

**SYNTHESIS, CHARACTERIZATION AND EVALUATION OF
SULFONATED POLYIMIDES AND SULFONATED PEEK
BASED PROTON EXCHANGE MEMBRANES**

POOJA CHHABRA



**CENTRE FOR POLYMER SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
HAUZ KHAS, NEW DELHI-110016**

JULY 2009

**SYNTHESIS, CHARACTERIZATION AND EVALUATION OF
SULFONATED POLYIMIDES AND SULFONATED PEEK
BASED PROTON EXCHANGE MEMBRANES**

by

POOJA CHHABRA

Centre for Polymer Science and Engineering

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110016

July 2009

CERTIFICATE

This is to certify that thesis entitled “**Synthesis, Characterization and Evaluation of Sulfonated Polyimides and Sulfonated PEEK Based Proton Exchange Membranes**” being submitted by **Ms. Pooja Chhabra** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research carried out by her. **Ms. Pooja Chhabra** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

Prof. (Mrs.) Veena Choudhary

Centre for Polymer Science & Engineering

Indian Institute of Technology, Delhi,

Hauz Khas, New Delhi - 110016

ACKNOWLEDGEMENT

I wish to express my deep dense of gratitude to my supervisor, Prof. (Mrs.) Veena Choudhary for her invaluable guidance and constant encouragement. Her caring attitude and co-operation have been invaluable throughout my research. Through her wealth of knowledge, direction and leadership I have been able to expand my knowledge in many areas of polymer science.

I am thankful to Prof. S.N.Maiti, Prof. A.K.Ghosh, Prof. B.L Deopura, Dr. S.Basu, Dr. Josemon Jacob, Dr. B.Sathpathy and Prof. A.K.Gupta for their constant encouragement and help throughout my project.

My special thanks to Mr. Surrender Kumar, Mrs. Rama, Mr. Shivkant, Mr. Ashok Kapoor and Mr. Devender Singh for their immediate help whenever needed.

I express my thanks to Dr. Pitchumani and Dr. A K Sahoo of Central Electrochemical Research Institute , CECRI, Chennai, in helping me setting up the facility for proton conductivity measurement in our lab.

Nothing could have been accomplished without my family support. I would like to extend my special gratitude to my family for their love, support and encouragement.

Much thanks is due to my husband Sanjay and my dear son Aayush. Their support, encouragement and patience enable me to pursue my career, while at the same time enjoying a lifetime of happiness with them.

I am extremely thankful to all my friends and colleagues Dr. Dipti Singh, Dr. Neetu, Piyush, Pravin, Shveta Mahajan, Geeta, Dr. Bala, Dr. Senthil, Dr. Sangeeta, Dr. Nimisha, Dr. Rashmi, Anju, Deeksha, Nikhil and Varsha for their constant encouragement.

The financial assistance provided by IIT Delhi is highly acknowledged.

Last but not the least I am thankful to the Almighty God in helping me to accomplish this task.

Pooja Chhabra

ABSTRACT

The main aim of the present studies was to synthesize and characterise sulfonated polymers [sulfonated polyimides and sulfonated poly (ether ether ketone)] and characterise them to evaluate their performance as proton exchange membranes for fuel cell applications. Sulfonated polyimides [SPI] were synthesized using sulfonated monomers whereas sulfonated PEEK [SPEEK] was synthesized using post sulfonation technique i.e. by sulphonating the commercially available polymer. Films based on polymer blends [SPEEK and SPI] and composites [sulfonated PEEK and inorganic fillers such as POSS or Laponite] were also prepared and evaluated.

The thesis has been divided into six chapters. Chapter 1 is a comprehensive review of the work reported in the literature by different groups on the synthesis of SPI's and SPEEK. It also covers the different techniques used for their characterization and applications.

The general procedures adapted for the synthesis of SPI's [from sulfonated monomers] and SPEEK [by post-sulfonation] are given in Chapter 2. The techniques used for characterization and evaluation of properties of sulfonated polymers are also described in this chapter.

The details of synthesis of sulfonated polyimides are reported in Chapter 3 of the thesis. Eleven sulfonated copolymers with varying degree of sulfonation were synthesised by reacting naphthalene tetracarboxylic dianhydride [NTDA] with varying molar ratio of sulfonated diamine [4, 4'-diaminodiphenyl ether-2, 2'-disulfonic acid [ODADS]: non-sulfonated diamines[4,4'-(hexafluoro-isopropylidene)bis(4-phenoxyaniline) [BDAF]/4,4'-(9-fluorenylidene)dianiline [BAPF]/4,4'- diaminodiphenyl ether [ODA] by one step method using cresol as solvent and benzoic acid and isoquinoline as catalysts. The molar ratio of ODADS: BDAF/BAPF/ODA was taken as 1:3, 0.75:1.25, 1:1 or 3:1 to investigate the effect

of degree of sulfonation and the structure of the non-sulfonated diamine on the properties of SPI's. Copolyimides based on BDAF, BAF and ODA have been designated as SPF, SPB and SPO respectively followed by numerical prefix representing the mole % of sulfonated diamine.

