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Semi-interpenetrating polymer networks of Nafion® and fluorine-containing polyimide with crosslinkable vinyl group

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ABSTRACT

Fluorine-containing polyimide with crosslinkable vinyl group (FPI) was synthesized from 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB), and 4-amino styrene (AS). The reinforced composite membranes based on semi-interpenetrating polymer networks (semi-IPN) were prepared via solution casting of FPI and Nafion®212, and crosslinking thereafter. The water uptake, swelling ratio, mechanical properties, thermal behavior, proton conductivity, and oxidative stability of the composite membranes were investigated. Compared with the recast Nafion® 212, the composite membrane shows better mechanical properties and improved dimensional stability. The tensile strength of the composite membranes ranges from 39.0 MPa to 80.0 MPa, which is higher than that of the recast Nafion® 212 membrane (26.6 MPa). The dimensional stability of the composite membranes increases with increasing FPI content in the membranes, whereas the proton conductivity decreases. The composite membranes show considerable proton conductivity from 2.0×10^{-2} S cm^{-1} to 8.9×10^{-2} S cm^{-1} at a temperature from 30 °C to 100 °C, depending on the FPI contents. The composite membranes with semi-IPN from FPI and Nafion®212 have considerable high proton conductivity, excellent mechanical properties, thermal and dimensional stabilities.

1. Introduction

Proton exchange membranes (PEMs) can be used either in polymer electrolyte membrane fuel cells (PEMFCs) or in direct methanol fuel cells (DMFCs) [1]. The polymers, which can be used as PEMs, have to combine various properties, such as excellent chemical stability especially against oxidative radicals, mechanical stability with reasonable swelling ratio and high proton conductivity [2–5]. Up till now, the most widely used material for PEM is the perfluorinated sulfonic acid polymers, such as Nafion®. They show high proton conductivity, good mechanical properties, and extremely high oxidative stability. However, they still suffer from high cost, poor dimensional stability, as well as low mechanical properties at high temperature and high humidity [6–12]. The reinforced composite membranes based on Nafion® can not only reduce the content and the cost of Nafion®, but also improve the mechanical properties and the dimensional stability. Besides these, the well-improved mechanical properties of PEMs can make the membrane thinner, thus reduce the impedance of the membrane, and improve the performance of the fuel cells. Recently, the reinforced composite membranes based on Nafion® mainly include Nafion®/porous polytetrafluoroethylene (PTFE), Nafion®/fibrous PTFE, Nafion®/carbon nanotubes, and Nafion/SiO_2 composite membranes [13–18].

Aromatic polyimide is a class of high performance engineering plastics. It has a variety of engineering and electrical applications due to its good mechanical properties, good chemical resistance, low dielectric constant, and high thermal stability [19–21]. The excellent chemical stability of Nafion® provides good durability; meanwhile, its chemical inertness makes the chemical modification difficult. By introducing crosslinkable polyimide to form semi-interpenetrating polymer networks (semi-IPN) with Nafion® may greatly improve the mechanical properties and the dimensional stability of the perfluorinated sulfonic acid membrane.

In present work, the crosslinkable fluorine-containing polyimide (FPI) was synthesized. By solution casting method, a new kind of PEM based on crosslinkable FPI and Nafion® 212 was prepared. The ethylene group in FPI can be polymerized and crosslinked by free radical polymerization during the membrane preparation and form semi-IPN structure. The properties of composite membranes, such as thermal stability, tensile properties, water uptake, swelling ratio, and proton conductivity were also examined. The proton transport in the semi-IPN structure is discussed.

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2. Experimental

2.1. Materials

4-Amino styrene (AS, >97%) was purchased from EHSY (Westingarea), 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, >99%), and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB, >98%) were purchased from Shanghai Darui Finechem Co. and used as received. Nafion®212 was from DuPont Co.. N-methylpyrrolidone (NMP), isoquinoline (spectroscopically pure), methanol (99.7 wt%, AR grade), and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Shanghai Chemical Reagent Co.

2.2. Synthesis of the crosslinkable polyimide

A synthetic procedure of the crosslinkable flourine-containing polyimide is described below using starting monomers of 6FDA/PFMB/AS (10/9/2, mol/mol) as an example. To a 100 mL completely dried three-necked flask, 3 mmol 6FDA, 2.7 mmol PFMB, and 12 mL NMP were added with the protection of N_2. The mixture was stirred under N_2 at room temperature for 12 h. 0.6 mmol AS was added thereafter and stirred at room temperature for another 12 h. Then acetic anhydride and triethylamine were added into the mixture and stirred at room temperature for 24 h. The mixture was poured into 200 mL methanol. The fiber-like precipitate was filtered off, washed with methanol thoroughly, and dried in vacuum at 120 °C for 24 h. The synthetic scheme and the chemical structure of the crosslinkable polyimide are shown in Fig. 1. FPI is named as FPI−*X*, in which *X*% represents the molar ratio of the C═C groups to 6FDA. The feed ratio of the monomers of FPI−*X* is listed in Table 1.

