SO_2 , an OH radical, and a carbon-based radical as earlier proposed by Wilkie and coworkers.²¹

It is seen that residual weight percentages at the final temperature are less than the original filler uptake as measured by a balance. This is understood to be due to degradation of the silicon oxide phase *via* the reaction:



DMA Analysis

Figure 6 contains plots of the mechanical storage modulus (E') and loss tangent ($\tan \delta$) *versus* temperature at 1 Hz for selected hybrids. The plots for pure Nafion®- H^+ and for the 1 : 1 hybrid, as well as plots at different oscillation frequencies, are omitted in Figure 6 in the interest of brevity. However, data at 1 Hz for the 1 : 1 sample are seen in Figure 7, which also shows plots for all applied oscillation frequencies in the range of 0.01 to 10 Hz. Likewise, Figure 8 consists of plots for all frequencies for the 2 : 1 hybrid to illustrate further the frequency dependence of the DMA spectra.

Two $\tan \delta$ peaks are seen for dry unfilled Nafion®- H^+ . A transition at around 240°C is in the temperature range of melting observed in the DSC scans in Figure 4, although this event is obscured in the scans for unfilled Nafion®- H^+ , as well as the Nafion®/ SiO_2 hybrid. On close inspection of the DSC scan for unfilled Nafion®- H^+ , a vestige of a transition occurs in the vicinity of 136°C. The distinctive drop in E' at this lower temperature is not profound, which suggests that long-range chain segmental motions in the sense of a glass transition are not involved. Shorter-ranged side chain motions within clusters might be hypothesized. In fact, Miura and Yoshida²² noted a DMA $\tan \delta$ peak at 120°C at 1 Hz for “dry” 1100 EW Nafion®- H^+ . This transition, labeled α , was rationalized as arising from motions within the po-

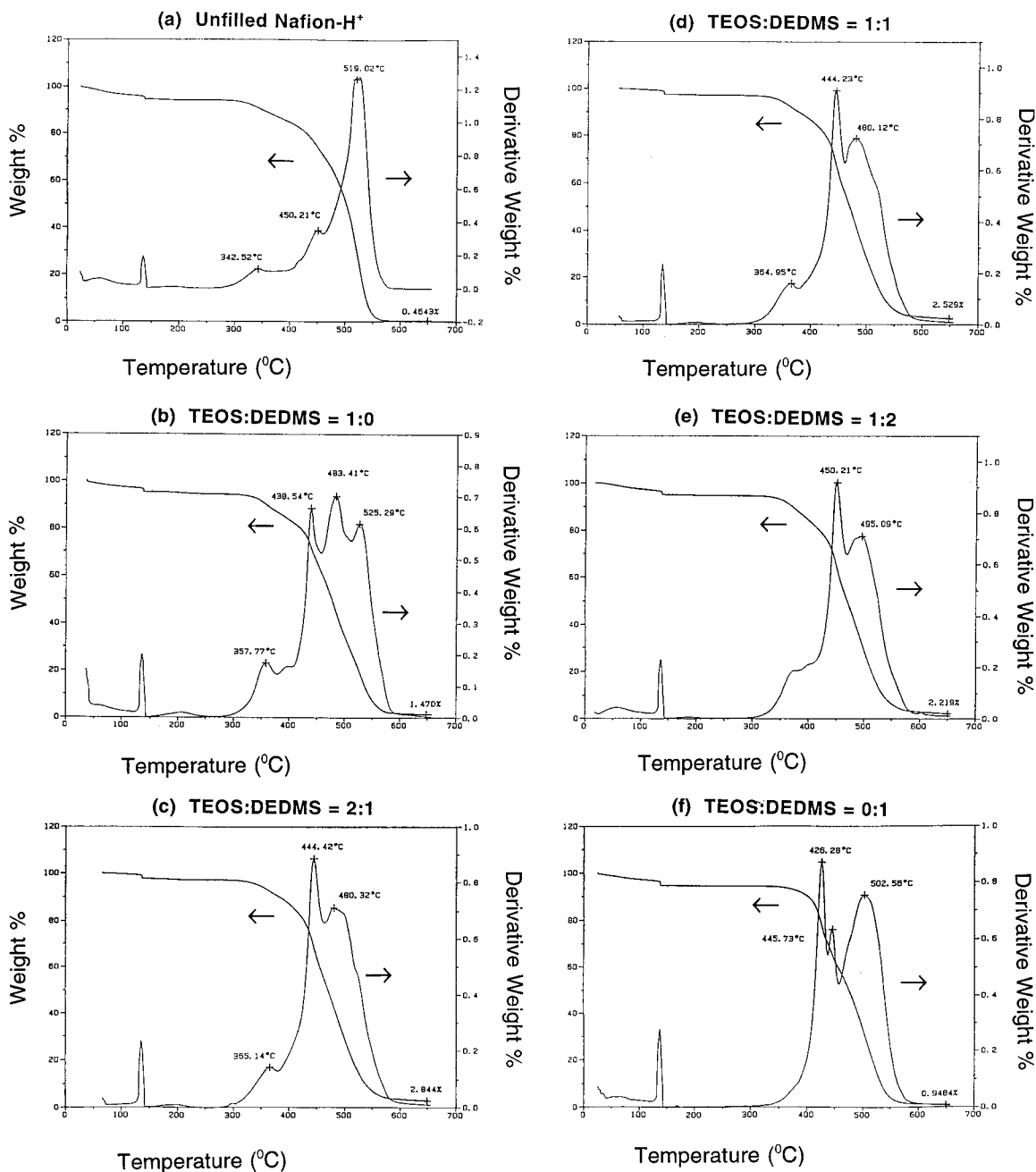


Figure 5 TGA thermograms, included derivative curves, for unfilled Nafion[®]-H⁺ and hybrids having indicated Q : D molar ratios.

lar clusters, because it was sensitive to cation type. A thermal event occurring close to this temperature was also observed in our earlier DSC studies of Nafion[®]-H⁺ and Nafion[®]/SiO₂ hybrids.¹⁰ We suggest that, whereas water may affect this transition, its volatilization is not the primary mechanism, owing to the fact that the mechanical modulus of Nafion[®] increases with decreasing water content,²³ as would occur upon heating, whereas the transition seen in Figures

6–8 (which we also refer to as the α transition) is characterized by a decrease in E' .

