Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 569-577

THERMAL BEHAVIOR OF NAFION MEMBRANES

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(Received April 15, 1998)

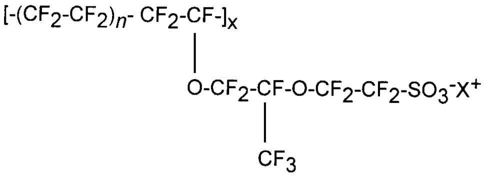
Abstract

The thermal behavior of Nafion-117 membranes was investigated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). TG measurements revealed that the mechanism of thermal degradation of a Nafion membrane in the acid form is different from that of Nafion in the sodium form. The DSC curves for the first heating, for both acid and salt forms, display two endothermic peaks, near 120 and 230°C. The high-temperature peak was assigned to the crystalline domains melting in Nafion, and the low-temperature peak was attributed to a transition into ionic clusters, since this transition exhibits significant changes depending on the nature of the counterion and the degree of hydration.

Keywords: counterion effect, DSC, membrane, Nafion-H, Nafion salts, TG

Introduction

Nafion® is a perfluorosulfonate ionomer used mainly in the form of membranes in electrochemical applications [1–3]. Nafion-117 membranes consist of a polytetrafluoroethylene (PTFE) backbone with side-chains terminated with a sulfonate group:
where n=6.5 and X^+ represents an exchangeable cation.



$$\begin{array}{l} [-(CF_2\text{-}CF_2)_n\text{-}\ CF_2\text{-}CF\text{-}]_x \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad O\text{-}CF_2\text{-}CF\text{-}O\text{-}CF_2\text{-}CF_2\text{-}SO_3^-X^+ \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad CF_3 \end{array}$$

In many ionomers, the ionic species are observed to aggregate and form ionic domains that are distributed through a polymeric matrix. The interactions between the ions act as physical cross-linking, changing the polymeric structure [4, 5]. In the

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Nafion membrane, these ionic aggregates can adopt a spherical structure of inverted micelles about 4 nm in diameter [6].

Nafion membranes are hydrophilic and the water sorbed is incorporated into the aggregates. The water content in hydrated Nafion membranes can vary up to 22 molecules of H_2O per sulfonic group [7].

In consequence of the interactions between the ions, each ionic aggregate is surrounded by a layer of chain segments of restricted mobility. These aggregates and chain segments of restricted mobility are defined by clusters [5]. The size or the stability of the aggregate may change with the content of counterion or the degree of hydration

This work investigates the thermal behavior of the Nafion membrane in acid and salt forms by means of thermogravimetric analysis (TG) and differential scanning calorimetric (DSC) measurements.

Experimental

A Nafion-117 membrane with an equivalaent mass (EW) of 1100 and 0.18 mm thick, from DuPont, was used.

TG measurements were carried out on a Shimadzu model TG-50 instrument. TG curves were recorded on Nafion membranes in the acid form (Nafion-H) and in the sodium form (Nafion-Na) at a heating rate of $20^{o}C\ min^{-1}$ under a nitrogen atmosphere ($30\ mL\ min^{-1}$).

DSC measurements were conducted on a DSC-10 differential scanning calorimeter from TA Instruments. A sample mass of about 10 mg was used in aluminum pans, purged with nitrogen, at a heating rate of $20^{o}C\ min^{-1}$. Indium was used as a calibration standard. The DSC traces were obtained for samples of Nafion-H and Nafion in different salt forms (Na^+, K^+, Rb^+ and Cs^+). The DSC traces were analysed with the DSC Standard Data Analysis Program, version 4.0, used with the TA Instruments Thermal Analyst 2000 system. The ΔH calculations were carried out by using the linear baseline type. Nafion in the salt forms was obtained by soaking Nafion-H membrane in a 1 M aqueous solution of the eletrolyte containing the desired cation for 24 h.

Results and discussion

Fluorocarbon polymers exhibit high thermal stability. The incorporation of ions into their structure reduces the thermal stability [8, 9].

