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SULPHONATED PEEK-SANTALUM ALBUM BASED COMPOSITE MEMBRANES FOR PEM FUELCELLS

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Abstract:

Santalum album (SA) incorporated Sulphonated Poly Ether Ether Ketone (SPEEK) binary composite membrane has been prepared by varying SA: SPEEK in five different ratios 0%:100% (SPEEK), 1%:99% (SA1), 2%:98% (SA2), 3%:97% (SA3), 4%96% (SA4) and 5%:95% (SA5) by solution casting technique at 80^{o}C environment. All the films are tested for their Ion Exchange Capacity (IEC), Chemical Stability (CS), Proton Conductivity (PC) and nonetheless Water Absorption (WA) performance. The observations on such parameters has identified obviously the sample SA5 ha accomplished the requisites for their suitability as an composite membrane for PEM fuel cells. To affirm its authenticity than the other samples in terms of its complexation of binary constituents,by FTIR; to explore it's crystalline/amorphous, phasical nature by XRD ; sustainance of its thermal stability by TGA have been anchored on all as prepared five samples. The FTIR vibrational studies confirm the adultration of PEEK by sulphonation, and degree of complexation of SPEEK with different concentration of SA. The SEM surface profile of SPEEK and SPEEK/SA composite reveal that increase in SA in the composite deteriates the texterity of the membrane is noted. The XRD reveal that SPEEK is found to loose its crystalline characteristics and found in high in SA5 suggest that amorphousity paves the way for good WA and protonic conductivity. The TGA thermal profile registers weight losses in stepwise three phase diminish and significant weight loss recording at 230 $^{\circ}$C suggests operational thermal stability of the membrane's heating capability. The optimised SA5 as identified, used for test fuel cell studies in real time PEMFC testing well augments its better performance eventually captivated in better OCV as well as good power density.

Key Words: Polymer Electrolyte Membrane Fuelcell, SPEEK/SA Composite, Proton Conductivity, Water Absorption & Realtime PEMFC Test

Introduction:

Fuel cells have been widely investigated, as clean and eco-friendly energy conversion systems, and attracted financial investment for wide applications in last decades [1, 2]. Proton exchange membrane fuel cells (PEMFCs) are a more suitable type of fuel cells as their special features like low-operating temperature, high power density and efficiency, low weight and compactness, fast start-ups, static nature, noiseless operation, tolerance to shocks and vibrations, and safety in usage handling [3-5]. In PEMFC, polymer electrolyte membrane plays vital role as a proton conductor and fuel crossover barrier [6]. A good proton exchange membrane material is expected to possess (i) high proton conductivity, (ii) good mechanical strength, (iii) high oxidation and hydrolytic stability, (iv) low fuel permeability, and (v) low manufacturing cost. The acidity, number and position of ionic groups, hydrophobic and hydrophilic components, and membrane morphology are the critical factors which decide the membrane function. Among them, the acidity and membrane morphology are identified to play a vital role, and they are closely related with each other. So, sulphonated and thermally and mechanically stable polymer has been studied extensively, and they exhibit better conductivity and structural stability [7, 8]. In the current applications, Nafion, a perfluoro sulfonic acid based membrane has been used extensively as PEM because of its appropriate fuel cell performance. Even though it has excellent proton conductivity and good stability, it has some major drawbacks such as high cost, high methanol permeability, dehydration problem and lower conductivity at temperature greater than 80°C have limited their commercial application [9-10]. Hitherto, researchers are working in the development of cost - effective and environmental friendly PEM from natural polymers as a substitute for Nafion [11-13]. So far, among different hydrocarbon polymers, SPEEK has the appropriate properties for fuel cell applications as compared to the Nafion membrane and some of them are commercially available such as the Fumapem membrane (Fumatech) [14]. The chemical structure of SPEEK membranes gives different microstructures with distinct electrochemical and mechanical properties, providing certain advantages of SPEEK membranes over Nafion as PEMs [15,16]. Portale et al. [16] portrayed a less phase separated structure of SPEEK at high water contents. It is due to more rigid matrix structure of SPEEK with respect to Nafion. The organic –inorganic composite membrane show improved water retention capacity and mechanical properties as well as reduced fuel permeation. Usage of such composite materials can be an effective and convenient way to improve the performance of PEMs [17-20].

Wood based Polymer Composites (WPC) are widely used for the automotive industries and building applications as flooring material, furniture, interior finishing materials including window frames, bathroom doors, outdoor applications such as garden fencing and decking [21, 22]. Wood based fillers are used to modify the thermoplastics such as polyethylene [23], polypropylene [24], polyvinyl chloride [25] and polystyrene [26]. Wood components may be wood flour and fiber from waste of timber/wood like as teak, maple and oak and fibers from jute and cotton, agricultural wastes such as wheat straw, cane bagasse and rice husk [27]. The WPC made out of jute, bamboo, sisal, coir, hemp, flax and pineapple leaves possess comparable properties, are environmental friendly and the composites could be reground and recycled [28–31].