2.3. Formation and crosslinking of the composite membranes

The preparation procedure of the composite membranes is described below using CM−20−15 as an example. 0.15 g FPI−20 (15wt%) and 0.85 g Nafion®212 (85wt%) were dissolved in 9 mL NMP (10wt%). 0.012 g AIBN was added to the solution and stirred at room temperature till AIBN was dissolved in NMP completely. The solution was cast on glass plates at 80 °C for 10 h to evaporate the solvent and initiate the polymerization of vinyl groups, and then heated at 130 °C for 24 h in vacuum. Then the plates were put into the deionized water until the membrane fell off naturally and dried in vacuum at 120 °C for 24 h. As a comparison, the non-crosslinked composite membrane was also prepared. By changing the weight ratio of FPI−*X* and Nafion®212 in the membrane preparation, a series of composite membranes with different contents of FPI−*X* can be obtained. FPI contents range from 5% to 25% (wt%) with the purpose to insure the membranes with relatively high mechanical properties and proton conductivities. The composite membranes can be assigned as CM−*X*−*Y*, in which *Y*% represents the content (weight percentage) of FPI−*X* in the membrane, *X*% represents the molar ratio of the C═C groups to 6FDA in FPI−*X*.

Table 1
The feed ratio of the monomers in FPI−*X* and the molecular weight of FPI−*X* by GPC.

Polyimide	6FDA (mol)	PFMB (mol)	AS (mol)	*X*% (AS/6FDA, mol/mol)	Mn	Mw/Mn
FPI−0	10	10	0	0	–	–
FPI−20	10	9.0	2.0	20	10,259	2.12
FPI−40	10	8.0	4.0	40	6073	1.93
FPI−60	10	7.0	6.0	60	5556	1.48
FPI−80	10	6.0	8.0	80	3917	1.28

2.4. Characterization of the membranes

FTIR analysis of the membranes was carried out on a Bruker EQUINOXSS/HYPERION2000 spectrometer. KBr pellet method was used. ^{1}H-NMR spectra of the polymers in deuterated dimethyl sulfoxide were measured on a Varian Bruker AC-250 instrument. Gel permeation chromatography (GPC) of the polymers was measured on Waters model 515 at room temperature and calibrated with standard polystyrene. Tetrahydrofuran was used as the solvent with a flow rate of 1 mL min^{-1}. Thermogravimetric analysis (TGA) of the samples was measured on a STA 449C (Netzsch Co.) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

The gel fraction of the crosslinked networks was measured by the method of solvent extraction [22,23]. 0.1 g to 0.3 g samples were placed in dimethyl sulfoxide (DMSO) and extracted in the Soxhlet apparatus for 24 h. After the removal of the solvent by drying at 120 °C for 24 h under vacuum, the remaining mass was

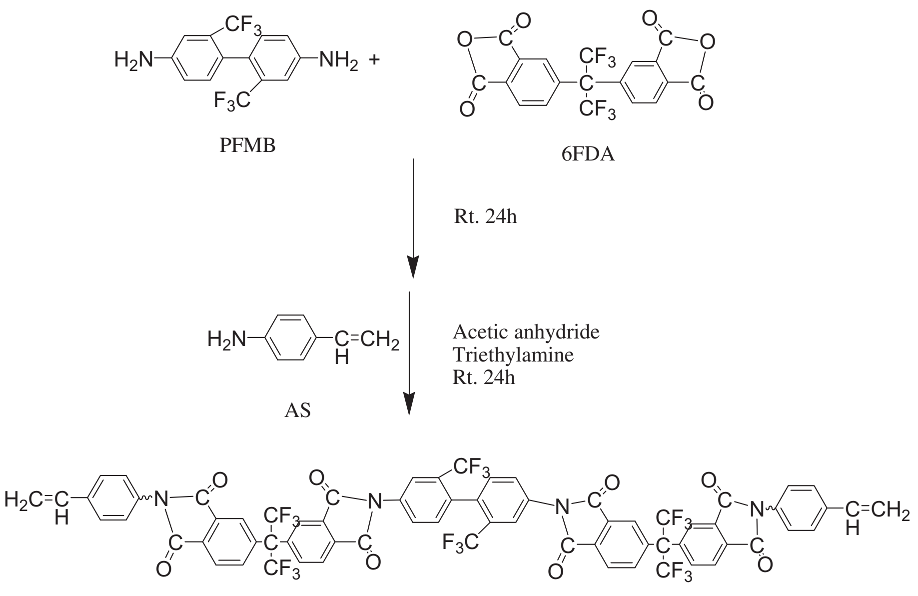

Fig. 1. Synthetic procedure of fluorine-containing polyimide.

weighed as gel. The gel fraction was calculated by dividing the weight of the gels by the initial weight of the samples.

Tensile properties of the composite membranes were performed on a universal material testing machine (DXLL-5000) according to ASTM D882-02 with a strain speed of 50 mm min^{-1}. Dynamic mechanical analysis (DMA) of the membranes was performed with a DMA 2980 (TA Instrument Co.) in tension mode at a frequency of 1.0 Hz and a heating rate of 10 °C min^{-1}. The initial static force was set to be 1.0 N.

The measurement of the water uptake of the membranes were carried out by immersing three sheets of membranes into water for 48 h at a temperature of 25 °C and 80 °C, respectively. Then the membranes were taken out, wiped with the tissue paper and quickly weighed on a microbalance. The water uptake (WU) of the membranes is calculated from Eq. (1) [22].

$$\mathrm{WU} = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100\% \qquad (1)$$

where W_{dry} and W_{wet} are the weight of dry and corresponding wet membrane sheets, respectively.

