IJNRD.ORG ISSN : 2456-4184
INTERNATIONAL JOURNAL OF NOVEL RESEARCH AND DEVELOPMENT (IJNRD) | IJNRD.ORG
An International Open Access, Peer-reviewed, Refereed Journal

# SULPHONATED POLY ETHER ETHER KETONE /ANIMAL HAIR (GOAT) COMPOSITE MEMBRANES FOR PEM FUEL CELLS

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**Abstract:**

Composite mem-branes with animal hair and S-PEEK(Sulphonated-polyetheretherketone) was prepared using solvent cast method. The molecular structure of the membranes was studied by FTIR. The thermal stability was found by TGA. SEM analysis revealed the composition of the membrane. XRD analysis revealed the crystallinity of the membrane. The proton conductivities of the membranes were found to be in the order of $10^{-3}$ S/cm. The crystalline properties were studied by X-ray diffraction analysis. The mechanical properties of the membrane were obtained from UTM studies. Solvent diffusion studies and accelerated stability tests were also conducted on the membrane. The results obtained were satisfactory and the membranes can be used for fuel cell applications.

**Keywords:** SPEEK, PEMFC, Composite polymer membranes

## Introduction:

Over the past few decades depletion of conventional sources of energy and environmental pollution has led to eco -friendly alternative energy devices that are sustainable and economic at the same time. Fuel Cells have the potent of replacing devices that depend on non-renewable energy sources. Polymer electrolyte membrane (PEM) fuel cells are a type of fuel cells which are currently in demand. PEM fuel cells are favored for their high efficiency and portability[1-3].

Traditionally Nafion$^{TM}$ (by Dupont) and Aciplex$^{TM}$ (by Asahi Chemicals) which are perflourinated polymers are used as the membrane in PEM fuel cells for its high mechanical strength, proton conductivity, thermal and chemical stability[4-9]. Owing to the many setbacks such as high cost, decrease in ionic conductivity at high temperature and environmental concerns due to the presence of fluorine in its composition[10-14], alternative membranes have been used in the development of fuel cells. Homopolymeric materials like polyamides[15-16], poly(phthalizinones) [17-20], polysulphones[21-23] and aromatic thermo stable nonperfluorinated polymers such as poly(aryl ether ketone)s (PAEKs) (e.g. PEEK), poly(ether sulphone), polybenzimidazole (PBI) with higher efficiency, lower cost, long-term stability, and, appreciable mechanical and electrical properties can be used to synthesize membranes for PEMFC[24-27].

The goal of this study was to synthesize membranes for PEMFC applications using Sulphonated-polyetheretherketone (S-PEEK) using goat's hair (*Capra aegagrus hircus)* as the composite. Membrane properties are altered by the addition of composites. Animal hair is used for its excellent moisture retention properties and its mechanical properties[28-30] as a reinforcement. The primary objective of this work is to prepare a series of sulfonated poly(ether ether ketone) (SPEEK) composite membranes of animal hair with different concentrations of hair, and to evaluate their mechanical properties for a successful application in PEMFC.

## 1. MATERIALS, SYNTHESIS AND PREPARATION OF MEMBRANES:

### A.Materials

PEEK G90P was purchased from Victrex. SPEEK was prepared by dissolving PEEK in sulfuric acid (98% purity).

### B.Synthesis of SPEEK:

PEEK, which is hydrophobic, is sulphonated to convert it into SPEEK (Sulphonatedpolyetheretherketone) which is hydrophilic in nature. Weighed amount of PEEK was transferred into a three necked round bottom flask and a known quantity of Sulfuric acid was used as the sulphonating agent. The reaction time was determined based on the previous trials conducted. Continuous stirring was maintained during the course of the reaction and the reaction was maintained at room temperature. The reaction was terminated by pouring the contents of the round bottom flask in excess of ice cold water. The sulphonated PEEK in the form of innumerable fibers was washed several times and the product obtained was dried at 80 $^{0}$C for 6 hours. The product then obtained was SPEEK (Sulphonatedpolyetheretherketone).