Extensive reviews on the composite membranes adhering to PEM fuelcells, none has attempted so far the wood polymer composite membranes and brings forth an insight to evolve the novel wood based composite membranes has been envisioned in the present investigation for PEM fuel cells.

Experimental:

Materials:

The PEEK powder (150XF) was purchased from Victrex (England) with purity of 99.9% was used as received. Sulphuric acid (H_2SO_4) and 1-Methyl-2-pyrrolidone (NMP) both of AR grades supllied by E-Merck india Ltd. were used as received. The cost effective materials for fabricating a test fuelcell were purchased from Sainergy Fuelcell India Pvt Ltd (Such as Carbon Vulcan XC-72, Carbon Cloth and 40% Pt in Vulcan XC-72). In addition, a 60% Teflon dispersion purchased from Sigma Aldrich, USA and Isopropyl Alcohol (IPA- AR grade) was purchased from Rankem Chemicals for fabrications were used as received for fabrication.

Preparation of SPEEK/SA Composite Membrane:

Sulphonation of PEEK:

A known quantity of PEEK powder was taken in a round bottom flask which was mixed with 150ml H_2SO_4 and stirred continuously for 6 hours using magnetic stirrer. The sulphonation reaction was arrested in an ice bath. [32-33]. The resulting Sulphonated PEEK (SPEEK) fibres were washed in double distilled water to have neutral pH and later dried for 3 hours in hot air oven at 60°C.

Preparation of Santalum album Wood Powder (SA):

Heartwood nucleus of SA wood powder was collected from the available source and was shallow dried for 24 hours and subsequently dried in hot air oven at 60 °C so as to remove certain moisture present. Later the SA wood powder was made into a coagulated paste formation using deionised water as a solvent. As prepared paste like SA wood powder conserved in a petri dish placed in an hot air oven as it was placed earlier for the same 24 hour duration. The resultant product furtherance made into finassy using a pistle/mortor setup and this time it was kept in oven for 48 hours at 60°C.

Preparation of SPEEK/SA Composite Membrane:

Step 1 Process: The SPEEK was dissolved in NMP at ambient temperature and the mixture was stirred continuously for an hour. The homogenous solution so obtained was then filtered and cast onto a dry clean petri dish. The petri dish was so filled kept in oven at 60°C for 24hours. The membranes so prepared in this process were found to be pale brown in colour as shown.

Step 2 Process: The measured quantity of SA was dispersed in NMP and the solution was stirred for 2 hours. The SA dispersion so prepared was then added in drop by drop into the SPEEK NMP Binary solution and the resulting terinary mixture was stirred for 4 hours till it turned into homogenity. This homogeneous solution was cast onto a clean petri dish and dried in the hot air oven at 60°C for slow evaporation of the solvent to avoid any fissures in the resulting membrane. After the complete evaporation, membranes were peeled off from the

container and subsequently treated with 0.5N H_2SO_4, and washed with deionized water. A set of five different composites with varying concentrations of 99% SPEEK - 1%SA, 98%SPEEK-2%SA, 97% SPEEK-3%SA, 96%SPEEK-4%SA, 95%SPEEK- 5% SA, were prepared using the solvent casting technique. These prepared membranes were found to have 80-100 microns in thickness.

Fabrication of Membrane Electrode Assembly (MEA):