Structural and thermal characterization of SPI's was done using FTIR, NMR and thermogravimetry respectively. In the FT-IR spectra of all the synthesized polymers, absorption bands due to naphthalimide carbonyl [1710 cm^{-1} (asymmetric) and 1668 cm^{-1} (symmetric)]; C-N-C vibration [$\sim 1345\text{ cm}^{-1}$] and SO_2 stretching [1080 (asymmetric) and 1030 (symmetric) cm^{-1}] were observed. The intensity of SO_2 stretching bands increased with increasing level of sulfonation. $^1\text{H-NMR}$ was used to calculate the degree of sulfonation and the values calculated agreed well with theoretical values based on the feed composition.

In the TG traces of all the polymers, three step degradation was observed. Thermal stability of SPI's having different structure and degree of sulfonation was compared by comparing the mass loss in the temperature range $50\text{-}200\text{ }^\circ\text{C}$ [which is due to the loss of physically and chemically bound water]; $200\text{-}450\text{ }^\circ\text{C}$ [attributed to the decomposition of sulfonic acid groups] and above $450\text{ - }800\text{ }^\circ\text{C}$ [due to main chain degradation]. The mass loss in the temperature range of $50\text{-}200\text{ }^\circ\text{C}$ and $200\text{-}450\text{ }^\circ\text{C}$ increased with increasing degree of sulfonation. Thermal stability of co-polyimides in the protonated and triethylamine salt form were also compared and it was found that in the salt form char yield at $800\text{ }^\circ\text{C}$ was lower as compared to its corresponding protonated copolymer.

Water uptake was measured for all the polymers at $80\text{ }^\circ\text{C}$ and it was in the range $14\text{-}56\%$. Hydrolytic stability of all the polymers was also checked at $80\text{ }^\circ\text{C}$. SPI's based on the non-sulfonated diamine BDAF had very good hydrolytic stability. Dynamic mechanical characterization of films in the tensile mode at a strain of 1% was measured at a frequency of

1 Hz. A heating rate of 5°C/min and sample size with length: 15 to 30 mm, width: 5 mm to 6.5 mm and thickness: 50 to 100 µm was used for recording DMA traces. SPI membranes had significantly higher values of storage modulus over the whole temperature range as compared to Nafion. Nafion became rubbery at temperature > 150 °C whereas SPI's retained their stiffness even up to a temperature of 350 °C.

For all the SPI series, proton conductivity [measured using two probe method, in the thickness direction] increased with increasing degree of sulfonation and temperature. The proton conductivity of the synthesized SPI's was in the range 0.42 – 4.72 mS/cm (90 °C) whereas proton conductivity of Nafion measured under similar conditions was 3.24 mS/cm. All the SPI's synthesized had methanol permeability in the range of 0.85-5.5 x 10⁻⁷ cm²/s which was lower than the methanol permeability of Nafion (11.2 x10⁻⁷ cm²/s).

Details of synthesis of SPEEK using conc. H₂SO₄ as the sulfonating agent and the preparation of blends based on SPEEK and SPI's are given in Chapter 4 of the thesis.

Structural and thermal characterisation of SPEEK was done using FTIR, NMR and thermogravimetry respectively. In the FTIR spectrum of SPEEK, bands corresponding to sulfonic acid groups 1080 cm⁻¹ (asymmetric O=S=O), 1024 cm⁻¹ (symmetric O=S=O) were observed and C-C absorption band at 1492 cm⁻¹ showed a split upon sulphonation (1472 cm⁻¹). ¹H-NMR was used to ascertain the degree of sulfonation of SPEEK. The ratio of peak intensity of the proton next to the carbon having sulfonic acid group to the rest of the protons was used to calculate the degree of sulfonation. The degree of sulfonation varied from 54-84%. Above 70% DS, the polymer was soluble in methanol, acetone and swelled in water. Therefore, for the preparation of blends SPEEK with degree of sulfonation ~ 60% was chosen.

