Chemical Engineering Journal 189–190 (2012) 1–4

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Proton conducting properties of nanocomposite membranes of chitosan

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ARTICLE INFO

Article history:
Received 19 December 2011
Received in revised form 31 January 2012
Accepted 1 February 2012

Keywords:
Preyssler type heteropolyacid
Chitosan
Nanocomposite membranes
Proton conductivity

ABSTRACT

Nanocomposite membranes of chitosan prepared in our earlier paper (see Ref. [1]) by incorporating different concentrations of Preyssler type heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$ (H_{14}-P_5) nanoparticles have been characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TGA) and dynamic mechanical thermal analysis (DMTA). Proton conductivity data of these membranes measured at varying temperatures have shown a systematic improvement in proton conductivity over that of the nascent chitosan membrane. Arrhenius activation parameter values obtained have been discussed in terms of the conduction transport mechanisms.

1. Introduction

In our previous paper [1], nanocomposite membranes (NCMs) of chitosan (CS), incorporated with the nanoparticles of Preyssler-type heteropolyacid $H_{14}[NaP_5W_{30}O_{110}]$ i.e., (H_{14}-P_5), have been explored for liquid separations. It was shown that membrane separation properties of NCMs have dramatically improved over that of the nascent CS membrane due to the desirable attributes of organic and inorganic components in a single composite membrane that will offer new synergistic properties [2–5]. In continuation of this work, we now report on the improvement of proton conducting properties of NCMs of CS membrane. These NCMs have been characterized by Fourier transform infrared (FTIR) spectroscopy, thermo-gravimetric analyzer (TGA) and dynamic mechanical thermal analyzer (DMTA). From the temperature dependence of proton conductivity data, Arrhenius activation parameters have been estimated and discussed in terms of conduction mechanism. The observed moderate improvement in proton conductivity by NCMs is due the conducting channels created by the added nanoparticles.

2. Experimental

All the materials and chemicals including the preparation of Preyssler type heteropolyacid as well as NCMs remain the same as discussed in our previous publication [1]. The average thickness of the membranes was around 40 ± 3 μm. The membrane nomenclature: nascent chitosan (M-0), whereas 5, 10 and 15% H_{14}-P_5 loaded chitosan nanocomposite membranes as NCM-5, NCM-10 and NCMM-15, respectively.

2.1. Spectral measurements

FTIR spectra of H_{14}-P_5 nanoparticles, M-0 and NCM-15 membranes were scanned in the range of 400–4000 cm^{-1} using Nicolet, Impact-410 (Milwaukee, WI), FTIR spectrophotometer by the KBr pellet method.

TGA thermograms were obtained using SDT 2960 (TA Instruments, USA). Measurements were done at the heating rate of 10 °C/min. The sample pan was conditioned in the instrument before performing the actual experiment.

Dynamic mechanical test analysis (DMTA) was done (courtesy of Dr. K.V.S.N. Raju, Indian Institute of Chemical Technology, Hyderabad) using a Rheometric Scientific, USA, DMTA IV instrument operated in a tensile mode at the frequency of 1 Hz and at the heating rate of 6 °C/min.

2.2. Ion exchange capacity (IEC)

Ion exchange capacity (*IEC*) indicates the number of milli-equivalents of ions in 1 g of the dry polymer. The membranes of similar masses were soaked in 50 mL of 0.01 N sodium hydroxide solution for 12 h at the ambient temperature and 10 mL of the remaining solution was titrated with 0.01 N sulfuric acid. The membrane was regenerated with 1 M hydrochloric

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doi:10.1016/j.cej.2012.02.002

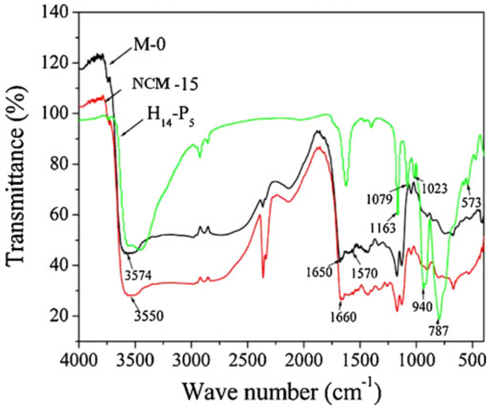

Fig. 1. FTIR spectra of H_{14}-P_5 nanoparticles along with chitosan (M-0) and NCM-15.

acid, washed with water until free from acid and dried to a constant mass. The *IEC* (mequiv/g) was then calculated as [6]:

$$IEC = \frac{(B - P) \times 0.01 \times 5}{m} \qquad (1)$$

where *B* is the volume of sulfuric acid required to neutralize the blank solution containing NaOH (mL), *P* is the volume of sulfuric acid required to neutralize NaOH solution in which membrane is soaked, 0.01 is the normality of sulfuric acid, 5 is a factor that corresponds to the ratio of volume of NaOH taken to dissolve the polymer and volume of NaOH used for titration and *m* is mass (g) of the membrane.