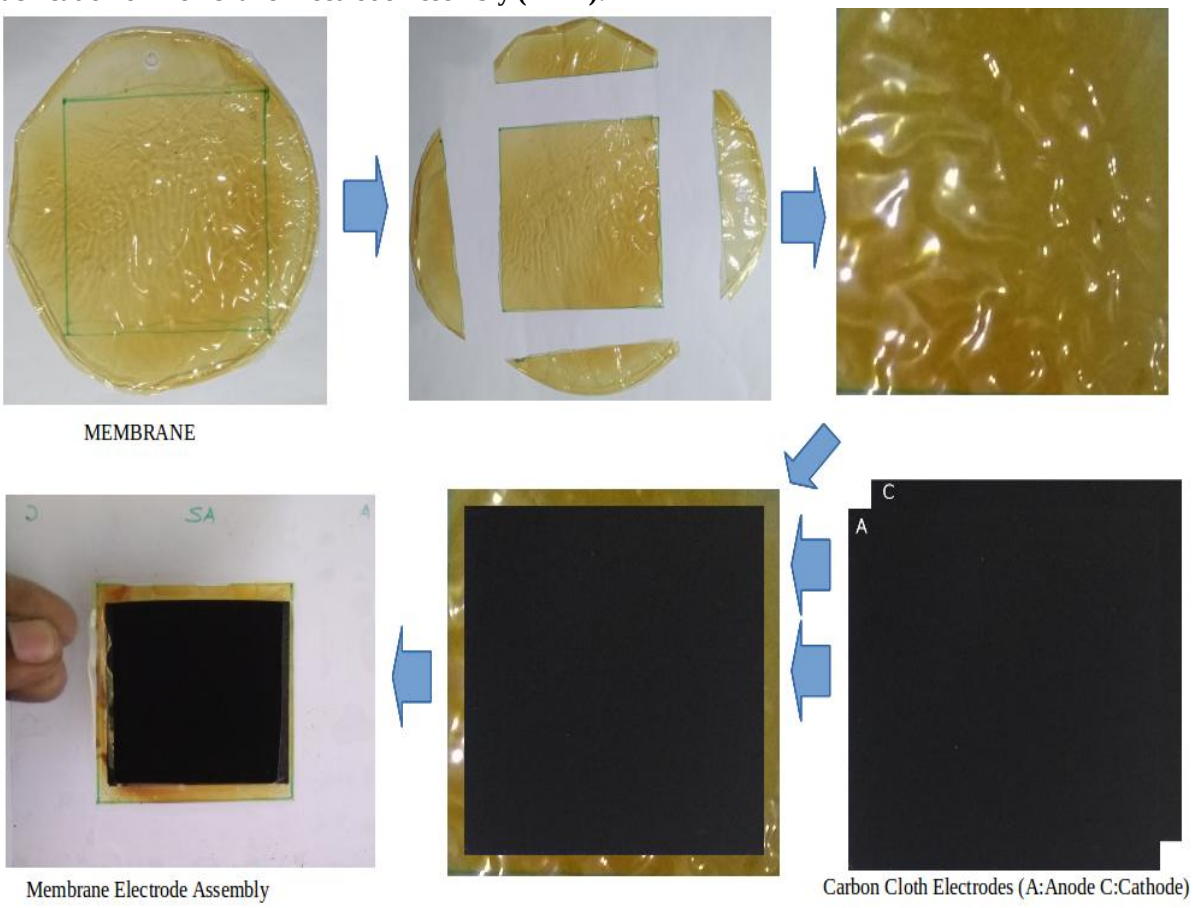

Figure 2: MEA Preparation stages

The procedure for preparing a MEA adhered to standard protocols [41].

A. Purification of membrane
B. Teflonization of porous carbon cloth
C. Carbonization of the teflonized carbon cloth
D. Catalyst layer first stage coating
E. Catalyst layer second stage coating
F. Hot pressing of the electrodes on the membrane

A. Purification of the Membrane: Purification of the membrane is very crucial and must be performed before the preparation of MEA. Initially, all membranes were allowed to boil in 3% H_2O_2 for 45 minutes which removed the impurities, if any, present on the surface of the membrane. It was then washed thoroughly with distilled water and boiled for 30 minutes in 10% H_2SO_4 to remove any inorganic impurities and to get the membrane in a complete protonated form. Finally, the membrane was washed with boiling water to remove any excess acid present on the surface of the membrane and later the membrane was dried.

B. Teflonization of the Porous Carbon Cloth: For the teflonization process, a 60% Teflon dispersion in water available commercially was procured and was further diluted with deionised water in the ratio of 1:5. The carbon cloth was highly porous in nature and was dipped in the above dispersion for 30 seconds. Then placed in a muffle furnace at 350°C for a span of 3 hours. The process of teflonization improve the hydrophobicity of the carbon cloth.

C. Carbonization of the Teflonized Carbon Cloth: This is also called as the Gas Diffusion Layer (GDL). Initially Vulcan XC-72 (3mg/cm^2) is mixed with 3ml of deionised water and sonicated for 10 minutes. The sonication was done to obtain a fine dispersion of the carbon particles. Then 2-3 ml of isopropyl alcohol (IPA) was added and sonicated again for 10 minutes. Finally, a drop of Teflon dispersion was added, mixed and immediately coated on the carbon cloth by means of a brush. The cloth was then kept in a muffle furnace at 350°C for 3 hours.

D. Catalyst Layer First Stage Coating:

- ✓ **Anode:** The catalyst used was Pt dispersed in carbon. For the first stage, the amount of Pt taken was 0.125 mg/cm^2. The required amount of the catalyst was weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of IPA was added and sonicated for another 10 minutes. Finally, one drop of Teflon dispersion was added, mixed with the help of a painting brush and coated immediately on the carbonized cloth. It was then heated in a muffle furnace at 350°C for 3 hours.
- ✓ **Cathode:** The first layer of catalyst was coated as done for anode.