Similar to the water uptake, the measurement of the swelling ratio of the membranes was carried out by immersing three sheets of membranes into water for 5 h at 25 °C and 80 °C, respectively. Then the membranes were taken out. The length of the swollen membranes was measured by micrometer screw calipers. Swelling ratio (SR) of the membranes is calculated from Eq. (2),

$$\mathrm{SR} = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \times 100\% \qquad (2)$$

where L_{dry} and L_{wet} are the length of dry and swollen membranes, respectively.

The proton conductivity (σ) of the composite membranes was measured by Electrochemical Impedance Lab CHI 604B (CH Instruments Inc.), which worked in the galvanostatic mode and produced a proton current across the membrane. The test cell (as shown in Fig. 2) was placed in a thermo-controlled water bath for measurement at relatively humidity (RH) of 100%. DC conductivity is calculated from Cole–Cole plots (Z'' versus Z').

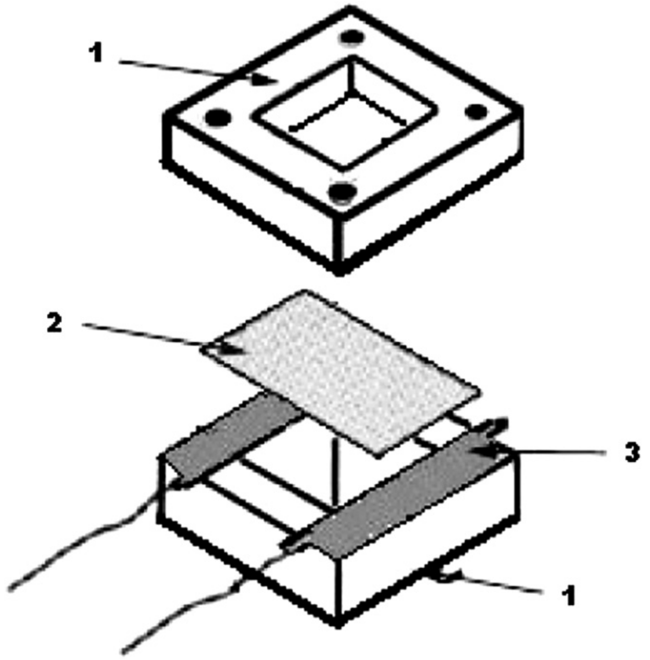

Fig. 2. Cell used for the determination of the proton conductivity of the membranes, (1) Teflon® block; (2) membrane sample; (3) blackened Pt foil.

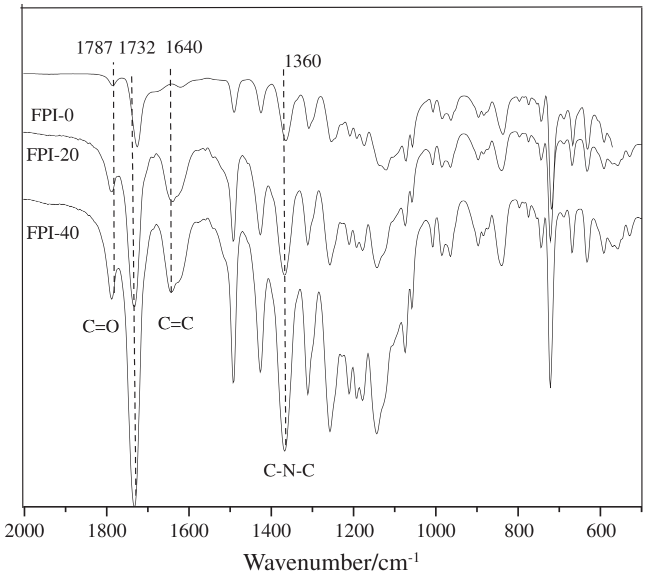

Fig. 3. FTIR spectra of crosslinkable fluorine-containing polyimide (FPI–*X*) samples.

The chemical oxidative stability of the composite membranes was examined by immersing the membranes in Fenton reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at room temperature [11]. It was characterized by the elapsed time that the membranes started to become a little brittle (the membranes were broken after being drastically shaken).

3. Results and discussion

3.1. Synthesis and crosslinking of fluorine-containing polyimide

As depicted in Fig. 1, the fluorine-containing polyimide was synthesized by polymerization of 6FDA, PFMB, and end-capped with AS. As a comparison, FPI–0 was synthesized from 6FDA and PFMB. By changing the molar ratio of AS and PFMB, a series of FPIs with different molar contents of crosslinkable groups ranging from 0 to 80% can be obtained. The feed ratio of the monomers of FPI–*X* and the molecular weight of FPI–*X* measured by GPC are listed in Table 1. The number-average molecular weight of FPI–*X* decreases

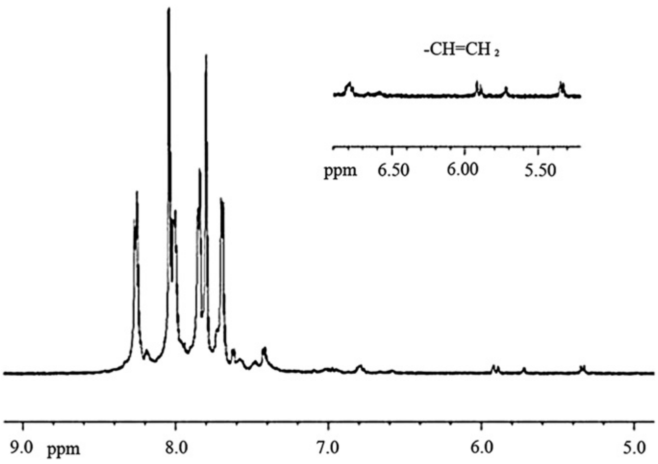

Fig. 4. ^{1}H-NMR spectrum of crosslinkable fluorine-containing polyimide (FPI–20).

with increasing X. The reason is that AS is an end-capping reagent, which certainly results in lower molecular weight when X increases. The chemical structures of FPI–0, FPI–20, and FPI–40 are characterized by FTIR and ^{1}H-NMR.