2.3. *Proton conductivity*

Proton-conductivity measurements were performed on all the NCMs using a two-probe cell by the AC impedance technique [7,8]. Conductivity cell comprised of two stainless steel electrodes, each of 50 mm dia. The membrane was sandwiched between the stainless steel electrodes fixed in a Teflon block kept in a closed glass container. Ionic conductivity of the membrane was measured under fully-humidified condition (RH = 100%) by keeping de-ionized water at the bottom of the test container and equilibrating up to 24 h. Subsequently, conductivity measurements were made between 30 °C and 110 °C in a glass container that has the provision to heat. Temperature of the conductivity cell was constantly monitored with a thermometer kept inside the container adjacent to the membrane. AC impedance spectra of the membranes were recorded in the frequency range of 1 MHz and 10 Hz with 10 mV amplitude using an Autolab PGSTAT 30. Resistance of the membrane was determined from a high-frequency intercept of the impedance with the real axis. Membrane conductivity was calculated [8] from its resistance, *R* as:

$$\sigma = \frac{h}{RA} \qquad (2)$$

where σ is proton conductivity (S/cm) of the membrane, *h* is its thickness (cm) and *A* (cm^2) is the cross-sectional area.

3. Results and discussion

3.1. *Fourier transform infrared spectroscopy (FTIR)*

FTIR spectra of pure H_{14}-P_5, M-0 and NCM-15 (typical) displayed in Fig. 1 exhibit characteristic peaks of H_{14}-P_5 assigned to the Preyssler structure [8]. The P—O stretching vibrations at 1163, 1079 and 1023 cm^{-1} as well as P—O bending frequencies at 573 cm^{-1} can be seen. Stretching frequencies of W—O—W and W=O are observed at 940 and 787 cm^{-1}, respectively. A strong and broad band around 3100–3500 cm^{-1} in H_{14}-P_5 and CS membrane (M-0) corresponds to O—H stretching vibrations of hydroxyl groups of H_{14}-P_5 as well as M-0. After introducing H_{14}-P_5 nanoparticles into M-0 matrix, the bands for O—H of M-0 were shifted from 3574 cm^{-1} to a slightly lower value of 3550 cm^{-1} (red-shift), due to the dissociation of hydrogen bond among the hydroxyl groups of M-0, confirming the formation of hydrogen bond between —OH groups of M-0 and H_{14}-P_5. The bands at 1650 and 1570 cm^{-1} are assigned [9], respectively to amino-I and amino-II functional groups of M-0. However, multiple bands appearing between 900 and 1100 cm^{-1} for CS (M-0) correspond to C—O stretching vibrations [10], but these bands experience a small shift to lower frequency in NCM-15, suggesting the retainment of Keggin ion geometry of H_{14}-P_5.

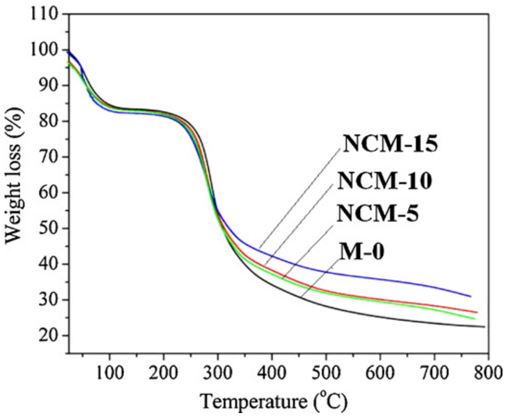

Fig. 2. TGA thermograms of M-0, NCM-5, NCM-10 and NCM-15.

3.2. *Thermogravimetric analysis (TGA)*

Thermal stability of NCMs studied by TGA displayed in Fig. 2 shows the weight loss before 110 °C for all the membranes due to sorbed water molecules and the extent of weight loss around this temperature range increased with increasing H_{14}-P_5 concentration in the CS matrix, implying the formation of CS–H_{14}-P_5 complex, due to which ion exchange capacity also increases. However, the first rapid weight loss observed at 260 °C is due to CS chain degradation, whereas the second rapid weight loss is due to the oxidative degradation of char formed from CS chain degradation. High H_{14}-P_5 concentrations of NCMs has resulted in high char yields around 700 °C that are almost coincident with the concentration of H_{14}-P_5.

3.3. *Dynamic mechanical thermal analysis (DMTA)*

DMTA gives important information on the microstructure of polymers. The tan δ plot as a function of temperature is displayed in Fig. 3, wherein T_g is related to peak temperature of tan δ curve, while the relaxation strength corresponds to the height of tan δ peak. Storage modulus E', cross-linking density, ν_e and number of moles of elastically effective network chains/cm^3, M_c or simply molar mass between crosslinks of the network polymer are reported in Table 1.

Table 1
Results of ion exchange capacity, storage modulus, crosslink density and molar mass between cross-links.

Membranes	*IEC* (mequiv/g)	E' (dynes/cm^2)	ν_e (mol/cm^3)	M_c (g/mol)
M-0	1.35	3.33×10^9	0.41	1.95
NCM-5	1.64	1.19×10^{10}	1.48	0.55
NCM-10	1.80	1.35×10^{10}	1.68	0.48
NCM-15	2.10	1.40×10^{10}	1.74	0.47