A single step degradation was observed in PEEK whereas SPEEK showed three step degradation i.e first step mass loss in the temperature range of 50-200 °C [due to the loss of physically and chemically bound water]; second step mass loss in the temperature range of 200-450 °C [is attributed to the decomposition of sulfonic acid groups] and third step mass loss was observed above 450 °C [due to main chain degradation]. PEEK was stable up to 500 °C.

Blend films were prepared by mixing DMSO solutions of SPI's [which as such gave brittle films but had good proton conductivity] and SPEEK [60 % DS]. All the blend membranes were transparent and did not show turbidity or phase separation during solution mixing or during drying. For the preparation of blend films SPB-25, SPB-37, SPB-50, SPO-50, SPO-75, SPF-75 were blended with SPEEK (DS 60%). In all 18 blend films were prepared by taking SPI and SPEEK in the ratio 1:3, 1:1 and 3:1 and were evaluated for their properties.

The membranes based on polymer blends irrespective of structure, degree of sulfonation or blend composition showed three step degradation, thus indicating that the two polymers degrade independently and the mechanism of degradation did not change upon blending. Dynamic mechanical analysis showed a significant increase in storage modulus values of SPEEK upon blending with SPI's and it was much higher as compared to Nafion. The membranes based on polymer blends retained their stiffness up to 300 °C whereas SPEEK and Nafion became rubbery above 150 °C. Water uptake in case of membranes based on polymer blends was higher as compared to SPEEK. However, stable membranes could not be prepared by taking SPI's with higher DS and in higher amounts. The proton conductivity of different blends varied from 0.44 to 3.12 mS/cm. Methanol permeability of the blend membranes varied in the range of $1.3 - 5.8 \times 10^{-6} \text{ cm}^2/\text{s}$ which was almost an order of magnitude lower than Nafion.

Chapter 5 of the thesis gives the details about the preparation of composite membranes based on SPEEK and the nano fillers i.e. tri silanol phenyl polyhedral oligomeric silsesquioxane [POSS] and nano clay [Laponite]. Several samples were prepared by mixing varying amounts [0.5 – 5 phr] of POSS or Laponite.

It was observed that addition of 2 phr of POSS and 0.5 phr of Laponite gave membranes with higher proton conductivity, water uptake and lower methanol permeability. Proton conductivity in the presence of POSS was almost double whereas methanol permeability was reduced by an order of magnitude as compared to Nafion. At higher concentration of POSS proton conductivity decreased which could be attributed to the agglomeration of POSS which hinders the mobility of protons.

Presence of nano particles in the composite membranes was confirmed by WAXD. Crystallinity of POSS was disturbed and instead of many crystalline peaks just a hump was observed. For the composite membranes based on Laponite intercalation was observed i.e. the layered structure of Laponite was disturbed. All the crystalline peaks corresponding to SPEEK were observed. In the SEM of composite membranes at lower concentration (0.5 and 1 phr) the distribution of nano fillers was homogenous i.e no agglomeration of nano particles was observed but composite films having higher amounts i.e. 2 and 5 phr of nano fillers, agglomeration was observed. In the SEM-EDX of the composite membranes with increasing amount of POSS in the SPEEK samples the intensity of the peak corresponding to Si increased which proved that POSS was evenly distributed in the polymer matrix. Thermal stability of composite membranes remained unaffected by addition of nano fillers. All the samples showed three step degradation.

Chapter 6 consists of the general summary and conclusions of the work done.

References are given at the end of each chapter.

Contents

	Page No.
Abstract	i-vi
List of Figures	vii-xi
List of Tables	xii-xv
List of Schemes	xvi-xvii
CHAPTER 1: INTRODUCTION AND LITERATURE SURVEY	1-66
1.1 Introduction	1
1.2 Sulfonation of Polymers	5
1.2.1 Mechanism of Sulfonation	6
1.3 Sulfonated Polyimides	8
1.4 Sulfonated Poly (ether ether ketone)	24
1.5 Blend Membranes	28
1.6 Composite Membranes	31
1.7 Characterization of Membranes	37
1.7.1 Water Uptake	38
1.7.2 Proton Conductivity	38
1.7.3 Methanol Permeability	41
1.7.4 Hydrolytic Stability	42
1.7.5 Thermal Properties	43
1.7.6 Mechanical Properties	44