As shown in Fig. 3, the absorption bands at 1787 and 1732 cm^{-1} are assigned to the stretch vibration of carbonyl groups of imido ring. The stretching vibration of C–N–C in the imido ring is observed around 1360 cm^{-1}. Compared to IR spectrum of FPI–0, the peaks at 1640 cm^{-1} of FPI–20 and FPI–40 are attributed to the vibration of the C=C in the ethylene group. From Fig. 4, the signals at 6.8–8.2 ppm are assigned to Ar–H. The peaks at 5.3 ppm, 5.7 ppm, 5.9 ppm, and 6.6 ppm are attributed to the ethylene groups. Therefore, it can be concluded that the ethylene groups are imported to FPI successfully.

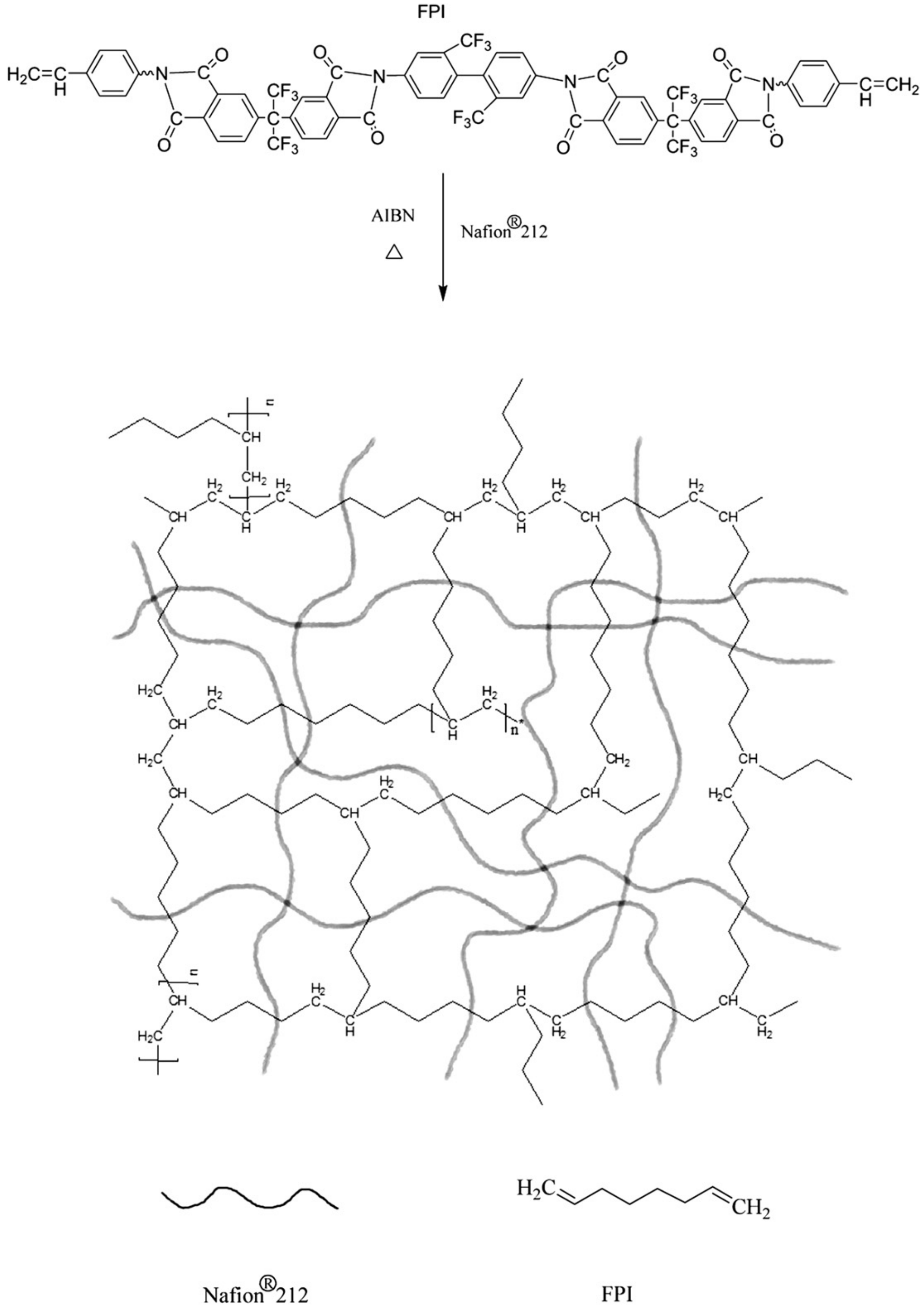

Fig. 5. Semi-IPN structure of the FPI/Nafion® 212 composite membrane.