For the 1 : 0 hybrid, there are two broad overlapping $\tan \delta$ peaks in Figure 6, centered around 160 and 250°C. It is assumed that these transitions reflect the same, but filler-modified processes exhibited by pure Nafion[®]-H⁺ (i.e., T_α and T_m , respectively). The increase in T_α from 136 to 160°C suggests restricted molecular mobility, perhaps the immobilization of side chains caused

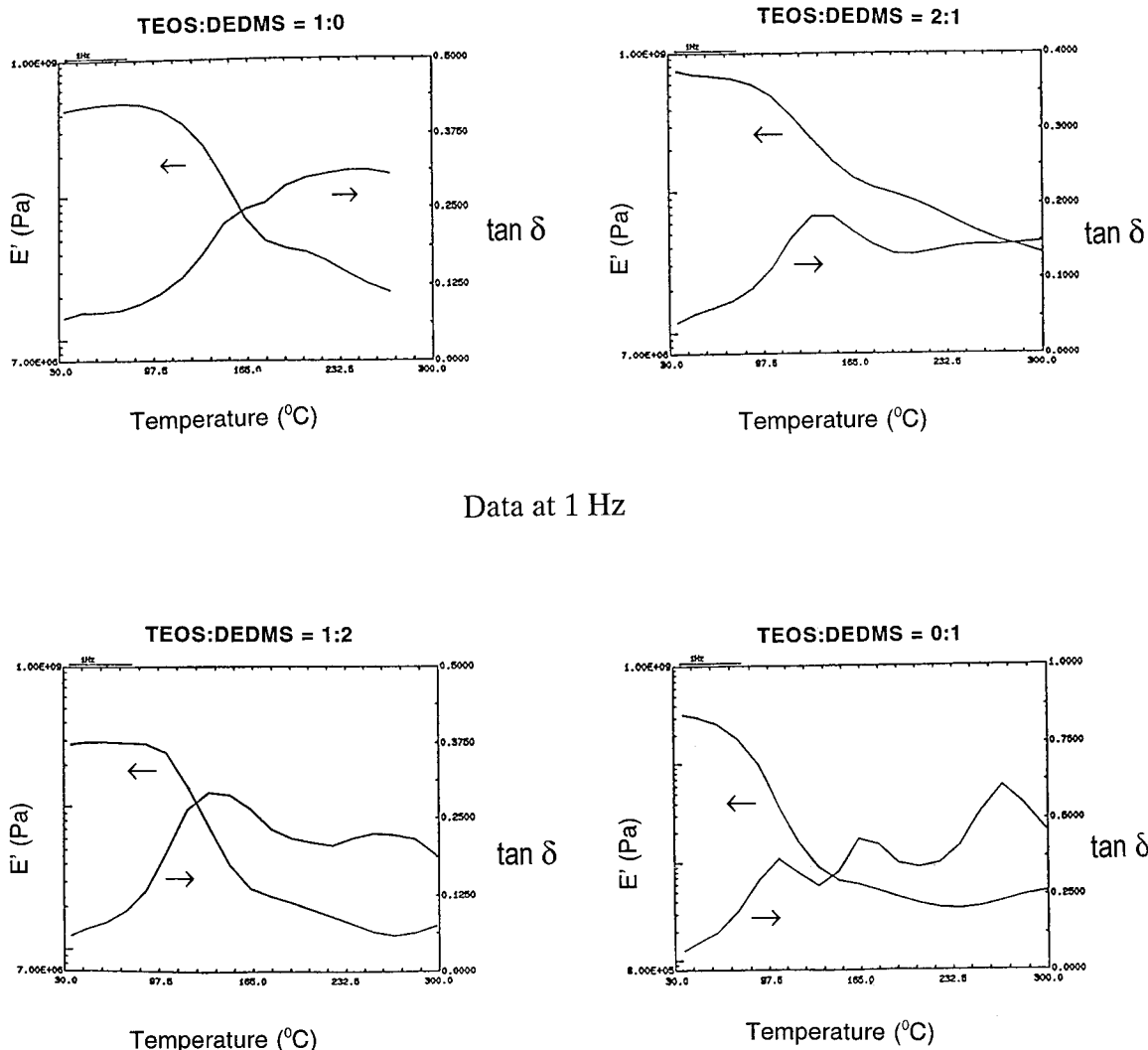


Figure 6 E' and $\tan \delta$ versus temperature for unfilled Nafion[®]-H⁺ and hybrids having indicated Q : D molar ratios at 1 Hz.

by their entrapment in rigid silicon oxide domains during the *in situ* sol-gel process. Side chains that are restricted in this way might also decrease main chain mobility, which in turn might account for the increase in T_m . In the case of this hybrid, E' initially increases on increasing the temperature from ~ 35 to 100°C . We suggest that increasing the temperature drives further condensation of unreacted $\equiv\text{Si}-\text{OH}$ groups within the clusters of Nafion[®], as described previously. This process would enhance material stiffness through increased silicon oxide crosslinking and the increased entrapment of side chains within this phase. Although the melting transition seems rather broad at 1 Hz, the family of scans at the different frequencies (not shown) shows that this peak in fact becomes narrower and shifts to lower temperatures with decreasing frequency, a conse-

quence of the fact that the time scale of the experiment is increasing.