E. Catalyst Layer Second Stage Coating:

- ✓ **Anode:** For the second stage, the amount of Pt taken was 0.125 mg/ cm^2. The required amount of the catalyst was weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then few drops of SPEEK solution was added and then coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It was then dried in a hot air oven at 80°C for 4 hours. The electrode obtained after drying can be used as the anode for the fabrication of the MEA.
- ✓ **Cathode:** For the second stage, the amount of Pt taken was 0.375 mg/cm^2 . The required amount of the catalyst was weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then few drops of SPEEK solution was added, mixed and coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It was dried in an oven at 80°C for 4 hours. The electrode obtained was the cathode that can be used for the fabrication of the MEA.

F. Hot Pressing of the Electrodes on the Membrane:

On either side of the membrane, a solution of SPEEK in NMP was applied and the electrodes were placed on either side. It was hot pressed at 80°C for 45 seconds with a load of 0.5 tonnes. The two electrodes stuck onto the membrane after the hot pressing treatment. The resulting assembly was the Membrane Electrode Assembly (MEA). This MEA was used in the PEMFC for performance evaluation.

Characterizations:

Membrane Characterization:

X-Ray Diffraction (XRD):

XRD measurements were performed using an Ultimate IV diffractometer of Rigaku, Japan. The dried samples were mounted on an aluminium sample holder. The scanning angle ranged from 10° to 80° at a scanning rate of 2° per min. All the spectra were taken at ambient temperatures (25 ± 2°C).

Fourier Transform Infrared Spectroscopy (FTIR):

The IR spectra for the dried membranes were recorded with a Perkin Elmer / Spectrum 2 Diamond UATR FT-IR spectrometer for wave number 400 – 4000 cm^{-1}. The samples were dried at 100°C for an hour before recording the spectrum.

Thermo Gravimetric Analysis:

TGA analysis is mainly carried out to determine the thermal stability of the composite membranes. The change in weight of the membrane with increase in temperature at a heating rate of 10°C/min in the range of the temperature between 30°C and 750°C is followed using a Thermo Gravimetric Analyzer SDT Q600 of TA Instruments, USA. All the runs were carried out under nitrogen atmosphere.

Scanning Electron Microscopy (SEM):

The surface morphology of the electrolyte membranes was analysed using SEM (Hitachi S – 3400 N). The samples were cut into sufficient size and sputter coated with gold to make the samples electro conductive. The samples were then analyzed under vacuum condition at an accelerating voltage of 10 KV.

Water Uptake:

The amount of solvent intake by the membranes was studied. The dried membranes were weighed and soaked in water and methanol separately and allowed to get equilibrated at room temperature for 40 hours, above which the weight was constant. The swollen membranes were then immediately weighed after blotting the surface water and the values noted. The swelling degree was determined using the formula,

$$SW = \frac{M\ wet\ - M\ dry}{M\ dry}$$

Where, M wet = Weight of wet membrane & M dry = Weight of dry membrane.

Ion Exchange Capacity (IEC):

The ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1g of the dry polymer. It was determined by titration method, repeated n times for confirmity. The membrane in its protonated form was weighed and then soaked in an aqueous solution containing a large excess of KCl in order to extract all the protons from the membrane. The electrolyte solution was then neutralized using a very dilute Na_2CO_3 solution of known concentration (0.01N). The EW (equivalent weight) values were calculated from the dry weight of the membrane divided by the volume and the normality of the Na_2CO_3 solution. The IEC values were mentioned as number of meq. of sulphonic groups per gram of dry polymer.

IEC was calculated using the formula,

$$IEC = \frac{\text{Titer value (in ml)} \times \text{Normality of the titrant } (Na_2CO_3)}{\text{Weight of the dry polymer membrane (in grams)}}$$

Proton Conductivity:

The proton conductivity measurements were taken using an alternating current impedance spectroscopy device over a frequency range of 1-10^7 Hz with 50 - 500mV oscillating voltage using a Hioki 3532-50 LCR HiTester. Films having 1cm^2, sandwiched between two stainless steel blocking electrodes with ~3 kg/cm^2 pressure, were placed in an open, temperature-controlled cell. The films were previously hydrated by soaking in deionised water for 24 hours at room temperature. The conductivity σ of in the transverse direction of the samples were calculated from the impedance data, using the relationship

$$\sigma = \frac{d}{RS}$$

Where, d and S are the thickness and face area of the membrane sample, respectively, and R found from the low intersection of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis.