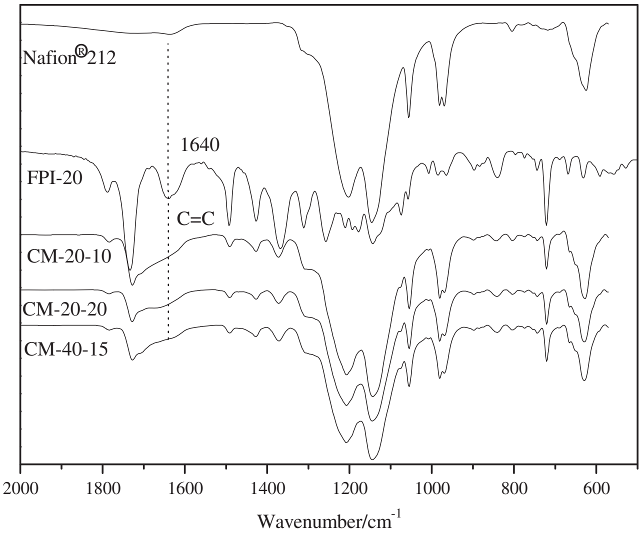

Fig. 6. FTIR spectra of Nafion®212 and composite membranes.

During the membrane preparation, the ethylene in FPI is polymerized with the help of the initiator AIBN and the network structure (Fig. 5) is formed within the composite membranes. At the same time, UCM–20–20 (uncrosslinked CM–20–20) is also prepared as a comparison. The chemical structures of Nafion®212 and composite membranes are characterized by FTIR as shown in Fig. 6. From FTIR spectra, the absorption of the ethylene groups in the composite membranes at 1640 cm^{-1} is getting weaker with increasing FPI content. This indicates the polymerization of the ethylene during the membrane preparation.

3.2. *Degree of crosslinking and gel fraction of the composite membranes*

During the membrane preparation, semi-IPN structure is formed within the composite membranes. Gel fractions of the crosslinked networks can be regarded as an indirect method for assessing the degree of crosslinking. The measured gel fractions of the crosslinked membranes are given in Table 2. As shown in Table 2, the gel fraction of CM–20–*Y* decreases with increasing *Y*. With increasing FPI–20 content in the composite membranes, more crosslinked polymers with lower molecular weight may form, which can be soluble in DMSO. This may be attributed to the reason that the amount of the crosslinked molecular chains increases with increasing crosslinker content, which results in the lower reactivity of the free radical of the macromolecular. According to CM–*X*–15 membranes, the gel fraction increases with increasing ethylene content in FPI–*X* when *Y* equals to 15. This proves that the ethylene group of FPI reacts with each other and forms networks. The higher the ethylene content in FPI–*X*–15 is, the higher the crosslinking density of the composite membrane is.

Table 2
Gel fraction of the composite membranes.

Membranes	Content of vinyl groups in FPI (*X*, mol%)	Content of FPI-*X* (*Y*, wt%)	Nafion®212 (wt%)	Gel fraction (%)
CM–20–5	20	5	95	88.5
CM–20–10	20	10	90	62.8
CM–20–15	20	15	85	59.8
CM–20–20	20	20	80	58.3
CM–20–25	20	25	75	50.7
CM–40–15	40	15	85	65.9
CM–60–15	60	15	85	67.0
CM–80–15	80	15	85	66.2

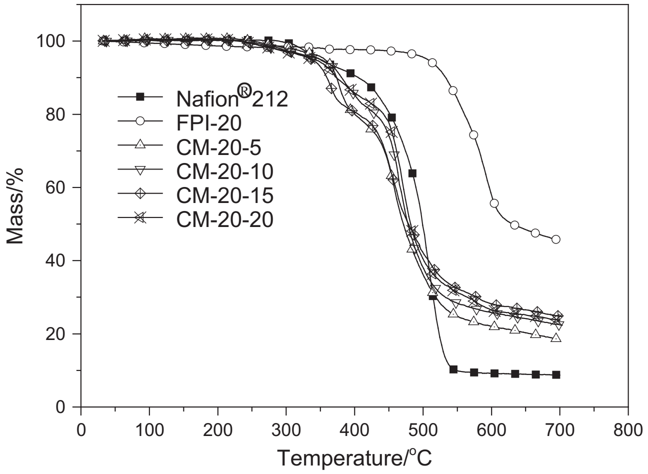

Fig. 7. Effects of the contents of FPI–20 on thermal degradation properties of CM–20–*Y*, nitrogen atmosphere, heating rate 10 °C min^{-1}.

3.3. *Thermal properties and chemical oxidative stability of the composite membranes*

The thermal stability of the composite membranes, Nafion® 212, and FPI–20 was examined by TGA, measured from 20 °C to 700 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Fig. 7 and Fig. 8 show the typical TGA curves of Nafion® 212, FPI–20, CM–20–*Y*, and CM–*X*–15. Two weight loss stages are observed for the recast Nafion®212 membrane. The first one is around 329 °C, which is attributed to the decomposition of the sulfonic acid group. The second stage of degradation around 509 °C is due to the degradation of the C–F bonds in Nafion®212 [24]. Only one obvious weight loss is observed in the TGA curve of FPI–20. The onset degradation temperature is around 544 °C, which is attributed to the decomposition of the main chain of FPI–20. Before 500 °C, FPI–20 still has a little weight loss, which may be due to the loss of the water produced from the imidization of the remained reactive groups in the polymer with the temperature increasing.