For the 2 : 1 hybrid, there is a strong $\tan \delta$ peak at $\sim 145^\circ\text{C}$ (T_α) corresponding to a drop in E' at 1 Hz. We propose that the decrease in T_α relative to that of the 1 : 0 hybrid is due to the fact that D units disrupt Q-based structures and render them more flexible, thus diminishing the cohesion among side chains as they are packed in a given cluster and embedded in the ORMOSIL nanophase. Although a significant feature is not present in the region of melting in Figure 6, it is clearly seen in Figure 8 that a broad peak does emerge, becomes stronger, and shifts to lower temperatures with decrease in frequency. E' for this, as well as for the following hybrids, does not undergo the initial increase with increasing temperature as seen for the 1 : 0 hybrid. This is attrib-

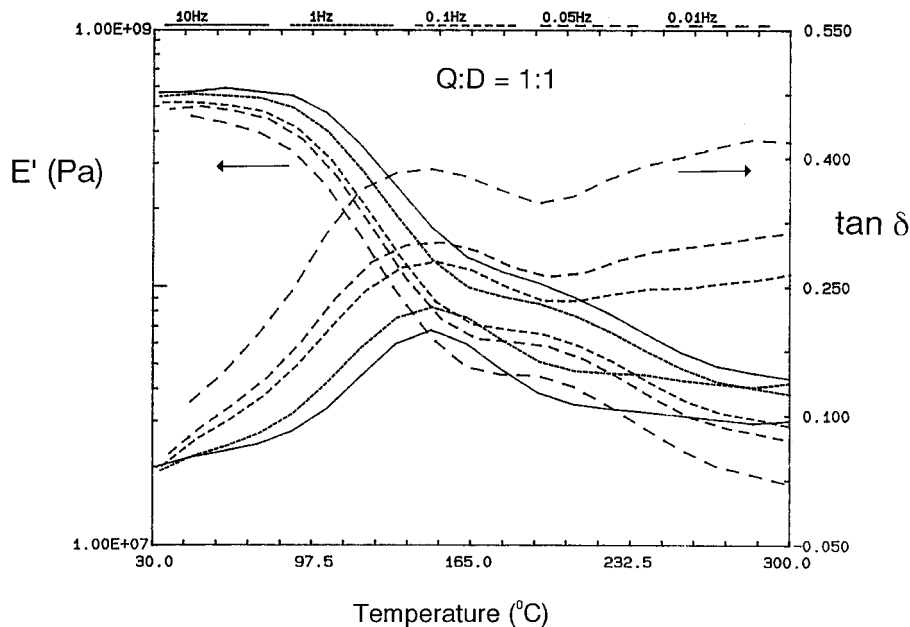


Figure 7 E' and $\tan \delta$ versus temperature for the hybrid having Q : D = 1 : 1 over the frequency range of 0.01–10 Hz.

uted to a lower fraction of unreacted $\equiv\text{Si}-\text{OH}$ groups that are available for crosslinking *via* condensation reactions owing to a larger fraction of D units that act as spacers between potentially reactive silanol groups.

For the 1 : 1 hybrid, T_α at 1 Hz is maintained at $\sim 145^\circ\text{C}$. Whereas Figure 7 illustrates the dependence of the E' and $\tan \delta$ curves on frequency

for the 1 : 1 hybrid, the same general behavior is in fact displayed for all of the hybrids. The first, T_α -related inflection point shifts to slightly higher temperatures with increasing frequency, although this kinetic effect is more pronounced for the 2 : 1 hybrid as seen in Figure 8. Regardless of whether the α or melting transition is involved, a decrease in frequency increases the time scale

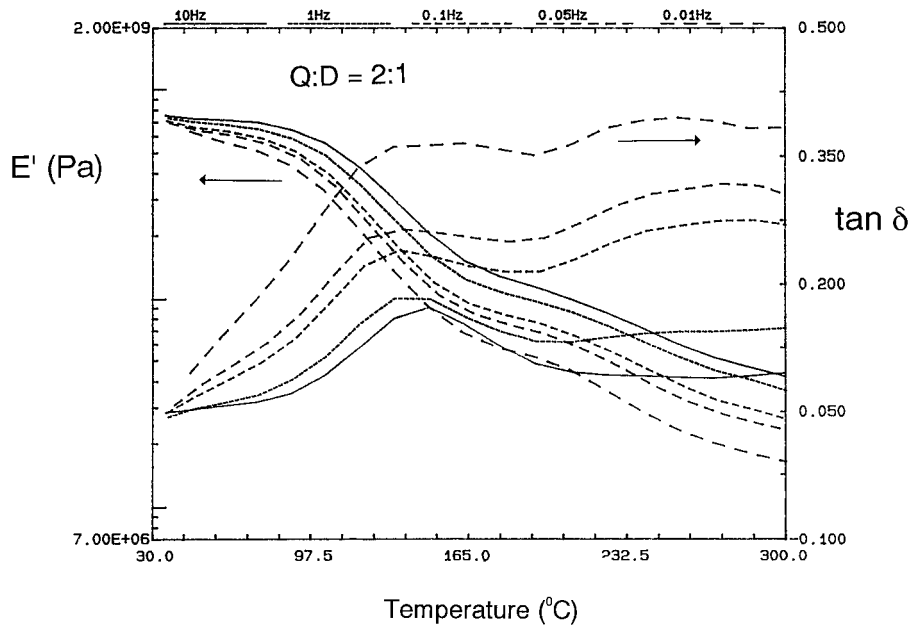


Figure 8 E' and $\tan \delta$ versus temperature for the hybrid having Q : D = 2 : 1 over the frequency range of 0.01–10 Hz.

of the experiment (i.e., cycle of driven oscillation) during which molecular motions can be monitored.

Two $\tan \delta$ peaks are present for the 1 : 2 hybrid at $T_\alpha \sim 135^\circ\text{C}$ and $T_m \sim 250^\circ\text{C}$. Finally, for the 0 : 1 hybrid, three $\tan \delta$ peaks appear around 105, 165, and 270°C . On inspection of the storage modulus curve, 105°C corresponds to the greatest decline in E' that reflects a greatly depressed T_α . Flexible dimethylsiloxane molecules within the clusters would seem to plasticize this phase to account for the low T_α . The event occurring at 270°C would seem to be melting, although the cause for the upward shift in this DMA-based T_m is unknown, especially because the DSC-based T_m is shifted downward with the trend.

