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

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by

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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.

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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'-(hexafluro-isopropylidiene)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 [~ 1345 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}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 50-200 °C [which is due to the loss of physically and chemically bound water]; 200-450 °C [attributed to the decomposition of sulfonic acid groups] and above 450 – 800 °C [due to main chain degradation]. The mass loss in the temperature range of 50-200 °C and 200-450 °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 °C was lower as compared to its corresponding protonated copolymer.

Water uptake was measured for all the polymers at 80 °C and it was in the range 14-56%. Hydrolytic stability of all the polymers was also checked at 80 °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} cm^2/s which was lower than the methanol permeability of Nafion (11.2 x10^{-7} cm^2/s).

Details of synthesis of SPEEK using conc. H_2SO_4 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}). ^{1}H-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 $x10^{-6}$ cm^2/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

BASED ON SPEEK AND INORGANIC FILLERS