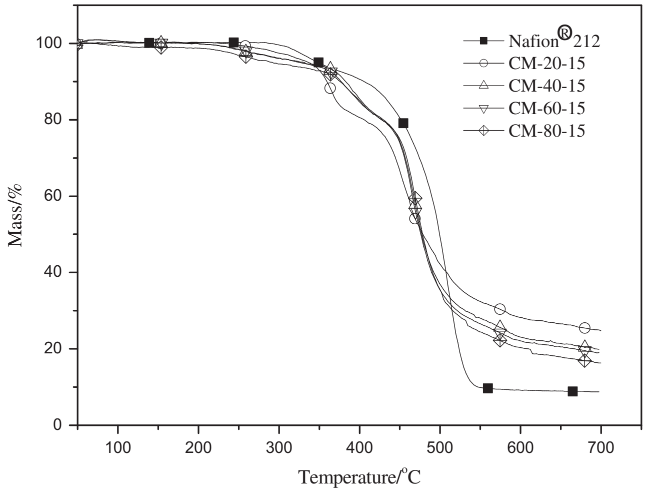

Fig. 8. Effects of the contents of vinyl groups in FPI on thermal degradation properties of CM–*X*–15, FPI content is 15%, nitrogen atmosphere, heating rate 10 °C min^{-1}.

For the composite membranes, they all exhibit a two-step degradation pattern, which is similar to that of Nafion®212. The first weight loss temperature of the composite membranes is in the range of 360–395 °C, which is higher than that of Nafion®212. The reason is that the crosslinked FPI and semi-IPN structure of the composite membranes restrict the activity of the backbone of the polymers. The second step of the composite membranes over 450 °C indicates the degradation of the main chain of FPI and Nafion®212. This is a little lower than that of Nafion®212. Because the crosslinked FPI contains the aliphatic C–H bond whose thermal stability is not as good as that of the aliphatic C–F in Nafion®212. The residual mass at 700 °C of the composite membranes is higher than that of the recast Nafion®212. All these data indicates that the composite membrane shows improved thermal stability to that of Nafion®212.

According to CM–*X*–15, both of the two onset temperatures for degradation are improved with increasing *X*. This is attributed to the higher content of the crosslinkable group and higher degree of crosslinking when *X* increases. As shown in Figs. 7 and 8, the residual mass of CM–20–Y increases with increasing *Y*, whereas that of CM–*X*–15 decreases with increasing *X*. For CM–20–*Y*, the FPI–20 content in the composite membranes increases with increasing *Y*. FPI–20 has better thermal stability than that of pure Nafion®212. So the residual mass of the composite membranes increases with increasing FPI–20 content (*Y*). For CM–*X*–15, the weight ratio of FPI–*X* and Nafion®212 is fixed. When *X* increases, the vinyl contents in FPI–*X* increase, which results the increase of the aliphatic $-CH_2-$ contents in the composite membranes. Therefore, the residual mass of CM–*X*–15 decreases with increasing *X*.

The oxidative stability of the composite membranes is also investigated in Fenton reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 25 °C. It is characterized by the elapsed time when the membranes start to break into pieces after being drastically shaken. The composite membranes maintain their integrality after being soaked in the Fenton reagent for more than four months. All the composite membranes show excellent oxidative stabilities.

3.4. *Mechanical properties of the composite membranes*

The adequate mechanical strength is one of the crucial factors for PEM in fuel cell regarding of the membrane-electrode-assembly (MEA) preparation. The tensile strength of the composite membranes and pure Nafion® 212 was examined at room temperature in dry state and the data are shown in Fig. 9. The tensile strength of the composite membranes is much higher than that of pure Nafion® 212. When the content of FPI–20 in CM–20–*Y* is lower than 20%, the tensile strength of the composite membrane increases with increasing FPI–20 content. This may be attributed to the existence of crosslinked FPI–20 in the composite membranes. Taking CM–20–20 as an example, the tensile property of the composite membrane with crosslinked FPI–20 is much higher than that of the membrane (UCM–20–20) with uncrosslinked FPI–20. The mechanical property of UCM–20–20 (30.4 MPa) is higher than that of pure Nafion® 212 membranes and much lower than that of CM–20–20 (48.6 MPa) with crosslinked network. FPI–20 is crosslinked during the membrane preparation and forms the semi-IPN structure within the composite membrane, which can improve the tensile property greatly. This can also prove the crosslinking of FPI–20 in the membrane. However, it declines when *Y* rises to 25%. The membrane with 30% FPI–20 is brittle and is not able to be tested. This may be due to the compatibility of Nafion® 212 and FPI, and it becomes worse when FPI content is higher.

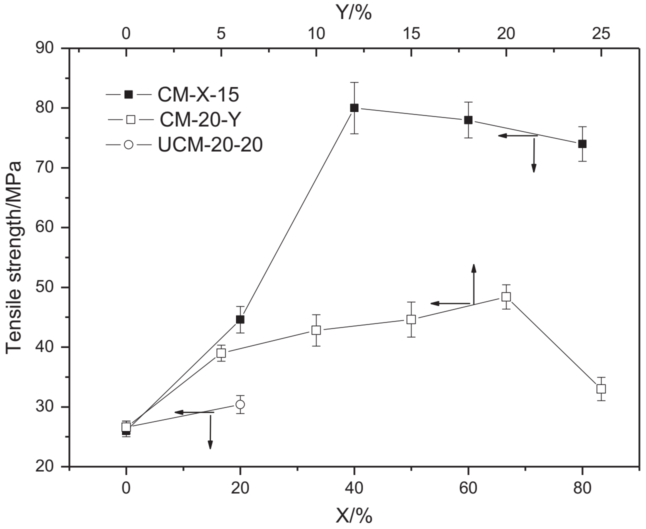

Fig. 9. Effects of the contents of FPI–*X* contents in the composite membrane on the tensile strength of CM–20–*Y* and CM–*X*–15.

