Journal of Thermal Analysis, Vol. 33 (1988) 1097–1102

STUDIES ON THE THERMAL STABILITY OF THE PERFLUORINATED CATION-EXCHANGE MEMBRANE NAFION-417

J. Surowiec and *R. Bogoczek*

TECHNOLOGICAL INSTITUTE OF CHEMICAL AND FOOD INDUSTRY, A. E., KOMANDORSKA 118–120, 53–345 WROCŁAW, POLAND

The thermal stability of the perfluorinated cationexchange membrane Nafion-417 was determined by means of simultaneous TG-DTA. The individual decomposition stages were studied via IR spectroscopy and ion-exchange capacity determinations. Nafion-417 is thermally stable up to 280 °C. Above this temperature, sulfonic groups present in the membrane are split off (T_{max} = = 345 °C. In the temperature range 420–590 °C, oxidative destruction of the perfluorinated matrix occurs, which is accompanied by practically total weight loss.

Perfluorinated ionomer membranes represent a major advance in membrane technology. Although a variety of applications have been found for these polymers since their appearance about fifteen years ago, the main driving force for their development has been their potential application as membrane separators in commercial alkali metal chloride solution electrolysis. This major chemical technology is in the process of being revolutionized through the use of these materials.

Among the polymeric synthetic ion-exchange membranes, special attention has been paid to the Nafion membranes, based on sulfonated fluorocarbons. Owing to their chemical inertness, thermal and mechanical stability, and high permeability and mechanical stability, and high permeability and selectivity, they have proved to be particularly suitable for many industrial processes [1, 2]. Nafion membranes have found wide application in the chemical industry, e.g. as separators in chloralkali electrolysis or as solid polymer electrolytes in fuel cells [3]. Perfluorinated ion-exchange polymers can also serve as "superacid" catalysts for many organic reactions [4].

The structures and physicochemical properties of Nafion membranes have been studied extensively by many authors [1,5–9]. Only a few papers have been published on the thermal stabilities of Nafion membranes; these have concerned the thermal behaviour of Nafion in solutions of chemicals up to 200–250°.

The purpose of our studies was to investigate the thermal properties of Nafion-417 in the temperature range 20–1000° through the use of thermogravimetry (TG) and differential thermal analysis (DTA). The combination

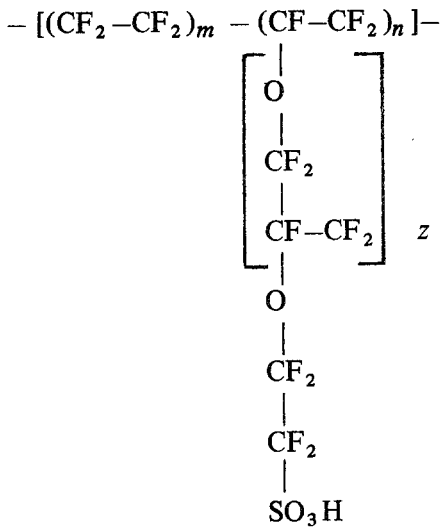
John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

of these techniques with other analytical methods (IR spectroscopy and ion-exchange capacity (IEC) determination) enabled us to study the thermal degradation of Nafion membranes.

Experimental

Materials

The Nafion products (Du Pont de Nemours and Co.) are copolymers of tetrafluoroethylene and monomers such as perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonic acid:



where:

$m = 5–13.5$,

$n =$ ca. 1000, and

$z = 1, 2, 3, \ldots$

The value of m determines the cation-exchange capacity, which according to the manufacturer's data varies from 0.55 to 1.05 mmolg^{-1}. For the ion-exchange membrane studied (Nafion-417), we determined an IEC of 0.31 mmolg^{-1}, probably because of the reinforcement fabric present in the membrane tested. This membrane was used in H^+ form, prepared by immersion for 24 h in 1 M HCl, followed by careful washing with distilled water. Before thermal studies, the samples were vacuum-dried at 60°.

Thermal studies

Thermal behaviour was studied with a MOM 102 derivatograph. First, the samples (ca. 250 mg) were heated in air atmosphere at a heating rate of 10 deg·min^{-1} in the temperature range 20–1000°. On the basis of the traces obtained, the main thermal transformations were determined. Then, other samples were heated under the same conditons, but up to the temperatures corresponding to the respective decomposition stages. For the partially decomposed residue, the IEC was determined and the IR spectrum was recorded.

