

# Hybrids of perfluorosulfonic acid ionomer and silicon oxide by sol–gel reaction from solution: Morphology and thermal analysis

R. A. Zoppi, I. V. P. Yoshida and S. P. Nunes\*

University of Campinas, Institute of Chemistry, C. Postal 6154,  
CEP 13083-970 Campinas-SP, Brazil

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NAFION®/silicon oxide hybrids were prepared from solution by hydrolysis/polycondensation of alkoxy silanes. Transparent, but brittle films were obtained when TEOS was used as the inorganic polymer precursor, showing a lamellar structure by transmission electron microscopy. Part of the TEOS was substituted by TMDES to increase the film flexibility. For substitution higher than 10% phase separation was clearly observed by scanning and transmission electron microscopy. The thermal analysis of NAFION® and hybrids with different inorganic contents showed two main endothermic transitions, one assigned to the NAFION® ionic clusters and the other to the melting of the perfluorinated matrix. The cluster transition temperature decreases as the TEOS content increases up to 50 wt%, but than increases as the TEOS content reaches 80 wt%. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

The development of organic/inorganic polymer hybrids<sup>1–15</sup> opened the possibility of tailoring new materials with a versatile morphology control, even in the nanoscale, combining a wide range of physical properties and extending their applicability.

A simple procedure to grow an inorganic phase inside an organic matrix is based in the sol–gel process, usually by hydrolysis and condensation of alkoxy silanes. A fine dispersion of the inorganic phase on the molecular level can be obtained and a progressive change of the film composition from pure organic to pure inorganic is possible. Growing the inorganic polymer in a hydrophobic medium, to give hybrids such as PMMA/silicon oxide<sup>1</sup> leads to phase separation, which may be followed by light scattering or electron microscopy. A similar reaction in a hydrophilic polymer matrix or in a matrix containing functionalized groups may lead to transparent films, in which no macroscopic phase separation can be detected. Phase separation should be avoided, for instance, in films developed for optical purposes.

A field of potential interest for polymer hybrids is the preparation of membranes for gas separation<sup>2</sup>, for facilitated transport<sup>10</sup> or for catalytic purposes. The introduction of an inorganic phase in an organic elastomeric membrane may have the effect of inhibiting swelling and therefore increasing the gas selectivity<sup>2</sup>. On the other hand, the introduction of organic crown groups in inorganic membranes may turn them selective, e.g. for carrier transport of potassium ions<sup>10</sup>.

NAFION® has been very successful in the membrane field due to its high chemical resistance, especially in the chlor-alkali process. NAFION® is an ionomer with a polymeric backbone similar to TEFLON® with pendant

sulfonic acid groups. The ionic groups are known to form hydrophilic clusters in the hydrophobic and chemical stable TEFLON® matrix which give unique permeability characteristics to the films as ion-exchange membranes. NAFION® has also already been used for immobilization of palladium complexes for catalytic purposes<sup>11</sup> in membrane reactors. Also due to its hydrophobic/hydrophilic structure, NAFION® has been investigated by Mauritz and co-workers<sup>12–15</sup> for the preparation of hybrid materials. NAFION® is supplied in quite insoluble films, which, however, swell in polar solvents. The films were swollen in water/methanol or water/propanol solutions and further immersed in alcohol/tetraethoxysilane (TEOS) solutions. The condensation and hydrolysis of TEOS promoted the growth of a silicon oxide phase inside the NAFION® clusters. Since the inorganic polymerization was restricted to the cluster regions, nanoparticles no larger than about 50 Å prevailed. By this procedure, the amount of incorporated inorganic component is also limited up to about 40 wt%.

Here in this work a new procedure for preparation of hybrids of NAFION® is reported, allowing the incorporation of continuously increasing amounts of the inorganic phase, going from the pure organic film up to the pure inorganic material. Since the hybrid films are formed from a mixed NAFION®/TEOS solution, instead of using a previously formed NAFION® film, the growth of the inorganic polymer is not restricted to small clusters. On the other side the form and size of NAFION® clusters are highly dependent on the silicon oxide content. The hybrids are characterized by transmission electron microscopy and by thermal analysis.