As shown in Fig. 9, the tensile strength of CM–*X*–15 increases with increasing *X* till 40, and then decreases. The content of the crosslinkable ethylene groups increases with increasing *X* and forms the crosslinked network. When *X* is higher than 40, the degree of crosslinking of the membranes decreases, which results in the lower tensile strength. CM–40–15 has highest tensile strength of 80 MPa, which is more than 3 times of Nafion® 212. The tensile strength of CM–60–15 and CM–80–15 is 78 MPa and 74 MPa respectively, which is a little lower than that of CM–40–15. According to CM–*X*–15, the tensile strength is affected by the molecular weight of the crosslinked FPI–*X* in the composite membranes. The molecular weight of the crosslinked FPI–*X* is determined by the molecular weight of the polymer FPI–*X* (M_n) and the degree of crosslinking. The higher the molecular weight of the polymer FPI–*X* and the degree of the crosslinking are, the higher the tensile strength of the composite membrane has. M_n decreases with increasing *X*, while the degree of crosslinking increases with increasing *X*. Under these two factors, the tensile strength of CM–*X*–15 increases first and then decreases with increasing *X*.

Fig. 10 shows DMA results of Nafion®212, CM–20–15, CM–20–20, and CM–40–15. The composite membranes have higher initial tensile storage modulus (E′) than that of Nafion®212. From 50 °C to 118 °C, the change of storage modulus is much

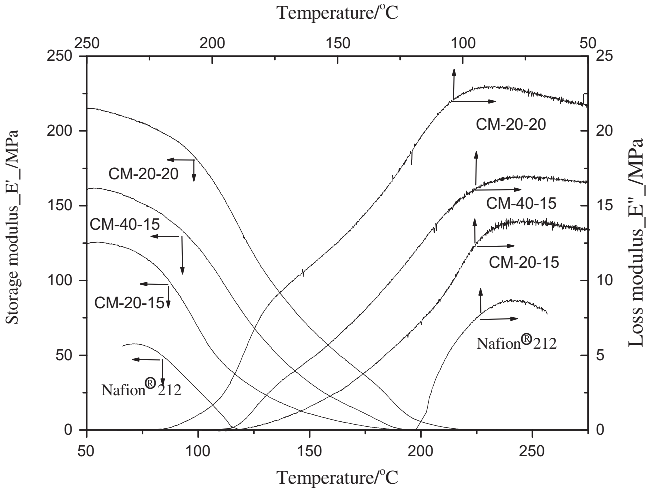

Fig. 10. Dynamic mechanical analysis (DMA) curves of CM–*X*–*Y* and Nafion®212.

smaller for CM–20–15 (71%) and CM–40–15 (48%) than that for Nafion®212 (100%). The initial storage modulus of CM–20–20 is higher than that of CM–20–15 because of the higher content of FPI–20 in the composite membranes. Meanwhile, CM–40–15 also has higher modulus than CM–20–15 for higher content of the crosslinkable groups in FPI–*X*. Both of the higher modulus and mechanical strength suggests better mechanical properties of the composite membranes than that of Nafion®212.

3.5. *Water uptake and swelling ratio of the composite membranes*

The proton conductivity of PEM strongly depends on the water uptake and the inside structure of the membrane. Only enough water can ensure the proton transport from the anode to the cathode. However, too much water brings on large swelling ratio and low tensile properties. Since current PEMs, like Nafion®, are used below 80 °C in PEMFC, herein the water uptake and the swelling ratio of the composite membranes were measured at both room temperature (25 °C) and 80 °C by dry and wet method.

From Table 3, the water uptake of the recast Nafion® 212 is much higher than that of the composite membranes at both 25 °C and 80 °C. The water uptake of the composite membranes decreases with increasing FPI–20 content in CM–20–*Y* because the density of the hydrophilic sulfonic group in the composite membranes decreases with increasing *Y*. As to CM–*X*–15, the water uptake increases with increasing *X*. This is due to the higher content of the aliphatic C–H in CM–*X*–15 with increasing *X* and the aliphatic C–H is more hydrophilic than that of C–F. The water uptake of the composite membrane increases with increasing temperature. This may be attributed to the high mobility of the polymer chain and larger free volume of the polymers in the membrane at a higher temperature.

The swelling ratio of the membrane is an important property for PEM since too high swelling ratio can lead to destruction of the membrane-electrode-assembly in PEMFC. The swelling ratio of the composite membranes was tested at room temperature and 80 °C. As shown in Table 3, the swelling ratio increases with increasing temperature, this is similar to that of water uptake. The swelling ratio of the composite membrane is much smaller than that of pure Nafion® 212 at both temperatures. This may be due to the introduction of the crosslinked FPI and the semi-IPN structure of the composite membranes, which restrains the swelling of Nafion® 212. The swelling ratio of the composite membranes decreases from 14.6% (Pure Nafion® 212) to 3.7%–6.9% at 80 °C. This data indicates that the composite membranes have much better dimensional stabilities than that of pure Nafion® 212.