	1.7.7 Morphological Studies	45
1.8	Aim of the Work	46
1.9	Format of Thesis	47
	References	48
CHAPTER 2:	EXPERIMENTAL TECHNIQUES: SYNTHESIS,	67-85
	CHARACTERIZATION AND EVALUATION OF	
	PROPERTIES	
2.1	Materials	67
2.2	Synthesis of Sulfonated Polyimides (SPI's)	72
2.3	Preparation of Sulfonated PEEK (SPEEK)	76
2.4	Characterization	76
	2.4.1 Structural Characterization	76
	2.4.1.1 FT-IR Spectroscopy	76
	2.4.1.2 ¹ H-NMR Spectroscopy	76
	2.4.2 Thermal Characterization	77
	2.4.2.1 Thermogravimetric Analysis	77
	2.4.2.2 Differential Scanning Calorimetry	77
2.5	Film Casting	77
	2.5.1 Sulfonated Polyimide Films	77
	2.5.2 Sulfonated PEEK Films	77
	2.5.3 Preparation of Films based on Blends of SPI's and SPEEK	78
	2.5.4 Preparation of Composite Films	78
2.6	Characterization of Films	78
	2.6.1 Ion-Exchange Capacity (IEC)	79

	2.6.2 Water Uptake	80
	2.6.3 Hydrolytic Stability	80
	2.6.4 Dynamic Mechanical Analysis	80
	2.6.5 Proton Conductivity	81
	2.6.6 Methanol Permeability	82
	2.6.7 Morphological Studies	84
	2.6.8 X-ray Diffraction	84
	References	85
CHAPTER 3:	SYNTHESIS AND CHARACTERIZATION OF	86-139
	SULFONATED POLYIMIDES	
3.1	Introduction	86
3.2	Experimental	88
3.3	Results and Discussion	88
	3.3.1 Structural Characterization	88
	3.3.1.1 FT-IR Spectroscopy	88
	3.3.1.2 ¹ H-NMR Spectroscopy	95
	3.3.2 Thermal Characterisation	109
	3.2.2.1 Thermogravimetric Analysis	109
	3.3.3 Film Characterization	117
	3.3.3.1 Water Uptake	119
	3.3.3.2 Dynamic Mechanical Analysis	123
	3.3.3.3 Proton Conductivity	126
	3.3.3.4 Methanol Permeability	136
3.4	Conclusion	137
	References	138

CHAPTER 4:	STUDIES ON BLENDS BASED ON SULFONATED	140-161
	POLYIMIDES AND SULFONATED POLY (ETHER	
	ETHER KETONE)	
4.1	Introduction	140
4.2	Experimental	141
	4.2.1 Synthesis of SPEEK	141
4.3	Characterization of SPEEK	142
	4.3.1 Structural Characterization	142
	(i) FT-IR	142
	(ii) ¹ H-NMR	142
	4.3.2 Thermal Characterisation	145
4.4	Preparation of Polymer Blends	146
4.5	Results and Discussion	147
	4.5.1 Thermogravimetric Analysis	147
	4.5.2 Dynamic Mechanical Analysis	154
	4.5.3 Water Uptake	155
	4.5.4 Proton Conductivity	156
	4.5.5 Methanol Permeability	158
4.6	Conclusion	159
	References	160
CHAPTER 5:	PREPARATION, CHARACTERIZATION AND	162-188
	EVALUATION OF COMPOSITE MEMBRANES	

BASED ON SPEEK AND INORGANIC FILLERS

5.1	Introduction	162
5.2	Experimental	164
	5.2.1 Composite Membranes Based on SPEEK and POSS	164
5.3	Results and Discussion	165
	5.3.1 Water Uptake	165
	5.3.2 Proton Conductivity	166
	5.3.3 Methanol Permeability	169
	5.3.4 Morphological Characterisation	169
	5.3.4.1 XRD	169
	5.3.4.2 Scanning Electron Microscopy	170
	5.3.4.3 SEM – EDX	171
	5.3.4.4 Atomic Force Microscopy	173
	5.3.5 Thermal Characterisation	175
	5.3.5.1 Thermogravimetric Analysis	175
	5.3.5.2 DSC Studies	177
5.4	Composite Membranes based on SPEEK and Laponite	178
	5.4.1 Water Uptake	178
	5.4.2 Proton Conductivity	179
	5.4.3 Methanol Permeability	180
	5.4.4 Morphological Characterisation	181
	5.4.4.1 XRD Analysis	181
	5.4.4.2 SEM	182
	5.4.5 Thermal Analysis	183
5.5	Conclusion	183

	References	185
CHAPTER 6:	SUMMARY AND CONCLUSIONS	189-198
6.1	Introduction	189
6.2	Synthesis and Characterization of Sulfonated Polyimides	190
6.3	Synthesis and Characterisation of Sulfonated PEEK	193
6.4	Preparation of SPI-SPEEK Polymer Blends	194
6.5	Preparation, Characterisation and Evaluation of Composite Membranes	196
6.6	Scope of future work	199
APPENDIX		
LIST OF PUBLICATIONS		
BIO-DATA		