## EXPERIMENTAL

### Materials

NAFION® is an ionomer with a polymeric backbone similar to TEFLON® (–CF<sub>2</sub>–CF<sub>2</sub>–) and pendant sulfonic

\* To whom correspondence should be addressed

acid groups. Although known as an insoluble polymer, under certain extreme conditions it may form a solution<sup>16,17</sup>. A 5 wt% solution in propanol was supplied by Du Pont with the trade name NAFION 1100 EW. Tetraethoxysilane (TEOS) was purchased from Aldrich. 1,1,3,3-Tetramethyl-1,3-diethoxy disiloxane (TMDES) was supplied by Hüls.

*Sample preparation*

Different volumes of TEOS were carefully added to a continuously stirring 5 wt% NAFION® solution in propanol, containing also about 10 wt% water. Drops of a 0.15 M HCl aqueous solution were then added. Usually 5 ml of solution were further stirred for 16 h at room temperature (25°C), maintained 24 h more without stirring and transferred to TEFLON® Petri dishes with 5 cm diameter. Glass dishes were avoided due to undesirable sample adhesion in some compositions. The dishes were kept inside a desiccator saturated with propanol vapour. A polymeric silicon oxide was grown by hydrolysis and condensation of TEOS. The desiccator was then kept semi-opened to allow slow solvent evaporation during 1 week. The samples were further dried under vacuum at 30°C during 1 week more before characterization. A considerable shrinkage was observed.

Samples with the following NAFION®/TEOS initial weight proportions were prepared: 100/0, 80/20, 50/50

and 20/80. Assuming total conversion of TEOS to silicon oxide, the final composition of the dry materials were respectively 100/0, 93.5/6.5, 78/22 and 46/54 wt% NAFION®/silicon oxide.

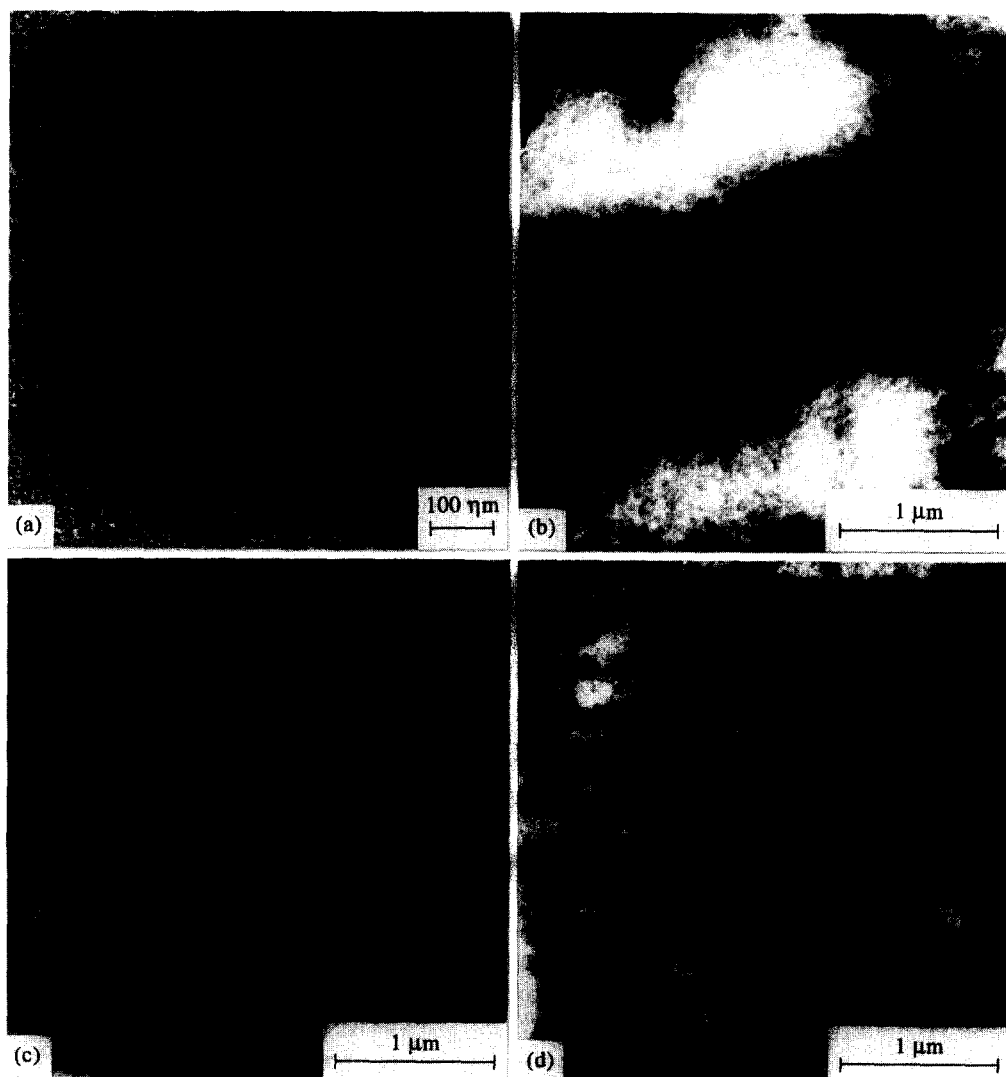
In an attempt to increase the film flexibility, part of the TEOS was up to 20 wt% substituted by TMDES. Through this procedure, more flexible siloxane segments were introduced into the inorganic part of the hybrid.