Upon thermal treatment (120–300^{o}C), Nafion-H samples exhibited a dark color that became darker with increasing temperature of duration of treatment. In contrast, the Nafion-Na membrane heated up to 300^{o}C did not undergo any color changes, but the photoacoustic infrared spectra exhibited a new band at $1790\ cm^{-1}$. This band could be related to the presence of C=O groups [10].

TG measurements

Figures 1 and 2 show TG curves of Nafion-H and Nafion-Na, respectively. The solid trace relates to the percentage mass loss, and the dashed one to the first derivative trace (DTG). The TG traces exhibit different profiles for Nafion-H and Nafion-Na. The Nafion-H membrane seems to decompose in at least 3 stages, which are clearly seen in the derivative trace. Similar curves were obtained by Stefanithis and Mauritz [11] in investigations of Nafion-117 in the acid form. The gradual mass loss of about 6.4% on heating from 25 to about 290°C can be attributed mainly to the loss

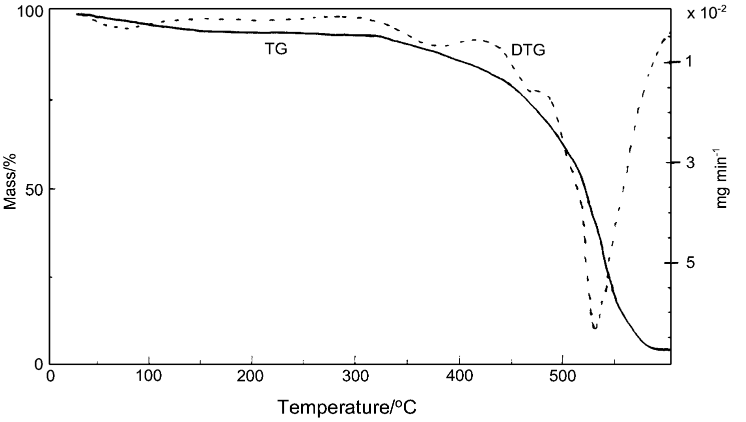

Fig. 1 TG (—) and DTG (- - -) traces of Nafion-H membrane at a heating rate of 20°C min^{-1} under N_2 atmosphere

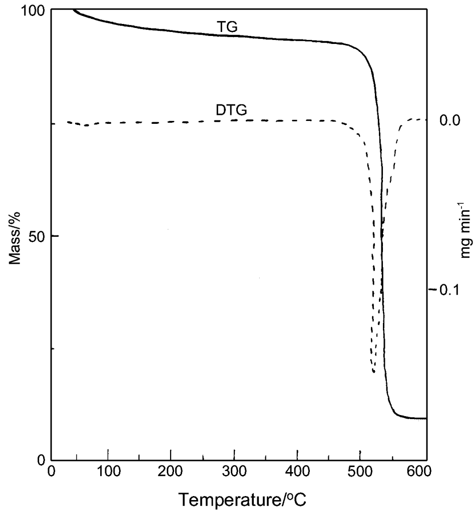

Fig. 2 TG (—) and DTG (- - -) traces of Nafion-Na membrane at a heating rate of 20°C min^{-1} under N_2 amosphere

of water molecules. The first stage (290–400°C) may be associated with a desulfonation process, while the second stage (400–470°C) may be related to side-chain decomposition and the third stage (470–560°C) to PTFE backbone decomposition. Wilkie *et al.* [12] reported that in the temperature range 25–355°C the gases liberated during the thermolysis of Nafion-H were H_2O, SO_2 and CO_2, while at higher temperatures typical gases from the degradation of fluorinated compounds, such as HF, SiF_4 and COF_2, were liberated. Nafion-Na membranes exhibit higher thermal stability and their thermal degradation seems to take place in only one stage. A small amount of water (~6.3%) is lost initially on heating from 25 to 390°C. The onset temperature of the thermal degradation of Nafion-Na is about ~150°C higher than that observed for the Nafion-H membrane. The TG traces of Nafion-Na are quite similar to those reported for other alkali metal salts of Nafion [13]. Formation of the ionic pair $–SO_3^-–Na^+$ seems to stabilize the C–S bond, since SO_2 production has not been detected during the degradation of this alkali metal salt. Wilkie *et al.* [12] reported that only CO_2 and SiF_4 were detected during the thermolysis of Nafion-K (375°C, 2 h).