IEC determination

The IECs were determined by the titration of samples (ca. 0.5 g immersed in 50 cm^3 1 M NaCl) with 0.1 M NaOH, a pH-meter and glass-calomel electrodes being used.

IR spectra

Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer 621 spectrophotometer, using KBr pellets (3 mg sample and 200 mg KBr).

Results and discussion

The TG, DTG and DTA curves and IR spectrum for Nafion-417 are presented in Figs 1 and 2A, respectively. Figures 2B and C show IR spectra for samples obtained by controlled decomposition.

It may be seen from Fig. 1 that the DTG-DTA curves exhibit three stages of decomposition:

1. The first endothermic effect occurs between 50° and 180° (T_{max} = 120°). The mass loss at the end of this stage, read from the TG curve, is ca. 4% and is caused by moisture elimination only. This was proved by the corresponding IEC increase for a sample separately heated up to 180°. Moreover, the IR spectrum revealed the disappearance of the characteristic O-H stretching vibration (free H_2O at 3650–3150 cm^{-1}) (Fig. 2B).

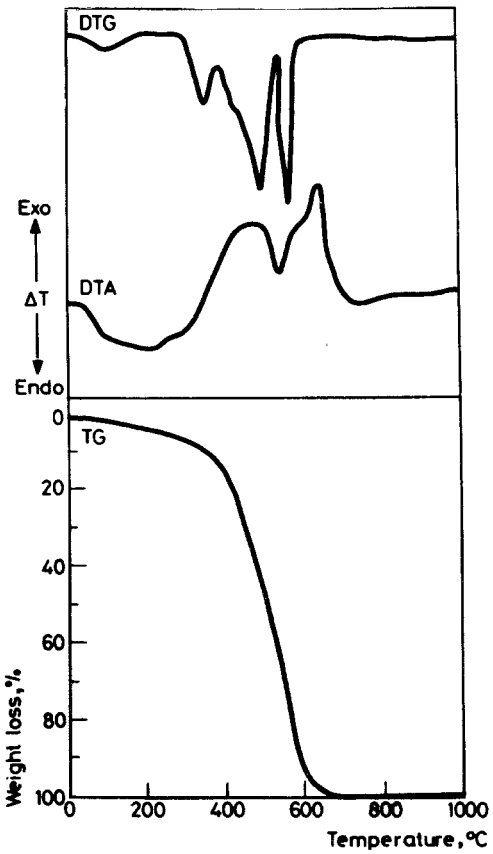


Fig. 1 TG, DTG and DTA curves of Nafion-417

Up to 280°, Nafion-417 is thermally stable and no thermal effects were recorded.

2. The thermal effect in the range 310–380° (T_{max} = 345°) is connected with a 7.7% weight loss. It is accompanied by the total loss of IEC, caused by the splitting-off of sulfonic groups.

3. Two very strong exothermic effects were recorded in the range 420–590°, with maxima at 500 and 565°. These decomposition stages, which are accompanied by practically total weight loss, are connected with oxidative destruction of the perfluorinated matrix.