*Transmission electron microscopy*

Thin cuts were obtained in a FC4E Ultracut Leitz-Reichert-Jung cryo-ultramicrotome at -80°C with diamond knife and observed in a Zeiss CEM-902 transmission electron microscope. The microscope has a spectrometer with a photomultiplier electron detector which evaluates the presence of specific elements by electron energy loss spectroscopy (EELS). In order to evaluate the presence of Si in different regions, spectra were obtained in a electron energy loss range between 1760 and 1900 eV.

*Scanning electron microscopy (SEM)*

Samples were fractured in liquid nitrogen and coated with gold by sputtering. The fracture surfaces were observed in a JXA 840A JEOL scanning electron microscope. The microscope was equipped with a energy



**Figure 1** Transmission electron microscopy of NAFION®/silicon oxide hybrids obtained from solution in propanol after in situ hydrolysis/condensation of TEOS: (a) 100/0, (b) 80/20, (c) 50/50 and (d) 20/80 wt% NAFION®/TEOS

dispersive spectrometer (EDS) which allowed the chemical analysis of different regions in the sample. For EDS analysis, the samples were coated with carbon instead of gold.

#### Thermal analysis

Thermograms were obtained in a 2910 MDSC TA Instruments differential scanning calorimeter (d.s.c.). About 10 mg of sample were heated at 10°C/min under nitrogen from -100 up to 300°C.

The stored ( $E'$ ) and dissipative ( $E''$ ) modulus and the  $\tan \delta$  of samples containing TMDES were evaluated at isothermal conditions at 25°C in a 938 TA Instruments dynamic mechanical analyzer (DMA). Samples without TMDES were too brittle to allow a successful evaluation under the same conditions.

#### Wide angle X-ray diffraction

Diffraction patterns of NAFION® and NAFION®/TEOS hybrids were obtained in a XD-3A Shimadzu equipment with  $\text{CuK}_\alpha$  source.