The assignments of the transitions in Figures 6–8 are basically reasonable within the context of DMA, coupled with a knowledge of thermal transitions observed for unfilled Nafion® in prior studies. It is known that physical transitions for Nafion®, other than melting appear weak, at best, using the DSC technique so that it is compelling to assign the major peak in Figure 4 to incorporated solvent volatilization as described at length previously. The major thermal event observed in Figures 6–8 is clearly not melting, and a higher temperature transition does exist on these curves, in the correct position, that can account for melting. The shifting of both DSC transitions (T_α , T_m) correlate well with the shifting of the major DMA transition (T_α) with filler composition, although the presence of an additional DMA peak for the 0 : 1 hybrid remains to be explained.

In comparing peak positions observed in DMA spectra with those appearing in DSC scans, it should be remembered that transition temperatures are a function of the time scale of the experiment (i.e., heating rate), as well as oscillation frequency (as seen in Figures 7 and 8). For this reason, the same transition may appear at somewhat different temperatures using the two methods.

Mechanical Tensile Analysis

Stress *versus* strain curves for these hybrids, as well as for the unfilled dry Nafion®-H⁺ control, are seen in Figure 9. None of the samples is brittle. Because unfilled Nafion®-H⁺ is ductile, brittleness might reflect a percolation of a glassy phase over macroscopic distances, which is apparently not the case. The fact that all hybrids exhibit ductility implies, as in earlier studies,⁹ that the filler particles exist in single isolation rather than

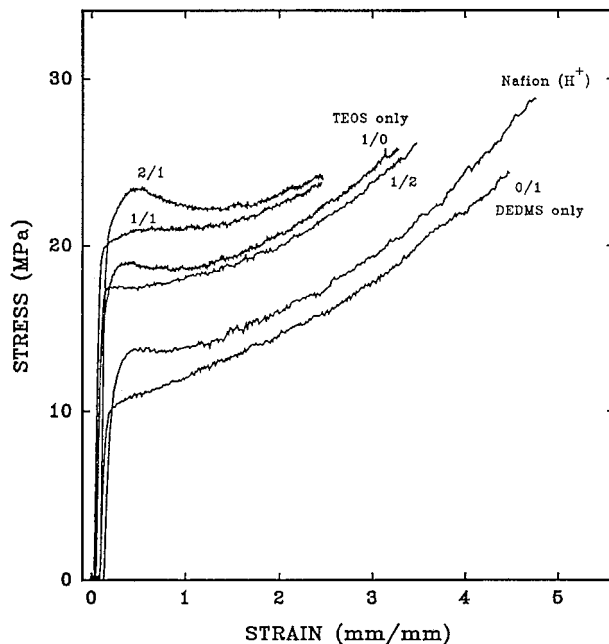


Figure 9 Mechanical tensile stress *versus* strain for unfilled Nafion®-H⁺ and hybrids having indicated Q : D ratios.

being contiguous. The 0 : 1 hybrid has the most ductility, approaching that of Nafion®-H⁺, but exhibits lower strength than the latter. Apparently, the dimethylsiloxane phase lowers material cohesion, as also implied by the DSC and DMA studies of this hybrid. On the other hand, for the hybrid progression 0 : 1 → 1 : 2 → 1 : 1 → 2 : 1, the curves monotonically shift upward to indicate increasing tensile strength, and elongation-to-break decreases in this order. All of the curves, save for the 0 : 1 case, lie above that of Nafion®-H⁺. The 1 : 0 sample curve, situated in the middle of the hybrid curves, is an exception to this rule. A significantly enhanced interfacial compatibility in the 2 : 1 and 1 : 1 hybrids, relative to the 1 : 0 hybrid, is envisioned; this might be attributed to the added hydrophobic D units contacting the hydrophobic perfluorocarbon matrix. Save for the 0 : 1 hybrid, material strength is enhanced in this way. We propose that strength is accounted for, in large part, by constraints posed by entanglements formed between the ORMOSIL or pure silicon oxide phases and the long Nafion® side chains during the sol-gel reaction.

A yield point is observed for unfilled Nafion®-H⁺. Whereas the processes operative during yielding for Nafion® are not known, the breaking of interchain interactions existing within the sulfonate clusters might be a primary agent. The lack of yielding shown by the 0 : 1 hybrid is in harmony

with this idea, in that the small oligomeric dimethylsiloxane rings constitute an uncrosslinked, weak hydrophobic phase that interacts rather weakly with the polar groups of the side chains of Nafion® and serve as a defect in the packing of side chains. It is also noted that, in the hybrid progression, 1 : 0 → 2 : 1 → 1 : 1 → 1 : 2 → 0 : 1 yielding character is gradually reduced to where it does not exist. The increasing “softness” of the nanostructured filler and structure-breaking effect on rigid Q structures of inserted D units is proposed as being responsible for this yield behavior; side chains become increasingly less constrained in clusters. Moreover, D units cannot hydrogen-bond with —SO₃H groups as can ≡SiOH groups in Q units. The 1 : 0 and 2 : 1 hybrids have more distinct yield points than unfilled Nafion®. In these two hybrids, the high Q unit content would cause nanophase rigidity.

The tensile moduli of all the curves seem to be about the same. Modulus is a property that has meaning for small (i.e. elastic) deformations. Thus, the mechanical tensile properties that are affected by the incorporation of these *in situ*-grown fillers are ultimate properties that are manifested at large deformations.

Solvent Uptake

The silicon oxide nanophase in the 1 : 0 hybrid formulated under acid catalysis was found to contain numerous ≡SiOH groups.³ When D units are inserted between Q units in the synthesis of an ORMOSIL nanophase, the network is more linear and flexible, as well as more hydrophobic than a nanophase based solely on Q units. Thus, in the hybrid progression from 1 : 0 to the 0 : 1, the sorption affinity for polar solvents is expected to be gradually reduced. Our primary motivation for these simple experiments was to establish relative liquid sorption affinities that might be relevant within the context of liquid pervaporation cells for solvent recovery, liquid product enrichment in industrial processes, gas separation technologies, and direct MeOH fuel cells.

The equilibrium weight percent uptakes of these three solvents by the 1 : 0, 1 : 1 and 0 : 1 hybrids, as well as unfilled Nafion®-H⁺ are represented by the bar graphs in Figure 10.