These results demonstrate that the mechanism of thermal degradation of Nafion-H is more complex than that of Nafion-Na.

Differential scanning calorimetry (DSC)

Figure 3 depicts DSC traces of Nafion-H (trace A) and Nafion-Na (trace B), in the same heat flow scale (W g^{-1}) shifted along the ordinate, concerning the first run at a heating rate of 20°C min^{-1}. Trace A shows a strong endothermic peak at 115°C (T_1) and a weak and broad endothermic peak near 230°C (T_2). The thermal events above ~250°C may be associated with thermal degradation of the Nafion-H membrane, according to the TG curve of this ionomer (Fig. 1). Between 250 and 300°C, a sharp peak is observed, which could be related to SO_2 liberation [12, 14]. A weak endothermic peak at ~325°C in the DSC trace of Nafion-H could be related to the desul-

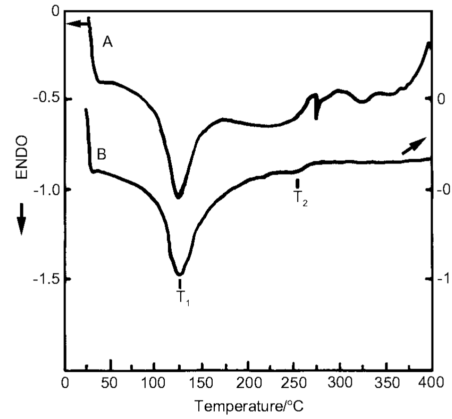

Fig. 3 DSC traces of the first heating for Nafion-H (trace A) and Nafion-Na (trace B) membranes at a heating rate of 20°C min^{-1} under N_2 atmosphere

fonation process that occurred during the heating, as observed in the TG curve of Nafion-H (Fig. 1).

Trace B exhibits two endothermic peaks, at about 122 and 250°C. The DSC traces of Nafion membranes usually reveal changes in the temperature and intensity of the peak at T_1 (~115°C) with the counterion, the degree of hydration and the aging time. The second heating, performed immediately after the first running, indicates suppression of the first peak, but when the second heating is performed some hours after the first heating, the peak at T_1 gradually increases, shifting to higher temperature with increasing sample aging. Similar behavior has been reported for ionomers in previous studies [15–20]. This behavior has been attributed to structural changes into ionic clusters and associated with the order destruction in these domains. Tadano *et al.* [15–18] assigned this endothermic peak to an order-disorder transition inside the ionic clusters. Mauritz *et al.* [21] studied Nafion membranes and concluded that this behavior is associated with the existence of a molecular rearrangement inside the polar phase of the base polymer.

Figure 4 presents a comparison between the DSC trace of Nafion-Na obtained in the first run up to 350°C with the DSC trace of the same sample recorded 3 weeks after the first heating. Samples aged for 3 weeks in air or in vacuum exhibit similar DSC traces. These results indicate that the water absorbed during the aging time is not responsible for the development of the endothermic peak at T_1. Weiss [20] also verified that sulfonate PS aged in air or in N_2 atmosphere exhibited similar DSC traces.

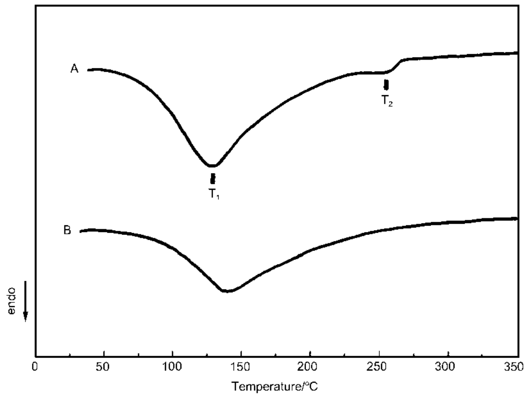

Fig. 4 Changes in DSC traces of Nafion-Na membrane: A – first heating, and B – second heating recorded 3 weeks after the first heating