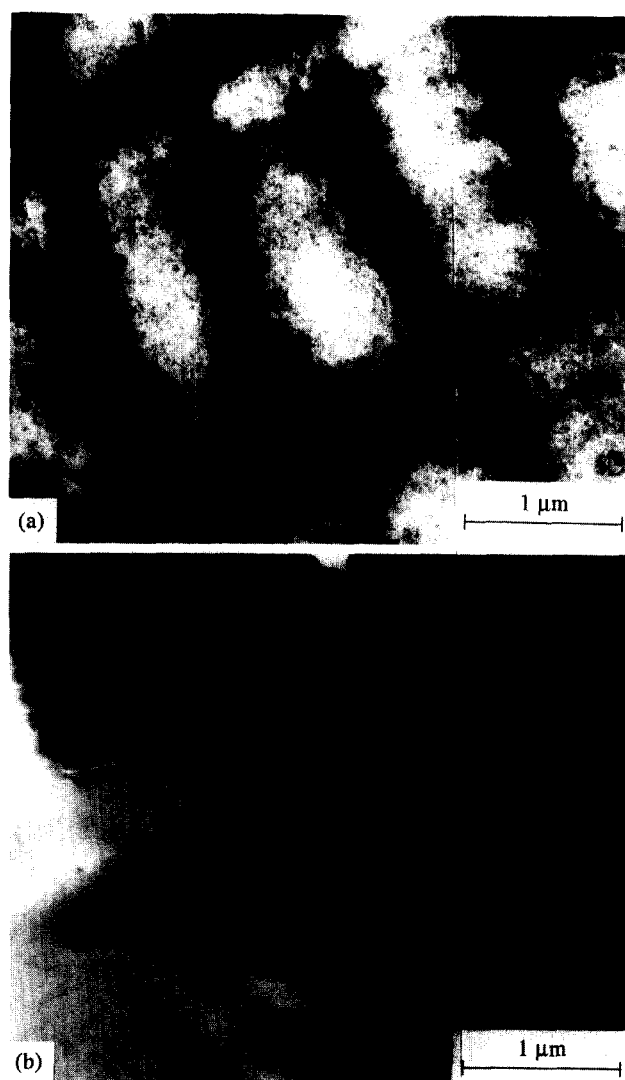
## RESULTS AND DISCUSSION

### Morphology

The main advantages of preparing hybrids of perfluor-sulfonic acid ionomers and silicon oxide from solution, using the procedure described here, instead of swelling a previously formed NAFION® membrane with TEOS, the procedure adopted by Mauritz and co-workers<sup>12-15</sup>, are the diversity of obtained morphology and the possibility of incorporating higher amounts of the inorganic component. The inorganic polymer growth is not limited to the already existent sulfonic acid clusters, but the clusters themselves are formed simultaneously to the inorganic polymerization reaction and solvent evaporation. The cluster morphology and distribution is also a function of TEOS content.

Figure 1 shows the different morphologies observed by transmission electron microscopy as a function of inorganic polymer content. Small (about 3 nm diameter) spherical clusters are observed regularly distributed all over a NAFION® film without TEOS. When 20 wt% TEOS was added to 80 wt% NAFION®, about 1.2  $\mu\text{m}$  wide stripes could be differentiated. They are aligned in the direction of solvent evaporation path, vertical to the film surface and also vertical to the cutting direction in the microtome. A finer structure can also be observed in each stripe. When the TEOS content increased, the distance between stripes decreased to about 0.3  $\mu\text{m}$  with 80 wt% TEOS.

When part of the TEOS was substituted by TMDES, the films which were originally transparent became turbid with TMDES substitution higher than 10 wt%. When observed by transmission electron microscopy, a phase separation could be detected for samples with 10, 15 and 20 wt% substitution, as shown in Figure 2. The dispersed domains had a lamellar structure with *ca.* 0.2  $\mu\text{m}$  between lamellae and the matrix was rather homogeneous. In samples with 5 wt% substitution, no large spherical domain was observed and the morphology was very similar to the morphology of an analogous sample without TMDES. TMDES also reacts by polycondensation and was incorporated into the silicon oxide network when the substitution was as high as 5 wt%. Since the inorganic segments incorporated by the TMDES polycondensation are much more hydrophobic than those



**Figure 2** Transmission electron microscopy of NAFION®/silicon oxide hybrids, obtained from a 50/50 wt% NAFION®/alkoxy silane mixture in propanol, where (a) 5 and (b) 10 wt% of TEOS was substituted by TMDES. A morphology very similar to that shown for 10% (b) was observed for 15 and 20 wt% substitution

coming from the TEOS reaction, a segregation occurs with substitution higher than 10 wt%.

EELS spectra of the dispersed domains and for the matrix in samples with phase separation were obtained and are shown in Figure 3. The domains are clearly rich in Si, a peak being observed in energy region characteristic for this element. The spectrum for matrix at the same energy range showed no sign of Si. This could be evidence that during the film formation the inorganic phase is completely segregated in domains, the matrix being constituted almost only by the organic polymer. The domains are rich in the inorganic polymer with homogeneously distributed silicon oxide and siloxane segments.

Using SEM, the same domains were observed in samples with high TMDES content, as shown in Figure 4. With EDS (Figure 5), it was confirmed that the presence of Si in domains is predominant and NAFION® is practically excluded, due to the higher hydrophobicity. The area under the Si peak is 130-fold larger than under the S peak. In the matrix, not only S but also Si could be detected by EDS, in contrast to the EELS results. The detection limit<sup>18</sup> of EDS is lower (0.1%). The reason why EDS could see Si