Oxidative Stability:

For checking the durability of the electrolyte membranes, the following procedure was adopted. Initially a 4 ppm ferrous ammonium sulfate in 3% H_2O_2 was freshly prepared and the temperature of the solution was maintained at 80°C. The electrolyte membrane with the dimension of 0.5cm 2 was cut and soaked in the solution. The time required for the physical disintegration of the membrane was noted down and reported.

Single Cell Fuel Cell Performance Test:

Selected sample was subjected to testing in real time PEMFC environment with hydrogen gas as fuel. Standard fuel cell grade graphite plates and copper current collectors were used for this purpose. The output voltage and the current were measured with a with a research grade digital multimeter (CD800a of Sanwa, Japan with accuracy of ±0.7% with resolution of 0.1mV) under different resistances as loads.

Results and Discussion:

XRD Analysis:

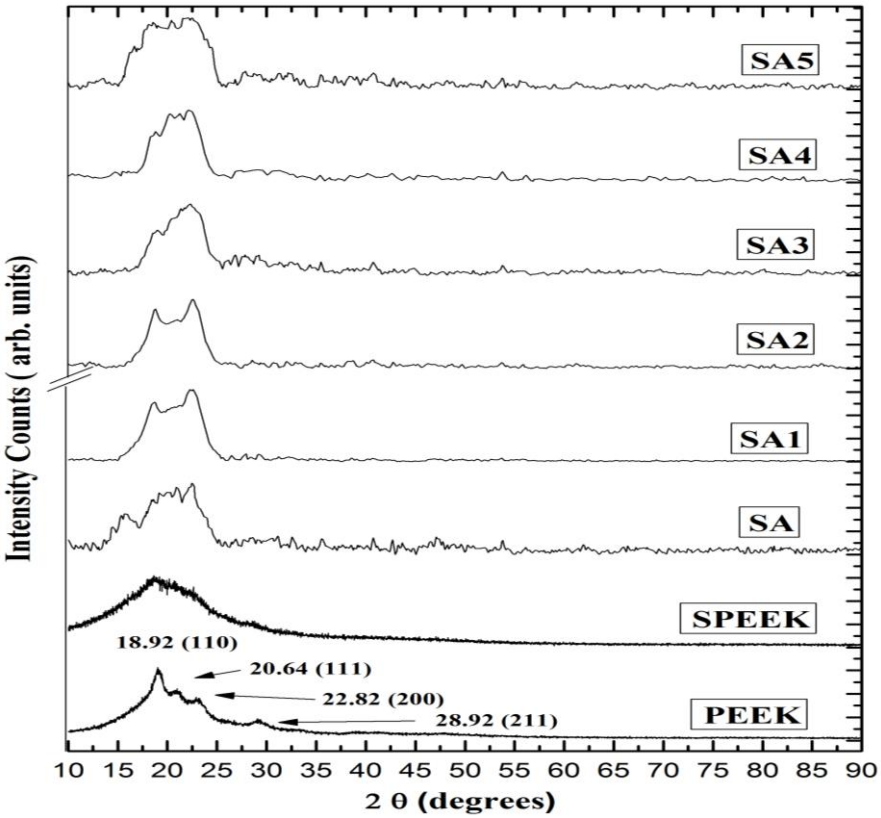

Figure 3: XRD pattern of virgin PEEK, SPEEK, SA, and SPEEK/SA composite membranes

The XRD pattern of PEEK, SPEEK, SA and various composites of different membranes are shown in fig3. PEEK shows XRD peaks at 18.7º, 20.6º, 22.6º and 28.6º due to its semi-crystalline nature. These peaks are ascribed to the diffraction at (110), (111), (200) and (211) crystalline planes respectively. Introduction of SO_3H group reduces the crystallinity of PEEK due to its restriction imparted by functional groups in ordered packing of polymeric chains. Thus intensity of (110) peak is reduced in SPEEK brings forth relative broadening and other crystalline peaks are not found in SPEEK reveals it becomes amorphous [34,35]. Diffraction peaks at 16.0° and 22.5° appear in the wood spectra, which originated from the crystalline region of the cellulose in the wood. [36] The broadness of its humps imply the amorphousity in wood powder. [37] In the case of composite membranes this peak slowly gets diminished and a new peak appeared around 22º. These get broadened as a

result the blended membrane become amorphous.