Water Uptake

Unfilled Nafion®-H⁺ exhibits 15% water uptake. The water uptake of the 1 : 0 hybrid, 20%, is greater than that of the unfilled membrane. We

attribute this increase to the insertion, within clusters, of numerous ≡SiOH groups to which H₂O molecules can be hydrogen-bonded. In proceeding to the 1 : 1 hybrid, the water uptake is 11%, which is significantly lower than that of the 1 : 0 hybrid and lower than that of pure Nafion®-H⁺. Our ²⁹Si solid-state NMR studies of this intermediate hybrid indicated that the internal Q : D ratio is also 1 : 1.⁵ The large fraction of D units renders the interior of this composite more hydrophobic than that of the aforementioned two membranes, which accounts for its lower uptake. The 0 : 1 hybrid shows the lowest water uptake, 9%, which is reasonable considering that the filler consists exclusively of D units that are predominantly in oligomeric rings.⁵ This uptake is lower than that for the 1 : 0 hybrid by 11%.

A significant conclusion of these simple liquid uptake studies is that hydrophilicity can be molecularly tailored to be more or less than that of pure Nafion®-H⁺ by adjusting the TEOS : DEDMS monomer feed ratio.

MeOH Uptake

Of the three materials, pure Nafion®-H⁺ has the highest MeOH uptake at 95%. In contrast, the MeOH uptake of the 1 : 0 hybrid was rather low at 51%. This order is reversed from that for the sorption of H₂O by these two particular membranes. MeOH is less polar than H₂O, so that it would interact less strongly than the latter with ≡SiOH groups. Also, the filling of the free volume within sulfonic acid clusters by silicon oxide structures might obstruct the penetration of these spaces by MeOH molecules. Although H₂O molecules would also be blocked from the cluster interior in this way, they could be attached, more strongly, to the numerous ≡SiOH groups at the nanoparticle surfaces.

The MeOH uptake for the 1 : 1 hybrid is 63%, which is considerably greater than the H₂O uptake for this hybrid (11%). The less-polar MeOH molecule is more energetically compatible with this ORMOSIL nanophase that contains around 50% D units. For the 0 : 1 hybrid, a slightly lower uptake of 61% is seen, despite the fact that the filler has a significantly different molecular structure.

The MeOH uptake of each hybrid, as well as of pure Nafion®-H⁺, is greater than its H₂O uptake. It is noteworthy that the MeOH : H₂O uptake ratio is lowest for the 1 : 0 hybrid, which is reasonable given the aforementioned rationale. In this discussion of sorption preference experiments, it

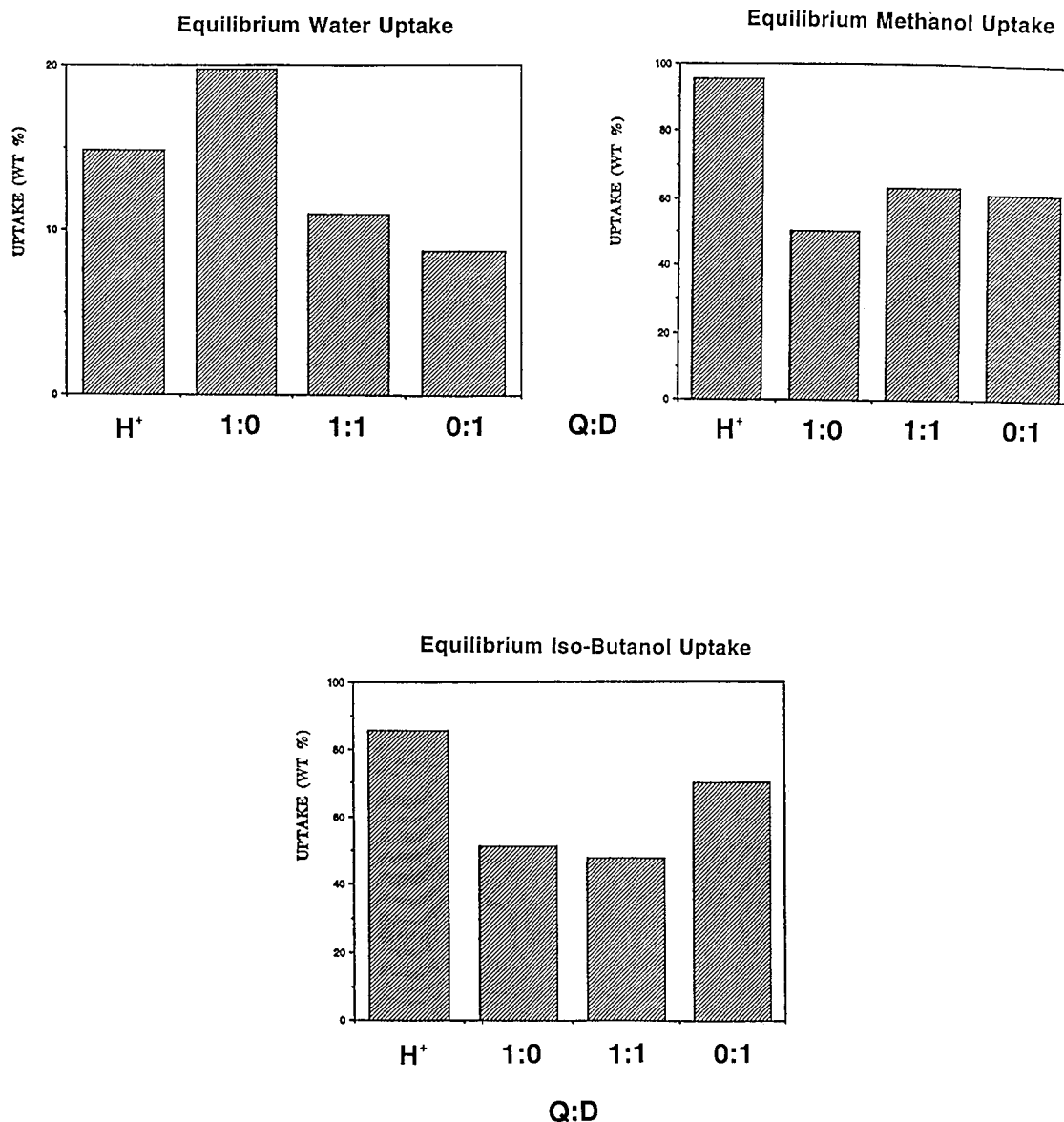


Figure 10 Equilibrium water, MeOH, *i*-BuOH percent liquid uptakes for unfilled Nafion®-H⁺ and hybrids having indicated Q : D ratios.

should be pointed out that pure solvents were used and the more complex internal partitioning of uptakes from binary liquid mixtures remains to be investigated.