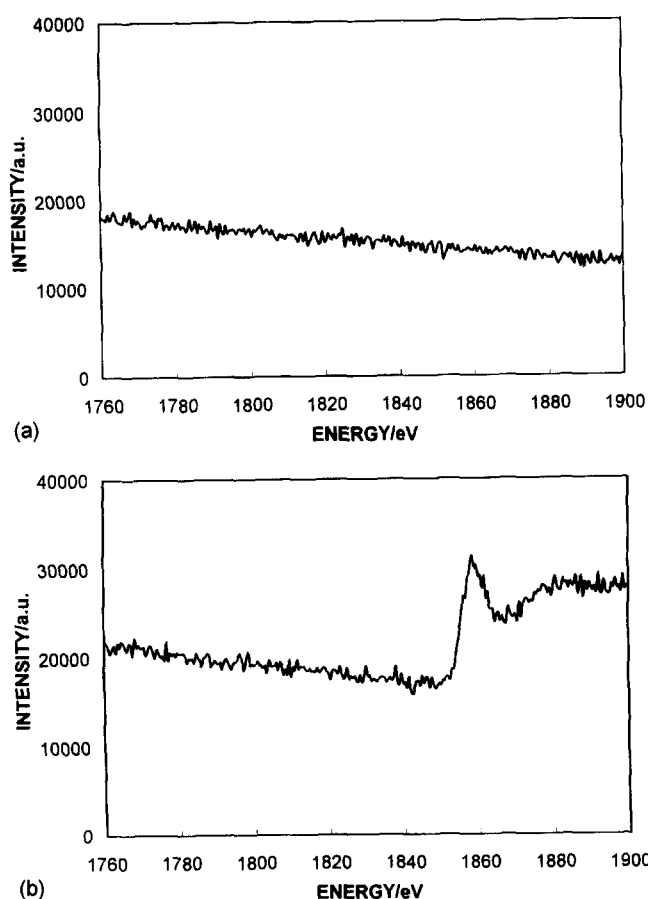


Figure 3 EELS spectra of (a) matrix and (b) domains in NAFION®/alkoxy silane hybrids, where 20 wt% of TEOS was substituted by TMDES

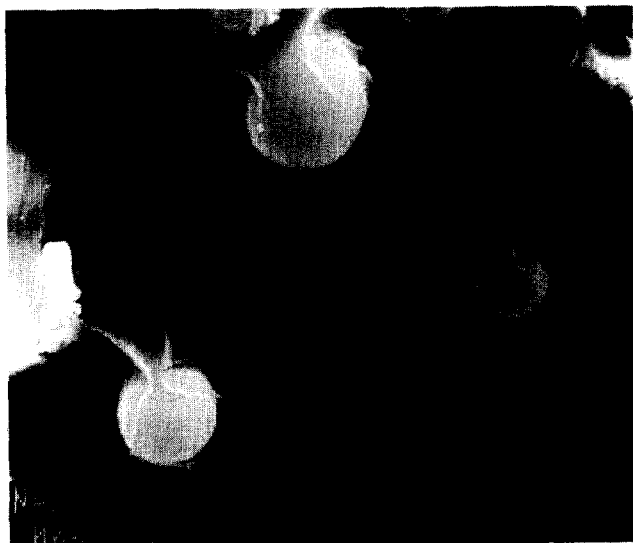


Figure 4 SEM of hybrids, obtained from a NAFION®/alkoxy silane mixture in propanol, where 20 wt% of TEOS was substituted by TMDES

which could not be detected by EELS is probably the space resolution. For EELS, the sampling volume is lower than  $\pi(100 \text{ \AA})^2 \times$  the film thickness. The film thickness is lower than 100 nm. For EDS, the sampling volume is larger than  $1 \mu\text{m} \times 1 \mu\text{m} \times 1 \mu\text{m}$  and it can not be disregarded that when sampling the matrix, part of the Si containing domains may be also contributing to the response assigned to the matrix. Anyway, a domain segregation with almost only Si