SEM Analysis:

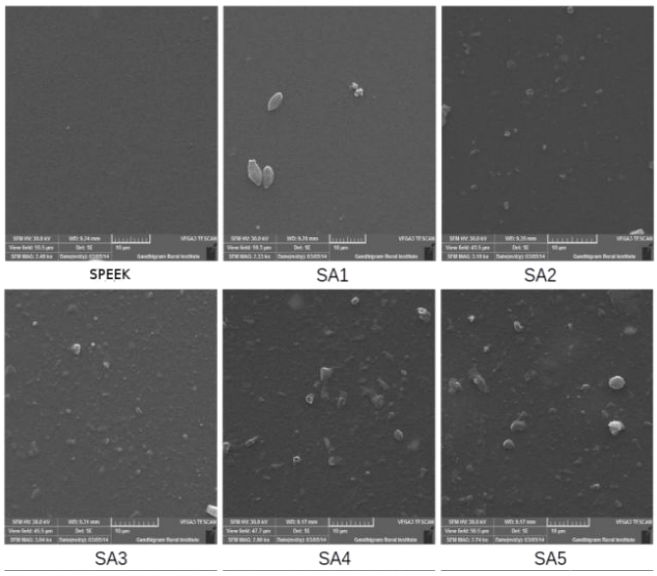

Figure 4: SEM images of Virgin SPEEK, and SPEEK/SA composites

The SEM images of virgin SPEEK and SPEEK+SA composite membranes are given in fig4. All SEM images appear dense and homogenous indicating a uniform distribution of Santalum album in the polymer matrix. No fissures could be observed in the virgin as well as composite membranes.

FTIR Studies:

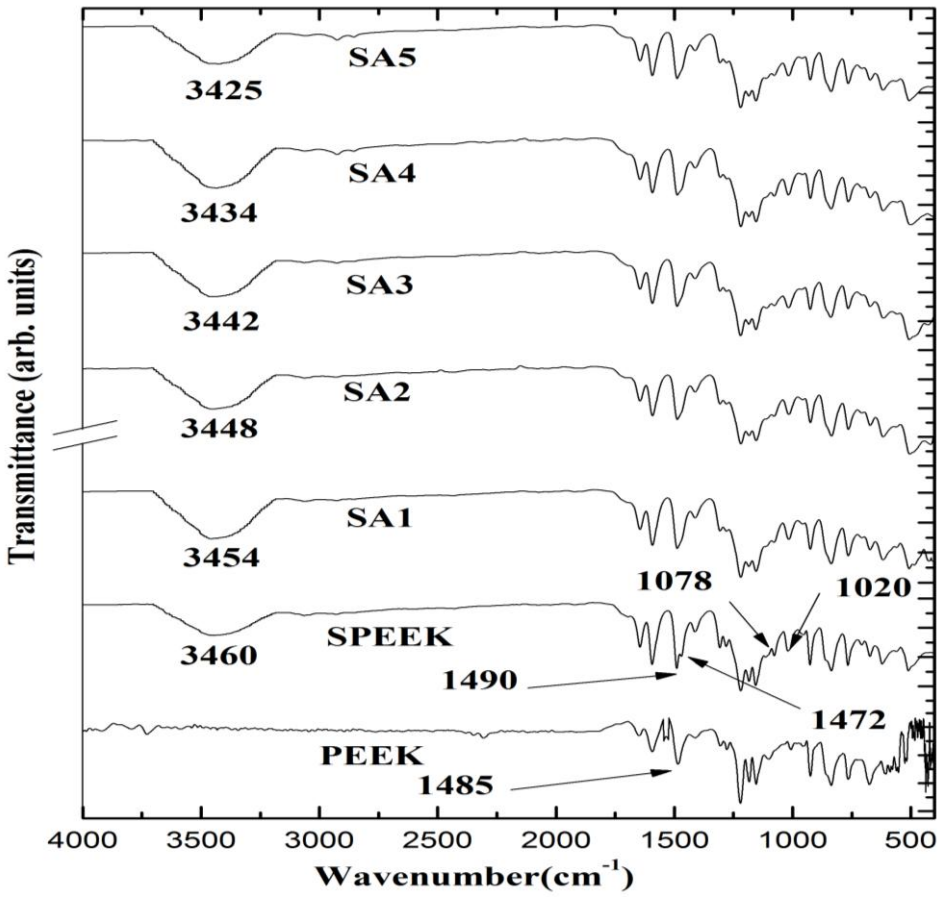

Figure 5: Shows the comparative FTIR spectra of PEEK, SPEEK and the various composite membranes.

The peak observed at 1485 cm^{-1} in PEEK is the aromatic C-C band, which is split into 1490 and 1472 cm^{-1} in SPEEK due to the new substitution from the sulfonation reaction. The new peaks observed at 1024 and 1080 cm^{-1} correspond to symmetric and asymmetric stretching vibration of the sulfonic acid group in

SPEEK.[38,39]. There is a significant broad peak at 3460 cm^{-1} in SPEEK assigned to OH vibration from sulphonic acid groups interacting with molecular water. [40] In the SPEEK composite membranes, the hydroxyl band is observed at 3460 cm^{-1} with a small shift in wavelength attributes to the effective hydrogen bonding interactions between SPEEK and the filler [41]. Most of the characteristic peaks of the filler are blocked due to the interference by the SPEEK matrix found highest percentages. [42]. The peak between 1600 cm^{-1} and 1750 cm^{-1} are due to the vibration of carbonyl group of SPEEK. The peaks at 1050 cm^{-1} and 1100 cm^{-1} confirm the presence of O=S=O groups.