3.6. *Proton conductivity of the composite membranes*

Proton conductivities of the composite membranes with various FPI contents were measured with temperature from 30 °C to 100 °C and in 100% relative humidity by AC impedance spectroscopy. All the membrane samples were soaked in water over 24 h for hydration before measurement. The results are shown in Figs. 11 and 12. The proton conductivity of the recast Nafion®212 is listed as a comparison under the same condition. All membranes show an increase in proton conductivity with increasing temperature. The proton conductivity of the composite membrane is lower than that of pure Nafion®212, and it decreases with increasing FPI–20 content in CM–20–*Y*. The reason is that FPI in the composite membrane has no proton conductivity and reduces the total number of the sulfonic groups with the increase of FPI content in CM–20–*Y*. However, all the composite membranes still have considerable high proton conductivities ranging from 2.0×10^{-2} S cm^{-1} to 8.9×10^{-2} S cm^{-1} (from 30 °C to 100 °C).

Table 3
Water uptake, swelling ratio of the composite membranes.

Membranes	Water uptake (%, w/w)		Swelling ratio (%)	
	25 °C	80 °C	25 °C	80 °C
Nafion®212	19.6	28.8	9.9	14.6
CM–20–5	6.8	18.7	3.3	6.3
CM–20–10	6.2	12.4	3.1	5.1
CM–20–15	5.8	12.1	3.1	4.9
CM–20–20	4.9	11.6	2.0	4.4
CM–20–25	4.6	10.6	1.1	3.7
CM–40–15	7.0	13.2	4.4	6.2
CM–60–15	7.8	14.3	5.2	6.9
CM–80–15	8.9	15.1	5.4	6.5

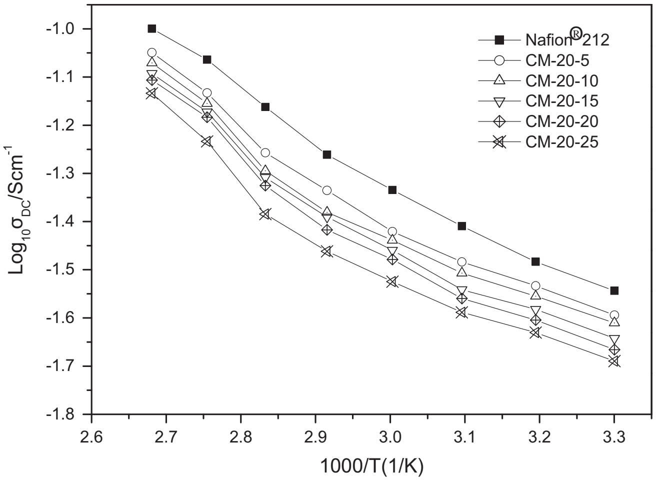

Fig. 11. Effects of the contents of FPI–*X* in the membranes on temperature dependence of proton conductivity of Nafion®212 and CM–20–*Y*, 100% relative humidity.

The values of the activation energy E_a for each of the composite membranes is calculated using the Arrhenius equation (Eq. (3)),

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where *R* is Boltzmann constant; E_a is activation energy; *T* is temperature. By calculation, the activation energy E_a of the composite membranes is in the range of 16.4–18.6 KJ mol^{-1}. The proton transport of the composite membranes might have been

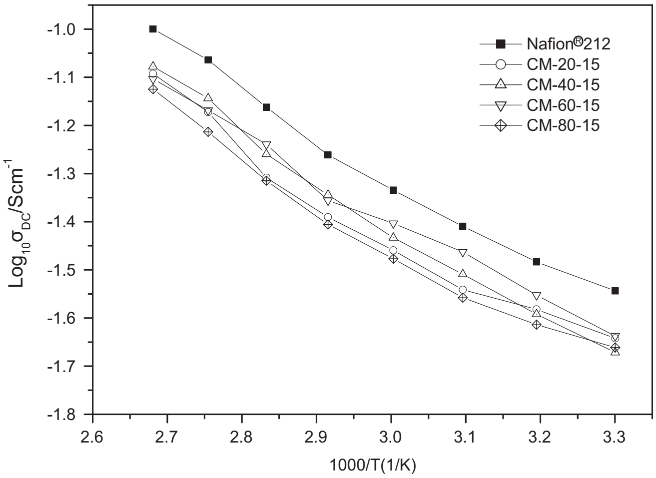

Fig. 12. Effects of the contents of vinyl groups in FPI–*X* on temperature dependence of proton conductivity of Nafion®212 and CM–*X*–15, 100% relative humidity.

occurred predominantly by the Vehicle mechanism [25,26]. The Vehicle mechanism suggests that the proton transport is controlled through H_3O^+ and $H_5O_2^+$ mediated proton transfer.

4. Conclusions

A series of fluorine-containing polyimides with crosslinkable vinyl group were synthesized from 6FDA, PFMB, and end-capped with AS thereafter. Nafion®212/FPI composite membranes with semi-interpenetrating polymer networks were successfully prepared through solution casting and crosslinking thereafter. The mechanical properties of the composite membranes with semi-IPN structure are much higher than that of the physically blended membranes of FPI and Nafion®212. Compared to pure Nafion®212, the composite membranes exhibit much improved tensile strength and dimensional stability. The proton conductivity of the composite membranes decreases with increasing FPI content, and is in the range from $2.0 \times 10^{-2}\ \mathrm{S\,cm^{-1}}$ to $8.9 \times 10^{-2}\ \mathrm{S\,cm^{-1}}$. The proton transport of the composite membranes was mainly contributed by Vehicle mechanism.

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