Isobutanol (i-BuOH) Uptake

i-BuOH swells Nafion®-H⁺, as well as the three hybrids, to a considerably greater degree than water. Because the *i*-BuOH molecule is considerably less polar than the MeOH molecule, the former would be more energetically compatible in the diffuse interfacial regions that were discussed by Yeager and coworkers²⁴ rather than in the centers

of the clusters of Nafion®. This might be implicated in the somewhat lower uptake of *i*-BuOH relative to MeOH. For pure Nafion®-H⁺, *i*-BuOH uptake is ~ 85% lower than that for MeOH by a difference of almost 10%. For the 1 : 0 case, *i*-BuOH uptake is the same as that for MeOH (51%). This is interesting because *i*-BuOH not only swells the Nafion® template to a lesser degree than MeOH, but the former interacts more weakly with the very polar pure silicon oxide phase.

In proceeding to the 1 : 1 hybrid, the uptake decreases but slightly to 48% relative to the 1 : 0 hybrid. Despite the fact that the 1 : 0 and 1 : 1

nanophases have significantly different structures and polarities, their *i*-BuOH uptakes do not differ greatly. Perhaps the simple steric blocking of the weakly interacting *i*-BuOH molecules from the clusters accompanied by little energetic discrimination is the dominant mechanism in both cases.

For the 0 : 1 hybrid, *i*-BuOH uptake greatly increases, relative to the values for the 1 : 0 and 1 : 1 hybrids, to 70%. In this case, sorption would be mainly governed by Van der Waals interactions between this rather nonpolar solvent and nonpolar nanophase. The uptake of H₂O, MeOH, and *i*-BuOH by the 0 : 1 hybrid increases from 8.7% to 61% to 70%, respectively, which reflects a broad range of polar interaction magnitude.

Dielectric Relaxation Studies

$\log_{10}\epsilon'$ and $\log_{10}\epsilon''$ are plotted as a function of $\log_{10}f$ for the hybrid series 1 : 0, 1 : 1, and 0 : 1, as well as for pure Nafion®-H⁺, at 22°C, in Figure 11. All sample types were sandwiched between the electrodes immediately after being dried and removed from the oven to minimize the effect of residual solvent and water. All relaxation spectra are reproducible with regard to major features.

The first significant observation is that all hybrids, as well as the unfilled control, displayed rather high values of ϵ' in the low-frequency regime. This phenomenon might be attributed, as in earlier reports of the dielectric relaxation spectra of electrolyte-imbibed Nafion®,^{25,26} as well as Nafion®/SiO₂ nanocomposites,⁷ to an internal interfacial polarization (i.e., a high volume polarizability resulting from the accumulation ↔ dissipation of charges at the interfaces between the clusters and perfluorocarbon phase).

A distinct ϵ'' peak is seen for the 0 : 1 hybrid around $f_{\max} = 1500$ Hz (average relaxation time $\approx 1.1 \times 10^{-4}$ s) and a weaker relaxation is visible at higher frequencies. The low-frequency peak corresponds to an inflection point at the same frequency on the corresponding ϵ' plot; the same holds for the weaker relaxation. On close inspection, weak relaxations are also seen in the same higher frequency range (10^4 – 10^5 Hz) for the 1 : 1 hybrid and unfilled Nafion®-H⁺, but not for the 1 : 0 hybrid. As plotted in log–log fashion, the ϵ'' curve for the 1 : 0 hybrid is very linear over a broad frequency range and therefore obeys a power law ($\epsilon'' \sim f^{-n}$) that might reflect long range (intercluster ion hopping) as discussed earlier.²⁷ As described previously, clusters in the 1 : 0 hybrid contain numerous ≡SiOH groups. It is con-

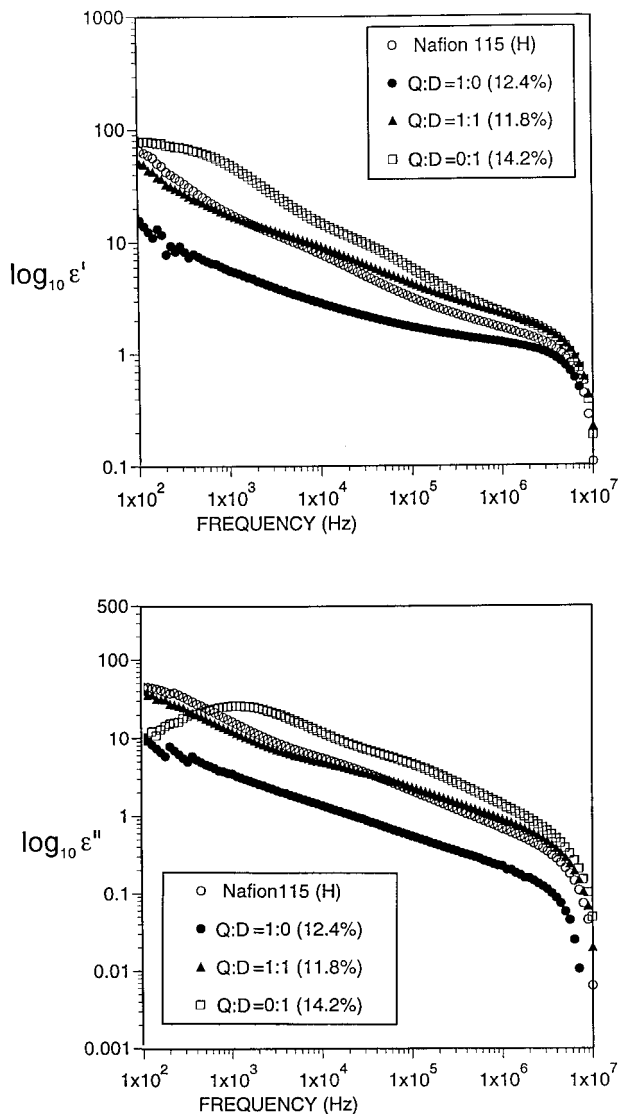


Figure 11 Dielectric storage and loss permittivity versus f , at 22°C, for unfilled Nafion®-H⁺ and hybrids having indicated Q : D molar ratios.