TGA Studies:

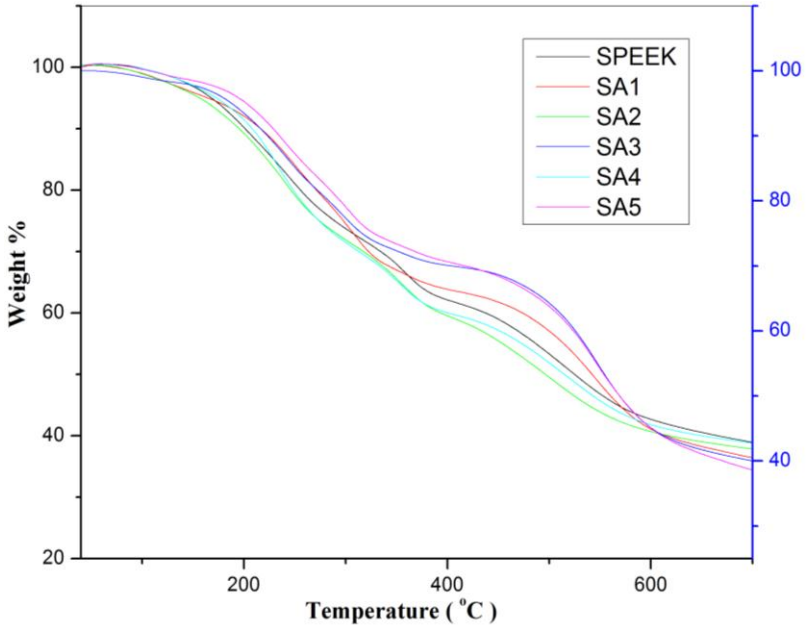

Figure 6: TGA of Virgin SPEEK and SPEEK/ SA composite membranes

The thermogram of SPEEK and various composite membranes are shown in fig.6 The thermogram of composite membranes are found to be similar to that of virgin SPEEK. A three stage degradation is observed for the electrolyte membranes. The first weight loss is observed between 80ºC and 150ºC. This weight loss may be attributed to the loss of physically and chemically adsorbed water. Even though the composite membranes exhibit a better water absorption capacity, the thermal energy available at temperatures over 120ºC is sufficient to break the interaction between water and wood material and thereby liberates water. However the weight loss extends upto 150ºC. The second major weight loss is between 230ºC and 350ºC. This may be reasoned be due to the liberation of sulphonic acid group attached with the polymer matrix. The third loss is found between 425ºC and 600ºC may be attributed to the degradation of the polymer matrix.

Ion Exchange Capacity:

The Ion- Exchange Capacity of pure SPEEK and SPEEK+SA composite membranes are given in table 1. It is observed that IEC of pure SPEEK is found to be 2.17 meq/g, and it might be due to the loading of Santalum album which could enhance the magnitude of IEC. Consequently, the enhancement of IEC are found to increase gradually with increase in concentration of Santalum album. This increasing trend may be due to the significant water absorbing capacity of the Santalum album. Before observing the role of organic content in the composite membrane, it was presumed that increase in organic content in the composite membrane would decrease the magnitude of IEC. But, it showed reverse trend, in empirical observations that IEC magnitude started to increase with increase of it.

Table 1: Observed results of Pure SPEEK and its composite membranes

Sample	Tests			
	IEC meq/g	Water Absorption wt%	Chemical Stability min	Protonic Conductivity mS/cm
SPEEK	2.17	14.16	267	8.53
SA1	2.21	15.31	261	8.79
SA2	2.23	16.50	257	9.04
SA3	2.28	17.48	250	9.36
SA4	2.30	18.60	246	9.74
SA5	2.33	19.73	236	10.1

Water Absorption:

The Table 1 Presents water absorption (wt%) and Chemical stability of samples virgin SPEEK , SA1

(99wt%SPEEK+1wt% SA), SA2 (98wt%SPEEK+2wt% SA), SA3 (97wt%SPEEK + 3wt%SA), SA4 (96wt% SPEEK+4wt% SA) and SA5 (95wt%SPEEK+5wt% SA) respectively. It is noted that the water absorption of virgin SPEEK is found to be 14.16 wt% whereas it is 19.73 against the sample SA5 wherein the maximum concentration of Santalum album is present. This suggests that the water absorbing capacity is found to vary as a function of the concentration of Santalam album. This may be due to hydrophilic sulphonic acid group is mainly responsible for the water absorption. With increase in the content of wood powder, the net content of sulphonic acid group decreases, even then there is increase in the water absorbing ability. This may be ascribed to the greater water absorbing capacity of the wood powder.