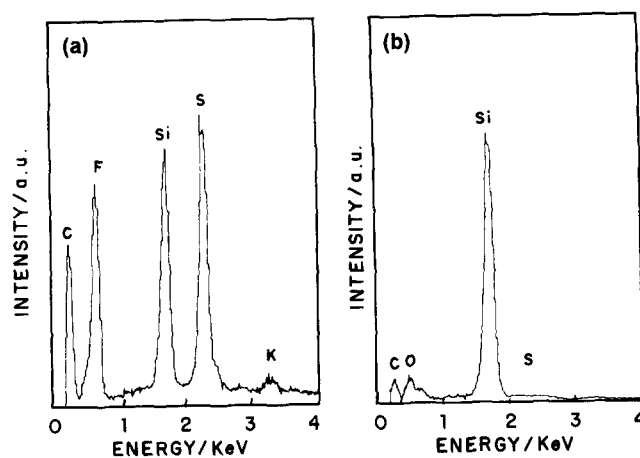


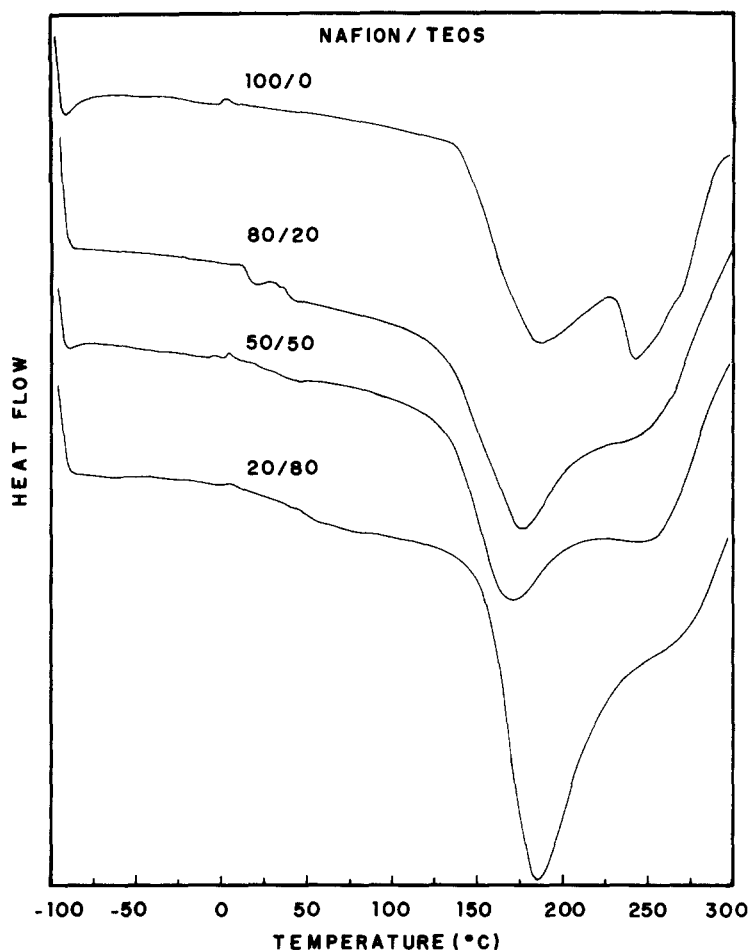
Figure 5 EDS analysis of (a) matrix and (b) domains in NAFION®/alkoxy silane hybrids, where 20 wt% of TEOS was substituted by TMDES

containing polymers occurs for TMDES substitution higher than 5 wt%. The NAFION® rich matrix may contain some Si. In this case, it can be expected that this Si comes preferentially from the TEOS condensation (and not from TDMES) oriented near or inside the sulfonic acid groups.

#### Thermal analysis

The thermal analysis of NAFION® is a matter of controversy in the literature<sup>13,19,20</sup>. Yeo and Eisenberg<sup>19</sup> assigned a transition near 111°C to T<sub>g</sub> of the non polar matrix. Another transition around 20°C was attributed to molecular motions within the ionic phase. Later, Kyu and Eisenberg<sup>20</sup> verified that the transition at higher temperature shifted in the presence of water and should then be assigned to T<sub>g</sub> of the polar phase, while the transition at 20°C should be T<sub>g</sub> of the non polar phase. Starkweather<sup>21</sup> mentioned a melting peak above 200°C. Stefanithis and Mauritz<sup>13</sup> investigating NAFION® membranes found a transition near 145°C and another at 230°C. The former was assigned to the polar cluster transition while the latter was assigned to the melting of the non polar phase. By swelling the membranes with TEOS and promoting its hydrolysis/polycondensation, only the lower transition changed. This transition almost disappeared in samples annealed at 130°C. It was concluded that the inorganic polymer invaded only the ionic clusters, disrupting the sulfonic group packing and leaving the melting transition unchanged.