Kyu *et al.* [22] observed two distinct thermal relaxations in the Nafion-Na membrane (EW=1365) in a dynamic mechanical analysis (DMA) study. These relaxations were attributed to the glass transition of the polymeric matrix (140°C) and to the glass transition inside the ionic clusters (235°C). In Nafion-H, these relaxations were observed at lower temperatures than those found for Nafion salts. The results for Nafion-H were observed at 230 and 111°C, respectively. DSC measurements have been performed on Nafion-Na [23] and an ionomer of Dow Chemical (which has a chemical composition similar to that of Nafion-117) [21, 24] and where one endothermic peak, at 150–180°C, was assigned to the T_g of the polymeric matrix, and one endothermic peak, at 260–286°C, was assigned to the T_g of the ionic clusters. The melting of crystalline regions was associated with a weak endothermic peak at 335°C. Investigations on Nafion-117 in the acid form [11] showed two endothermic peaks; the first endotherm, at 145°C, was attributed to a transition in the ionic clusters, while the transition at 230°C was assigned to the melting of crystalline regions. The weak endothermic peak at 335°C was not observed by Stefanithis and Mauritz [11]. Nafion-H yields a weak endothermic peak at 325°C in the DSC trace, which could be related to the desulfonation process, as observed in the TG trace in Fig. 1. The presence of side-chains and ionic aggregates (which could hamper the crystallization of the polymer chains) probably leads to the Nafion crystallites melting at a temperature lower than that observed in PTFE (327°C) [25]. Thus, the endotherm at 335°C could not be related to crystallite melting. The endothermic peak at 120°C could be related to the same phenomenon in Nafion-Na and in Nafion-H, since the two membranes exhibit similar behavior relative to the effects of the degree of hydration and of sample aging.

Since the peak at temperature T_1 depends on the counterion and the degree of hydration, this peak could be associated with the transition into ionic clusters instead of destruction of the aggregates. Small-angle X-ray scattering experiments revealed an ionic scattering peak at a temperature higher than that of ionomer melting [26]. The disappearance of the endothermic peak at T_1 in the second heating and its appearance after sample aging can be explained by assuming that increase of the temperature to higher than T_1 (in the first run) induces a molecular rearrangement inside the clusters, allowing a higher mobility of the chain segments. When the second heating is performed soon after the first heating, there is not enough time for the system to return to the initial state and the endotherm at T_1 is not observed, but after some time the system returns slowly to conformational equilibrium, so the endothermic peak appears with increase of the aging time. This behavior is consistent with the changes observed in the electronic absorption spectrum profile during the aging of Nafion-Na submitted to thermal treatment, the results of which were assigned to the conformational changes in the ionomer [27].

The transition T_2 observed at 230–250°C in the different salt forms may be associated with the region of crystalline melting of the ionomers. The DSC studies performed by Starkweather [28] on Nafion-117 precursor material (where no ionic aggregates exist) demonstrated an endotherm at 231°C, which was attributed to the melting of this material. This assignment is consistent with the X-ray diffraction results of Gierke *et al.* [6] on Nafion precursor (ME=1379) and of Fujimura *et al.* [26] on Nafion-H (ME=1100). In both studies, the crystalline peak ($2\theta=18^\circ$) disappeared when the samples were heated up to 275°C. Since the acid and salt forms of the membrane melted at temperatures lower than that for PTFE (327°C), the endothermic peak observed at 230–250°C could be related to the crystalline region melting of Nafion, in both acid and salt forms.

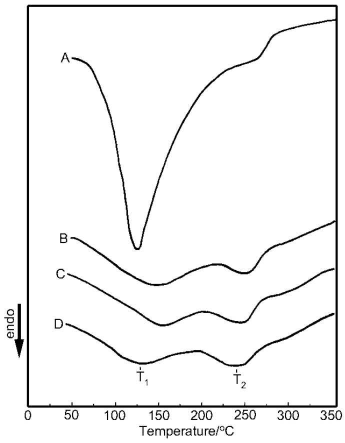

Fig. 5 DSC traces of the first heating for Nafion salts: A – Nafion-Na; B – Nafion-K; C – Nafion-Rb; and D – Nafion-Cs (20°C min^{-1} under N_2 atmosphere)

Effects of counterions

Figure 5 presents DSC traces of Nafion membranes with different cations (Na^+, K^+, Rb^+ and Cs^+). These traces are on the same heat flow scale (W g^{-1}), but are shifted along the ordinate to allow comparison between the traces. The DSC traces of the Nafion salts exhibit two endothermic peaks (T_1 and T_2). The Nafion-Na trace displays an endothermic peak at T_2; it is not well resolved, due to the first endothermic peak superposition.