ceivable that protons supplied by —SO₃H groups can hop along hydrogen bonding pathways within hydration structures that are bound to ≡SiOH groups. Moreover, the clusters are close enough so that energetic barriers for intercluster proton hopping would conceivably be low. Based on the positions of similar weak peaks observed in earlier studies of like systems, we suggest that the high-frequency relaxation is due to the cluster/matrix interfacial polarization mechanism,²⁶ although this assertion certainly needs to be verified.

The ϵ' and ϵ'' versus f curves for the 0 : 1 sample are positioned above the respective curves for

all of the other materials. On the other hand, the curves for 1 : 0 hybrid, at the other extreme of the Q : D compositional series, are positioned below those of all the other materials. The Nafion®-H⁺ and 1 : 1 hybrid curves are rather close to, and cross each other. Within the general concept of molecular mobility, or relaxations, it seems that the 0 : 1 hybrid is the most and the 1 : 0 hybrid the least motionally facile over this frequency range. Regardless of mechanistic detail, this result would seem to reflect the inherent conformational flexibility of pure D structures contrasted with the rigidity of pure Q structures.

The pure D oligomeric phase in the 0 : 1 hybrid would be the most energetically compatible with the Nafion® hydrophobic matrix. Assuming that the peak at ~ 1500 Hz is related to chain segmental or, more likely, side chain mobility at this temperature, incorporated dimethylsiloxane molecules might act as a plasticizer to increase molecular mobility. The fact that the 0 : 1 hybrid has the lowest DMA-based transition and greatest elongation-to-break in the mechanical tensile experiment is in harmony with this view. The fact that D units cannot hydrogen bond with —SO₃H groups and can block hydrogen bonding between —SO₃H groups, is also relevant within this context. Given this interpretation, the weakest dielectric activity and absence of relaxation peaks for the 1 : 0 hybrid can be rationalized in terms of a matrix-incompatible and rigid silicon oxide phase in which the long sulfonate-ended perfluoroalkylether side chains are embedded and thereby immobilized.

In the future, these preliminary dielectric relaxation spectra experiments will be performed at higher temperatures, in part, to determine activation energies.

CONCLUSIONS

Unfilled Nafion®-H⁺ exhibits a broad endothermic DSC transition with a peak at ~ 215°C, which significantly shifts upward for the 1 : 0 sample to ~ 235°C, but then progressively shifts downward with decreasing Q : D. We rationalized that this endotherm arises mainly from the release of H₂O molecules that were bound to surface ≡Si—OH groups in the silicon oxide and ORMOSIL nanophases, as well as to condensation reactions among these groups.

A higher temperature peak in the melting region exhibited a gradual shifting to lower temperatures with decreasing Q : D. For the 1 : 0 hybrid,

it was proposed that the main chains, *via* coupling through the side chains, are tethered in silicon oxide nanoparticles so as to hinder their mobility with the result that T_m increases. However, progressive insertion of D units into silicon oxide nanostructures reduces ORMOSIL conformational rigidity so that the side chains are anchored in this softer phase to a lesser degree. In this way, T_m would shift to lower temperatures with decreasing Q : D. The decrease in T_α observed in the progression from the 1 : 0 to 0 : 1 hybrid is rationalized in terms of an increasing fraction of D units that disrupt Q-based structures and render them increasingly more flexible, thus diminishing cohesion among packed side chains.

TGA degradation profiles for all materials indicate that the first loss step for Nafion®-H⁺ shifts to significantly higher temperatures as the ratio D : Q increases and we hypothesize that an increase in D unit fraction inhibits Q unit degradation by evolved HF with concomitant SiF₄ evolution.

Two DMA tan δ peaks are seen for unfilled Nafion®-H⁺ and the hybrids: (1) a transition, labeled α , is proposed to arise from side chain motions within clusters and (2) a higher temperature transition is due to crystallite melting. We suggest that the increase in T_α that is observed in passing from unfilled Nafion® to the 1 : 0 hybrid is due to immobilization of side chains by their entrapment in rigid silicon oxide domains. This side chain restriction might also decrease main chain mobility that would account for the observed increase in T_m .

Mechanical tensile analysis showed that the 0 : 1 hybrid has the greatest ductility and least strength. The hybrid progression 0 : 1 → 1 : 2 → 1 : 1 → 2 : 1 generates increasing tensile strength and decreasing ductility, with the 1 : 0 case being an exception; all stress-strain curves, save for the 0 : 1 case, lie above that of Nafion®-H⁺. We propose that this strength enhancement is due to constraints posed by entanglements formed between the ORMOSIL and pure silicon oxide phases and the long side chains of Nafion®. In the progression 1 : 0 → 0 : 1, yielding is monotonically reduced, presumably due to the increasing filler softness and the structure-breaking effect of D units so that side chains are increasingly less constrained in clusters.