Figure 6 shows the d.s.c. curves for NAFION®/silicon oxide hybrids obtained from different initial TEOS contents here in this work. Two endothermic peaks can be seen for pure NAFION® at about 186 and 243°C (considering the peak minimum). According to the literature<sup>13</sup>, both could be considered first order transitions, the lower one being the polar cluster transition and the higher one the melting of the non polar phase. However, melting could not be confirmed when observed under polarized optical microscope. Furthermore, the sample becomes darker when heated above 243°C, indicating that an irreversible transition occurs. In a modulated d.s.c., at 5°C min<sup>-1</sup>, both the first and the second transitions did not behave as reversible (in this time scale). When the d.s.c. was repeated after some time with the same sample, the first peak was observed again. It probably takes some hours to complete the cluster transition. This would explain why in d.s.c. experiments performed by Stefanithis and Mauritz<sup>13</sup>, annealing NAFION® during some minutes at 130°C, and then increasing the temperature, the first



**Figure 6** The d.s.c. thermograms of NAFION®/TEOS hybrids with different initial TEOS contents. Heating rate  $10^{\circ}\text{C min}^{-1}$ , all thermograms in the same heat flow scale

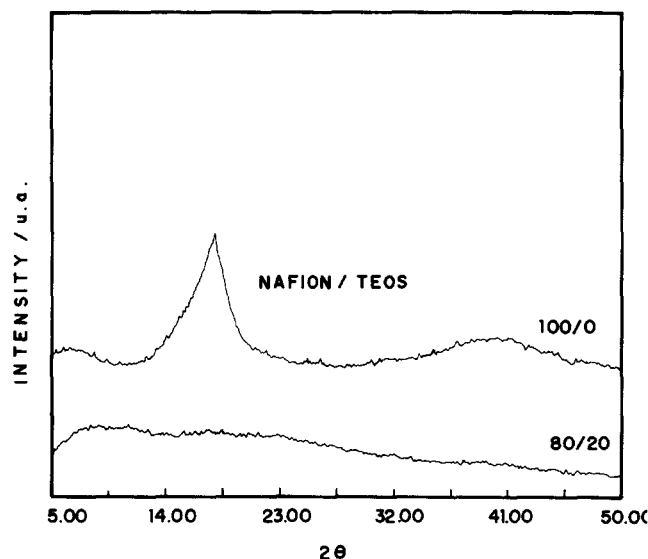
**Table 1** Thermal transition<sup>a</sup> for NAFION®/TEOS hybrids

NAFION®/TEOS	Cluster phase transition (°C)	Melting (°C)
100/0	186	243
80/20	176	235
50/50	172	250
20/80	186	Indeterminate

<sup>a</sup>The error in the determination of the transition temperatures is  $\pm 5^{\circ}\text{C}$

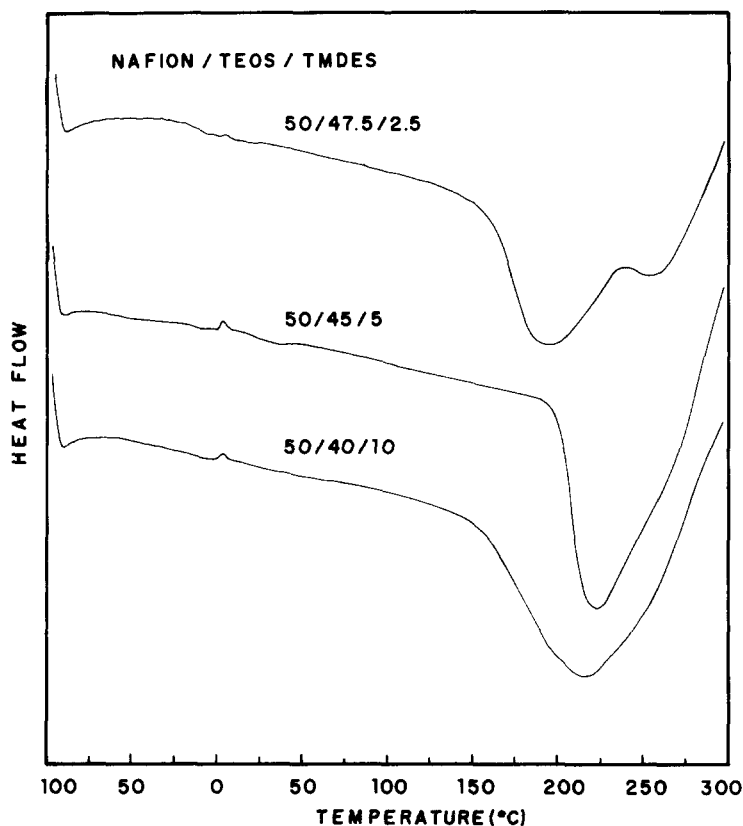
transition disappeared. Probably after some hours the transition would be observed again.

