

연료전지 전해질막으로의 응용을 위한 산-염기 폴리이미드
**Acid-Base Polyimide Blends for the Application as Electrolyte Membranes
for Fuel Cells**

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INTRODUCTION

The search for alternative fuel got intensified from the mid of the 20th century, due to depleting natural resources and hiking petroleum prices. The alternative energy sources suggested earlier, especially for transport applications enjoyed only brief stints and they were unable to cope to the market demands. Conceived of in 1840s, fuel cells are still looms on the horizon as automotive El Dorado. They not only mean alternative to petrol fuels but promises much more, as they have quieter engines - there is no combustion and they are eco friendly - they emit nothing more harmful than water vapor. PEMFC and DMFC are identified as more suitable for automation purpose owing to high charge density, low temperature operation and simple operating conditions [1, 2].

Polyaromatics having good thermal, thermo-oxidative and chemical stabilities are screened for their application as electrolyte membranes and polyimides are one among them. Polyimides, possessing all the virtues properties of polyaromatics also have few unique advantageous. Polyimides show very little sensitivity to external conditions due to the vitreous nature of their polymer chain which is very useful in the development of commercial PEMFC products. Moreover, unlike most of the membranes, the number of watermolecules per ionic group is independent of equivalent weight and conductivity is not related to the water content in the membrane. In sulfonated polyimides the monomers contain an internal structure of ionic domains which are not water droplets, but an ionic part of the polymer chain and the microstructure of the membrane is probably lamellar or disc-like, and fundamentally different from the other ion exchange membranes which are essentially spherical ionic domains. Because of this anisotropy of the microstructure, the existence of nano-scale porosity and the fact that this microstructure is formed of hydrophobic domains embedded in a continuous ionic phase composed of ionic sticks and a large quantity of freevolume. These make polyimides as an interesting new class of ion exchange membranes,

having properties which are fundamentally different from those of per-fluorinated membranes.

Despite the fore mentioned salient properties the hydrolytic stability is the primary obstacle in the application as electrolyte membrane in fuel cell. Various approaches have been put forth to develop membranes of higher hydrolytic stability that includes (1) incorporating monomers having flexible linkages, (2) incorporating monomers not having both sulfonic acid group and amine group in the same ring, (3) diamine monomers having high nucleophilicity, (4) using aliphatic diamines, (5) using naphthalenic dianhydrides and (6) diamines having sulfonic acid group in side chain.

Acid-Base blend membranes otherwise described as organic-organic composite membranes are new class of interesting materials that exhibit improved thermal stability and good resistance to swelling. Kerres et.al. reported several acid base blends in polysulfones using various basic polymers. These blend membranes are synthesized by a combination of polymeric nitrogen-containing bases (N-bases) with polymeric sulfonic acids. The formation and properties of the blend membranes are based on the interaction between the sulfonic group acids and the N-bases. This may lead to the formation of hydrogen bonds or the protonation of the basic N-sites. This paper reports the synthesis and characterization of novel Acid-Base blend polyimides for the first time.

A novel polyimide having polymeric base containing tertiary nitrogen group is synthesized and it was blended with polyimide having sulfonic acid group. Ionomeric polyimide blends by mixing different molar ratio of base polyimide to acid polyimide was synthesized and their properties are reported. Tough, flexible membranes having good mechanical stability are obtained. Variation in the properties and morphologies were accomplished by variation of blend compositions.

EXPERIMENTAL

Materials and Synthesis of Polyimides

1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), 4,4'-diaminobiphenyl 2,2'-disulfonic acid (BDSA), 2-bis [4-(4-aminophenoxy)phenyl]hexafluoropropane (HFBAPP) and *m*-cresol were purchased from Tokyo Kasei Co. Diaminoacrydine hemisulfate (DAA) was purchased from Aldrich Co. Triethylamine (Et₃N) was purchased from TEDIA. Benzoic acid was purchased from Duksan Co. NTDA, HFBAPP and BDSA were dried under vacuum before use. *m*-Cresol was distilled under reduced pressure. All other chemicals were used as received.

To synthesize base polymer, DAA (8 mmol), HFBAPP (8 mmol), *m*-cresol (60 mL)

and triethylamine (6 mL) were successively added to a 250 mL 3-neck flask under nitrogen flow. When the monomers are completely dissolved, 20 mmol of NTDA and 28 mmol of benzoic acid were added. The mixture was stirred at room temperature for a few minutes until it became homogeneous and then they were chemically imidized. The synthesized polyimides are precipitated in acetone and dried in vacuum.

RESULT AND DISCUSSION

FT-IR Analyses

The $>C=O$ vibration of the anhydride (1778 and 1737 cm^{-1}) shifted to lower frequency upon conversion into imides. The characteristic absorption band of imide carbonyl group around 1717 cm^{-1} (asymmetric) and 1672 cm^{-1} (symmetric) confirmed the formation of polyimides. The SO_2 vibration of the sulfonic acid group was observed as a broad band around 1173 and 1092 cm^{-1} . The out-of-phase bending of imide ring was observed around 765 cm^{-1} . The C-N-C absorption of the imide ring was observed around 1345 cm^{-1} . It shows that all the sulfonated polyimide films were successfully synthesized.