Proton Conductivity:

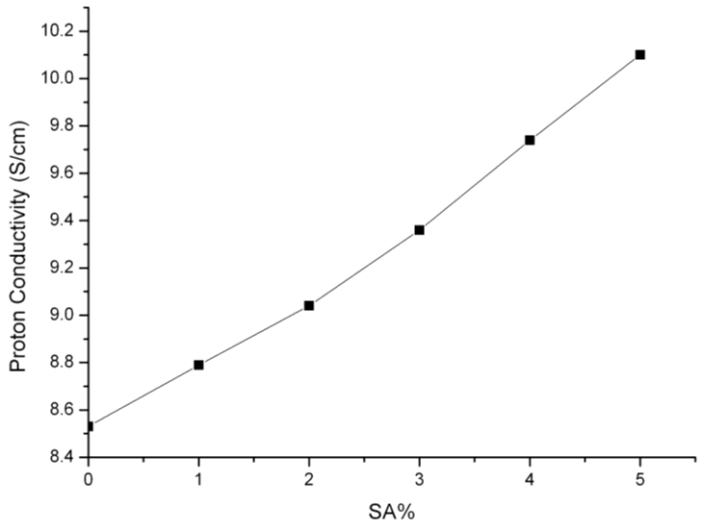

Figure 7: Proton conductivity at variation of SA concentratetion

The proton conductivity of SPEEK with various concentration of Santalum album is given in the fig. The sulphonic acid group available in SPEEK is primarily responsible for the transportation of protons. The proton conductivity of the composite membranes are found to be in an increasing trend when compared to SPEEK. This clearly shows that the composite membranes are capable of transporting protons better than virgin SPEEK even though there is a decrease in the net sulphonic acid group with increase in the wood content. This inherent nature may be due to the increased water holding capacity of the composite membranes as compared to SPEEK.

Chemical Stability:

The experimental results of chemical stability of various electrolyte membranes were given in Table1. The hydrolytic stability of SPEEK was found to be 267 minutes. The oxidative stability of the composite membranes found to decrease with increase in the wood content. It was noted that increasing the composition of the wood content, the continuity in the polymer matrix was disturbed and hence there could be regions where breaking was relatively easy. This might be the reason for the decrease in the chemical stability of the composite membranes.

Single Cell Performance:

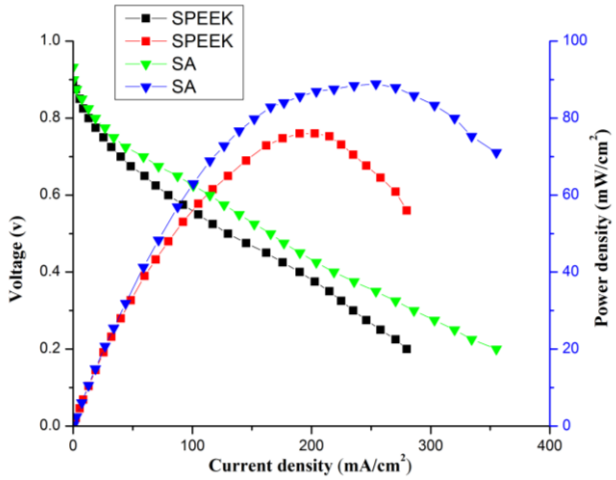

Figure 8: Single cell performance studies for virgin SPEEK and SPEEK/SA composite membranes

The prepared pure SPEEK and SPEEK/SA membranes were subjected to single-cell test in order to evaluate their suitability for fuel cell applications. Figure 8 display the single-cell performance of fabricated composite membrane at room temperature at 30 °C. The open circuit voltage for the composite was observed to be 0.932V comparing to that of pure SPEEK at 0.896V. The peak power density attained by SPEEK/SA composite was 89 $mWcm^{-2}$ which was comparatively higher than that of Pure SPEEK 76 mW cm^{-2}. This result indicate that the prepared membrane could be used as potential candidate for PEMFC.

Conclusion:

The Eco-friendly, low cost SPEEK/SA wood-polymer membrane as a novel composite membrane has been fabricated and found compatible in terms of its electrochemical performance than Nafion, the commercially available high cost membrane for PEM fuel cells. All physical characterisations have well augmenting the 5 wt% SA incorporated SPEEK matrix anchored its suitability has been testified. Fabrication of the PEM fuel cell performance has well been brought into limelight in terms of open circuit voltage and better power density as the prominent factors of the membrane recommended for PEMFC.

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