Table 1 shows that decreasing ionic radius (Rb^+, K^+ and Na^+) causes a temperature T_1 decrease; Cs^+ is an exception. The temperature decrease could be associated with a water plasticizing effect in the membrane, since the small cations can absorb greater contents of water molecules. The absorbed water content increases the free volume, increasing the chain mobility and decreasing the temperature T_1. Figure 5 and Table 1 show that increase in the ionic radius produces a reduction in the area of the first endothermic peak (ΔH_1). On increase in the ionic radius, the anion-cation electrostatic interaction becomes weaker and the corresponding clusters are less stable. Therefore, lower energy (ΔH_1) is required to promote an ionic rearrangement. Nafion-Cs exhibits different thermal behavior as compared to the T_1 of the other

Table 1 Temperature and ΔH changes for endothermic peaks in Nafion membranes as functions of the counterions

Counterion	T_1/°C	ΔH_1/J g^{-1}	T_2/°C	ΔH_2/J g^{-1}
Na^+	122	60.4	250	
K^+	144	13.8	245	4.5
Rb^+	150	8.2	243	4.0
Cs^+	123	11.0	237	4.4

salts. Such behavior could be associated with a hydrophobic cation, such as Cs^+, staying preferentially in interfacial regions, rather than inside the ionic aggregates, resulting in different behavior from that of the other alkali metal cations. This phenomenon has been observed by other workers [29].

The effects of different cations are also observed in the second endothermic peak (Table 1). Increasing ionic radius produces a slight decrease in the temperature T_2. If this endothermic peak is related to crystallite melting, the decrease in T_2 could be attributed to a reduction in the size of the crystallite, which has been observed when the ionic radius increases [26].

Effects of water absorption

The experiments demonstrated that an increase in the degree of hydration in Nafion-H causes an increase in ΔH_1 and a decrease in temperature T_1. Similar results were observed for hydrated Nafion-Na, although to a lesser extent than for the Nafion-H membrane. The decrease in temperature T_1 with the membrane hydration can be attributed to the water plasticizing effect, which favors the mobility of the chain segments. The increase in ΔH_1 with hydration may be due a change in the state of ion aggregation with increasing water content. According to Gierke *et al.* [6], an increase in the water sorbed by the membrane simultaneously leads to a higher number of sulfonic groups per aggregate and an increase in the size of the aggregate, and more highly organized clusters and more cohesive interactions are expected. Consequently, higher energy is required to overcome the ionic interactions and to cause higher mobility of the chains.

Conclusions

The TG results indicate that the thermal stability of Nafion membranes depends on the nature of the exchangeable cation and that the mechanisms of thermal degradation of Nafion-H and Nafion-Na are distinct.

The DSC traces of the Nafion acid and salt forms exhibit two endothermic peaks, near 120 and 230°C, on the first heating. The endothermic peak at 120°C is not present in the second heating, performed immediately after the first running, but this endothermic peak gradually appears with sample aging. This phenomenon may be caused by a molecular rearrangement during the polymeric relaxation process. The dependence of this endotherm on the type of the counterion and the degree of hydration suggests that the endothermic peak is associated with ionic clusters and may be attributed to a transition order-disorder inside the clusters, as suggested by Tadano *et al*. [16–18]. The endothermic peak observed at 230–250°C could be assigned to the melting of microcrystalline regions of the Nafion membranes.

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S. H. Almeida thanks CAPES/PICD for a fellowship and Y. Kawano thanks CNPQ for a research fellowship and FAPESP for financial support.

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