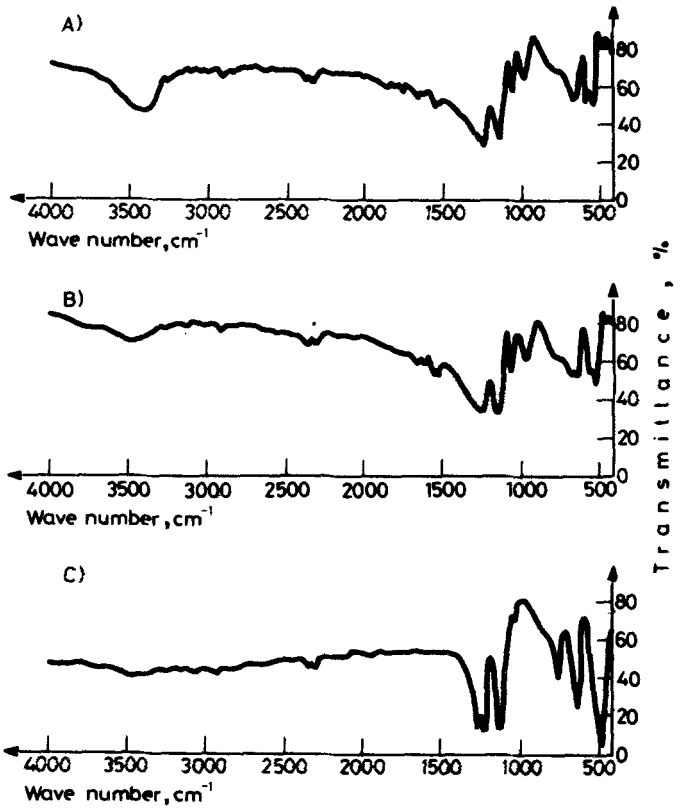


Fig. 2 Infrared spectra of Nafion-417 (A) and products of its thermal decomposition: up to 180 °C (B) and up to 380 °C (C)

Conclusions

Studies on the thermal behaviour of Nafion-417 have shown that this membrane is thermally stable up to 280°. Below this temperature, only moisture elimination is recorded. However, at higher temperatures, sulfonic groups are split off. Consequently, the membrane loses its IEC and can then serve neither as a cation-exchanger nor as an acidic catalysts. Our studies have proved the much higher thermal stability of cation-exchangers based on perfluorinated monomers (Nafion products) in comparison with traditional ion-exchangers manufactured on a styrene-divinylbenzene copolymer base (e.g. Amberlite, Dowex or Wofatit), which can be used up to ca. 120°.

IR spectroscopy proved to be a useful method for estimation of the structural changes of these products during heating, but only in certain regions. For the Nafion membrane, the strong CF_2 vibration overlaps part of the spectrum, so that some spectral details of the SO_3H bands can not be observed. However, a strong band is visible at 1060 cm^{-1}, which is assigned to the symmetric stretching vibration of SO_3^-.

References

1 A. Eisenberg and H. L. Yeager, Perfluorinated Ionomer Membranes, ACS Symp. Ser. No 180, Washington 1982, chapters 14–19.
2 J. Surowiec, Przem. Chem., 65 (1986) 409.
3 H. J. R. Maget, Handbookof Fuel Cell Technology, Prentice-Hall, Englewood Cliffs, New York 1967.
4 R. Bogoczek and J. Surowiec, Chem.-Ing-Tech., 59 (1987) 178.
5 C. Heitner-Wirguin, Polymer, 20 (1979) 371.
6 A. Eisenberg and M. King, Ion Containing Polymers, Polymer Physics Volume 2, Academic Press 1977 (and references therein).
7 J. Ostrowska and A. Narębska, Colloid and Polymer Sci., 261/1983.
8 S. C. Yeo and A. Eisenberg, J. Appl. Polym. Sci., 21 (1977) 875.
9 M. Lopez, B. Kipling and H. L. Yeager, Anal. Chem. 48 (1976) 1120 and 49 (1977) 629.

Zusammenfassung – Die thermische Stabilität der perfluorierten Kationenaustauscher-Membran Nafion 417 wurde durch simultane TG-DTA untersucht. Die einzelnen Zwischenstufen der Zersetzung wurden durch IR-Spektroskopie und Messung der Ionenaustauschkapazität charakterisiert. Nafion 417 ist thermisch stabil bis 280 °C. Oberhalb dieser Temperatur werden die vorhandenen Sulfonsäuregruppen abgespalten (Maximum bei 345 °C). Im Temperaturbereich 420–590 °C findet oxidativer Abbau, verbunden mit völliger Gewichtsabnahme, statt.

РЕЗЮМЕ — Для определения термоустойчивости полностью фторированной катионо-обменной мембраны Нафоин—147 был использован термический анализ. Для изучения отдельных стадий разложения были применены метод ИК спектроскопии и ионо-обменной хроматографии. Установлено, что Нафион—147 термически устойчив до температуры 280°. Выше этой темпреатуры ($T_{макс.}$ = 345°) происходит отщепление сульфогруппы, а затем в температурном интервале 420—590° происходит окислительно-восстановительный распад перфторированного образца, сопровождающийся практически полной потерей веса.