Table 1 lists two transitions for hybrids of different composition. The temperature at which the first transition occurs slightly decreases at least up to 50 wt% TEOS (22 wt% silicon oxide incorporation). Being a cluster transition, it is altered by the introduction of silicon oxide, which perturbs the sulfonic acid group environment. The first transition becomes much more pronounced than the second one, as the TEOS content increases. This is expected, since silicon oxide is amorphous and the total amount of crystalline segments is decreasing, as confirmed by wide angle diffraction (Figure 7). Also it must be mentioned that silica obtained from hydrolysis/polycondensation of TEOS (without NAFION®) has a wide endothermic transition above  $120^{\circ}\text{C}$ , probably due to volatilization of low molecular weight reaction by-products. A weight decrease can be observed by thermogravimetric analysis. This transition due to volatilization in d.s.c. experiments may be overlapping the NAFION® cluster transition in hybrids.



**Figure 7** Wide angle diffractograms of NAFION® and 80/20 NAFION®/TEOS hybrids

Figure 8 shows curves and Table 2 lists the transitions for 50/50 NAFION®/alkoxy hybrids for which part of the TEOS was substituted by TMDES. As the TMDES content substitution increases to 10 wt%, the temperature of the first transition also increases. It seems that the cohesion between sulfonic groups increases. The TMDES segments



**Figure 8** The d.s.c. thermograms of 50/50 NAFION®/alkoxy hybrids, substituting part of the TEOS by TMDES. Heating rate 10°C min<sup>-1</sup>, all thermograms in the same heat flow scale

**Table 2** Thermal transition<sup>a</sup> for 50/50 NAFION®/alkoxy hybrids, for which TEOS has been partially substituted by TMDES

TMDES substitution (wt%)	Cluster phase transition (°C)	Melting (°C)
0	172	250
5	196	255
10	224	Indeterminate
20	Indeterminate	Indeterminate

<sup>a</sup>The error in the determination of the transition temperatures is ± 5°C

**Table 3** E' and E'' at 25°C for 50/50 NAFION®/alkoxy hybrids for which TEOS has been partially substituted by TMDES

TMDES substitution (wt%)	log E'	log E''
10	8.53	8.51
15	8.16	8.11
20	8.08	8.14

are more hydrophobic than those of TEOS. The inorganic polymer growing from TDMES is therefore less able to interact with the hydrophilic sulfonic acid groups in the cluster. Above 10 wt% substitution, phase separation occurs and the NAFION® rich matrix has a very low content of inorganic polymer, which can no longer interfere in the cluster transition. For samples with 20 wt% substitution, the three transitions which are probably taking place (cluster transition, melting of NAFION® matrix and volatilization of polycondensation by-products) overlap in a wide endothermic peak. The melting temperature of the NAFION® crystalline regions seems not to change.

The DMA (*Table 3*) gave information on the flexibility of samples with TMDES incorporation. In DMA analysis, E', the storage modulus is related to elasticity and E'', the dissipative modulus, is inversely related to flexibility. When silicon oxide is incorporated in NAFION®, the hybrid becomes obviously much more rigid. A higher value for E' was expected, but the sample was also too brittle to allow a satisfactory evaluation in the same conditions.

The role of TMDES was to increase flexibility. As TMDES substituted TEOS and its content increased, both E' and E'', measured at room temperature, decreased again, reaching values even lower than for pure NAFION® (log E' = 8.18, log E'' = 8.18).

**CONCLUSION**

NAFION®/silicon oxide hybrids were obtained with a wide range of compositions using NAFION® solutions to form the organic phase and TEOS as the inorganic polymer precursor. No phase separation could be detected, but lamellar structures with different dimensions were observed by transmission electron microscopy. Part of the TEOS was substituted by TMDES to increase the hybrid flexibility, as confirmed by dynamic mechanical analysis. Above 10% substitution, phase separation took place due to the higher hydrophobicity of TMDES. Cluster transitions and melting of the organic polymer matrix were observed by d.s.c.

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