The water affinity of the 1 : 0 hybrid is greater than that of Nafion®-H⁺, due to the insertion of numerous hydrophilic ≡SiOH groups. The water affinity of the 1 : 1 hybrid is lower than that of the 1 : 0 hybrid and pure Nafion®-H⁺, owing to

the large fraction of hydrophobic D units in the former, and the 0 : 1 hybrid shows the lowest water uptake. It is significant that hydrophilicity can be chemically tailored to be more or less than that of pure Nafion®-H⁺. Of the three materials tested, Nafion®-H⁺ has the highest MeOH uptake, and the uptake of the 1 : 0 hybrid was the lowest, because MeOH interacts less strongly than H₂O with ≡SiOH groups. MeOH uptake for the 1 : 1 hybrid is considerably greater than that for H₂O as less polar MeOH molecules are more compatible with this partially organic nanophase. For the 0 : 1 hybrid, uptake is only slightly lower, despite the fact that there are twice as many D units present. *i*-BuOH swells Nafion®-H⁺, as well as the three hybrids, to a considerably greater degree than water but somewhat less than MeOH. For the 1 : 0 case, *i*-BuOH uptake is the same as that for MeOH; *i*-BuOH uptake for this hybrid is lower than that of Nafion®-H⁺. The affinity of the 1 : 1 hybrid for *i*-BuOH is only slightly less than that of the 1 : 0 hybrid although the two nanophases have different structures and polarities. *i*-BuOH uptake of the 0 : 1 hybrid greatly increases relative to those of the other hybrids. The uptake of H₂O, MeOH, and *i*-BuOH by the 0 : 1 hybrid increases from 8.7 to 70%, reflecting a broad range of polar *versus* nonpolar interactions.

In dielectric relaxation experiments, all hybrids displayed high ϵ' values at low frequencies, which is tentatively attributed to internal interfacial polarization. A distinct relaxation for the 0 : 1 hybrid around 1.5 kHz might be related to side chain mobility that is facilitated by plasticizing dimethylsiloxane molecules. A weaker relaxation in the range 10⁴–10⁵ Hz exists for the 0 : 1 and 1 : 1 hybrids and Nafion®-H⁺, but not for the 1 : 0 hybrid and might arise from relaxation of cluster/matrix interfacial polarization. The 1 : 0 hybrid exhibits the behavior $\epsilon'' \sim f^{-n}$ over a broad frequency range, suggestive of intercluster proton hopping. The weakest dielectric response for the 1 : 0 hybrid is rationalized in terms of a rigid silicon oxide phase in which side chains are immobilized.

It is generally concluded that silicon oxide, ORMOSIL, and dimethylsiloxane nanostructures in Nafion®—and the properties of these hybrid materials—can be tailored by *in situ* sol–gel chemistry.

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REFERENCES

1. T. D. Gierke, G. E. Munn, and F. C. Wilson, *J. Polym. Sci.: Polym. Phys. Ed.*, **19**, 1687 (1981).
2. K. A. Mauritz, I. D. Stefanithis, S. V. Davis, R. W. Scheetz, R. K. Pope, G. L. Wilkes, and H.-H. Huang, *J. Appl. Polym. Sci.*, **55**, 181 (1995).
3. Q. Deng, R. B. Moore, and K. A. Mauritz, *Chem. Mater.*, **7**, 2259 (1995).
4. Q. Deng, K. M. Cable, R. B. Moore, and K. A. Mauritz, *J. Polym. Sci.: B: Polym. Phys. Ed.*, **34**, 1917 (1996).
5. Q. Deng, W. Jarrett, R. B. Moore, and K. A. Mauritz, *J. Sol-Gel Sci. & Technol.*, **7**, 177 (1996).
6. Q. Deng, Y. Hu, R. B. Moore, C. L. McCormick, and K. A. Mauritz, *Chem. Mater.*, **9**, 36 (1997).
7. K. A. Mauritz and I. D. Stefanithis, *Macromolecules*, **23**, 1380 (1990).
8. Z. D. Deng and K. A. Mauritz, *Macromolecules*, **25**, 2369 (1992).
9. K. A. Mauritz, R. F. Storey, and C. K. Jones, in *Multiphase Polymer Materials: Blends, Ionomers and Interpenetrating Networks*, ACS Symposium Series No. 395, L. A. Utracki and R. A. Weiss, Eds., American Chemical Society, Washington, DC, 1989, Chap. 16.
10. I. D. Stefanithis and K. A. Mauritz, *Macromolecules*, **23**, 2397 (1990).
11. M. Falk, in *Perfluorinated Ionomer Membranes*, A. Eisenberg and H. L. Yeager, Eds., ACS Symposium Series 180, American Chemical Society, Washington, DC, 1982, Chap. 8.
12. J. Ostrowska and A. Narebska, *Colloid & Polym. Sci.*, **261**, 93 (1983).
13. J. Ostrowska and A. Narebska, *Colloid & Polym. Sci.*, **262**, 305 (1984).
14. D. J. Barnes, in *Structure and Properties of Ionomers*, M. Pineri and A. Eisenberg, Eds., D. Reidel, Dordrecht, The Netherlands, 1987, p. 501.
15. M. Escoubes and M. Pineri, in *Structure and Properties of Ionomers*, M. Pineri and A. Eisenberg, Eds., D. Reidel, Dordrecht, The Netherlands, 1987, p. 341.
16. C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, Inc., Boston, 1990, p. 627.
17. L. L. Hench and J. K. West, *Chem. Rev.*, **90**, 33 (1990).

18. R. K. Iler, in *The Chemistry of Silica*, Wiley, New York, 1979.
19. J. Kratochvila, Z. Salajka, A. Kazda, Z. Kadlc, J. Soucek, and M. Gheorghiu, *J. Non-Cryst. Solids*, **116**, 93 (1990).
20. J. Y. Ying and J. B. Benziger, *J. Am. Ceram. Soc.*, **76**, 2561 (1993).
21. C. A. Wilkie, J. R. Thomsen, and M. L. Mittleman, *J. Appl. Polym. Sci.*, **42**, 901 (1991).
22. Y. Miura and H. Yoshida, *Thermochim. Acta*, **163**, 161 (1991).
23. W. G. F. Grot, G. E. Munn, and P. N. Walmsley, *141st Natl. Meet. Electrochem. Soc.*, Houston, TX, 1972.
24. H. L. Yeager and A. E. Steck, *J. Electrochem. Soc.*, **128**, 1880 (1981).
25. Z. D. Deng and K. A. Mauritz, *Macromolecules*, **25**, 2369 (1992).
26. S. Su and K. A. Mauritz, *Macromolecules*, **27**, 2079 (1994).
27. K. A. Mauritz, *Macromolecules*, **22**, 4483 (1989).