Morphology of blend membranes

From the SEM micrographs of Acid-Base polyimide blends and pure acid polymer, it can be clearly seen that the polymers exhibit very fine microstructures indicating homogeneous morphology without phase separation. A very fine island like, somewhat larger microstructure was observed in the AB-10% and AB-20% compositions. The larger microstructure in these two compositions may be due to partial microphase separation due to the clustering of ionic groups i.e., sulfonic acid groups. This phenomenon disappeared with increase in base polymer content and looks like as if a homo-polymer matrix. The other blends with higher base content and the parent acid polyimide have homogeneous morphology. This is due to the increase in the stronger attractive force between the blend components due to the interaction of acid and basic groups in the polymer. The larger structures observed in few of the SEM micrograph could be both gel or dust particles.

Ion exchange capacity

Many important properties of the sulfonated polyimide like the proton conductivity and the water uptake depend on IEC. The IEC decreased in the order AB-0% > AB-10% > AB-20% > AB-30% > AB-40% > AB-50% > AB-75%. The decrease in the IEC despite the same sulfonic acid content can be attributed to the neutralization of acid group by the tertiary nitrogen group in the base polymer. Hence the IEC of the polyimide blends was reduced accordingly. The hydrogen bond between the acrydine molecule and the hydrogen is strong due to the high basicity of the pyridinium nitrogen and it does not break in the presence of

NaOH. Also with increase in the base polyimide weight ratio, the weight percentage of nonsulfonated fragment in the blend increases. IEC is measured for a particular weight of the polyimide.

Water Uptake

All the films exhibited rapid water uptake initially and reached an equilibrium beyond which the variation in the water uptake is small with time. The water uptake decreased with increase in base polymer content. The water uptake varied as follows AB-0% > AB-10% > AB-20% > AB-30% > AB-40% > AB-50% > AB-75%. Water uptake value primarily depends on the sulfonic acid content i.e., IEC [34]. It is well known that the water uptake increase with increase in sulfonic acid content. The tertiary nitrogen groups in the base polymer preferentially interact with sulfonic acid group and decrease the amount of free sulfonic acid group available to form hydrogen bond with water molecules.

Hydrolytic Stability

Sulfonated polyimides are vulnerable to hydrolytic degradation which is a severe problem in commercialization of these membranes despite many advantages. Several approaches were adopted to increase the hydrolytic stability of the polyimide. In view to improve the hydrolytic stability, Acid-Base polyimide blends were prepared and their corresponding hydrolytic stability was evaluated. The poor hydrolytic stability may arise from two reasons. Due to the hydrophilic modifications in the polyimide backbone, the swell in water increases leading to poor mechanical properties of the film. The second reason is due to the chemical degradation of the polyimide backbone. The polyimide blends exhibited higher hydrolytic stability than the pure acid polyimide and the hydrolytic stability increase with increase in base polymer content. This may be because, with increase in base polymer content the ionic cross link density increase due to increase in the amount of polysalt formation between the sulfonated polyimide and the tertiary nitrogen in the polymeric base. Due to the increased interaction between the two polymers, the swelling of the polyimide blends are greatly reduced. This increase the mechanical stability of the polymer blends.

Proton conductivity

Generally, the proton conductivity of the polymer increases with increase in IEC and water uptake. This is because, with more IEC and water uptake, the formation of the hydrophilic domain increase and hence the proton conductivity increases. The water uptake and IEC decreased with increase in the basic component and hence it is expected that the proton conductivity also decrease with increase in base polymer content. The conductivity for all the sulfonated polyimides and the Nafion[®] 115 were done at four different temperatures namely 30 °C, 50 °C, 70 °C and 90 °C. With increase in temperature both the

proton diffusion and molecular diffusion merge together and result in the increased proton conductivity. When compared with benchmark Nafion membrane, the polyimides AB-0%, AB-10%, AB-20% and AB-30% showed higher conductivity than Nafion at all temperatures. AB-40% showed lower conductivity upto temperature 50 °C and showed comparable conductivity at high temperature. Among the Acid base blends, the proton conductivity decreased as AB-0% (0.197) > AB-10% (0.124) > AB-20% (0.122) > AB- 30% (0.088) > AB-40% (0.080) > AB-50% (0.034) > AB-75% (0.025). The proton conductivity of the blends decreased with increase in basic component. Especially, polyimide blend AB-100% did not show any conductivity. This is due to the decrease in free sulfonic acid group that are available to transfer protons due to the ionic crosslinking between the base polymer and sulfonic acid in the sulfonated polyimide.

CONCLUSION

The effect of different base to acid molar ratio on the properties of polyimide blends were evaluated using thermal stability, IEC, water uptake, hydrolytic stability and proton conductivity. Among the Acid-Base blends the thermal stability increased with increase in base polymer content which is due to the stabilization of sulfonic acid groups due to the polysalt formation. A notable increase in hydrolytic stability as well is observed with increase in base polymer content, which is attributed to the increase in ionic crosslink which resist polymer swelling in water and thus increasing the mechanical stability of the membrane. IEC and water uptake decreased with increase in base polymer content which must be due to the strong interaction of acrydine group with the sulfonic acid group which reduce the free sulfonic acid group in the polymer blends. Proton conductivity also found to decrease with increase in base polymer content similar to IEC and water uptake showing the dependence of proton conductivity on IEC and water uptake.

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