### C.Preparation of Composite Membranes:

The required quantity of SPEEK was taken and was dissolved in NMP by gentle heating. Then the reinforcement (Animal hair) was added accordingly. The mixture was stirred for about 30 minutes. This mixture was cast on a glass petri dish and was kept for drying in the oven for 18 hours at 80$^{0}$ C. Two sets of membrane containing varying reinforcement percentage of 0%, 2%, 4%, 6%, 8%, 10% of animal hair was cast. The obtained membranes were off white to pale brown in color. It was peeled from the petri-dish and was stored under room conditions for further analysis. The variations in concentration are as follows

**Table 1.1: Composition of Matrix and Reinforcement**

| S.No. | Composition of SPEEK( in %) | Composition of reinforcement(animal hair) ( in wt%) |
|---|---|---|
| 1 | 100 | 0 |
| 2 | 98 | 2 |
| 3 | 96 | 4 |
| 4 | 94 | 6 |
| 5 | 92 | 8 |
| 6 | 90 | 10 |

## 2. CHARECTERIZATION OF MEMBRANES:

### A. ION EXCHANGE CAPACITY:

Ion exchange capacity is the technique for measuring the number of milliequivatents of ions per gram of dry polymer. A known quantity of dry membrane in its protonic form is immersed in a solution of saturated KCl in order to extract all protons from the membrane. This solution is left undisturbed for 24 hours after which it is titrated with $Na_2CO_3$ of a known normality. The equivalent weight values (EW) were calculated from the dry weight of the membrane divided by volume and normality of $Na_2CO_3$ solution. The IEC values were expressed as milli equivalents of sulphonic groups per gram of dry polymer.

$$EW = \frac{Dry\ weight}{Volume\ of\ \text{Na2CO3} * \text{Normality of Na2CO3}}$$

### B.SWELLING STUDIES:

This test is to understand the retention properties of the membrane. Weighed amounts of dry membranes were kept soaked in water and methanol respectively for 24 hours. The membranes were removed and surface liquid was blotted and the wet weight of the membranes were taken. The swelling degree was determined by the following formula:

$$SW = \frac{\text{Wwet} - \text{Wdry}}{\text{Wdry}} * 100\%$$

Where $W_{wet}$ is the wet weight of the sample and $W_{dry}$ is the dry weight of the sample.

### C.ACCELARATED STABILITY TEST:

This test is used to check the physical stability of the membrane in a corrosive environment. A solution of water containing $H_2O_2$ and FAS was prepared.

The membrane was subjected to this solution at a constant temperature of $80^0$ C and the time taken for physical degradation for different compositions was noted.

D.FT-IR STUDIES:

FT-IR is an analytical technique, performed by passing infra red radiation through the sample, to identify composition of the sample. FTIR spectra was collected within the range of 4000-550 $cm^{-1}$. FTIR studies of SPEEK were carried out using KBr pellets in an FTIR NICOLET iS10 Thermo scientific spectrophotometer. The apparatus was set to transmission mode and the spectra obtained were recorded. The difference between the characteristics of PEEK and SPEEK was analyzed using the FTIR.

E.SEM ANALYSIS:

The surface morphology of the composite was analyzed using a scanning electron microscope (SEM, Carl Zeiss MA15 / EVO 18 Scanning Electron Microscope). A piece of membrane was spluttered with a thin layer of gold prior to examination. The nature of pores and nature of dispersion of the reinforcement in the matrix was examined.

F.THERMO GRAVIMETRIC ANALYSIS:

This is carried out to examine the thermal stability of the membrane. It measures the sample's weight as it is heated/ cooled in the furnace. The change in weight of the membrane with increase in temperature is determined at a heating range of $10^0$ C/min at a temperature range of $30^0$ C- $800^0$ C using a SDT Q-600 US analyser.

G.X-RAY DIFFRACTION STUDIES:

To know the level of dispersion of the reinforcement in the membrane and to study the crystallinity of the membrane, XRD study is useful. The scanning angle ranged from $1^0$ -$80^0$ with a scanning rate of $2^0$ /min performed using Bruker X-Ray diffraction meter. And all patterns were taken at room temperature as reported [7].

H.MECHANICAL PROPERTIES:

This is measured by the Universal testing machine. The mechanical properties were tested using Zwick/ Roell Z010. The samples were cut into a size range of 10mm * 50mm with a cross head speed set at a constant value of 1mm/min.

I.PROTON CONDUCTIVITY TEST:

This test is used to measure the ionic conductivity of the membrane. Proton conductivity was measured using a CHI600E- CH instruments AC impedance analyzer with a frequency of range 0.1Hz – 100 kHz. Rectangular shaped membranes were cut and placed in a cell containing NaCl as the electrolyte and Ag/ AgCl as the reference electrode. The polymer membrane was taken to be working electrode. Ionic conductivity is highly dependent on temperature. This test was performed at standard testing conditions.

## 3.RESULTS AND DISCUSSIONS:

### A. FT-IR:

FT-IR images of S-PEEK-Animal hair for different compositions are given below:

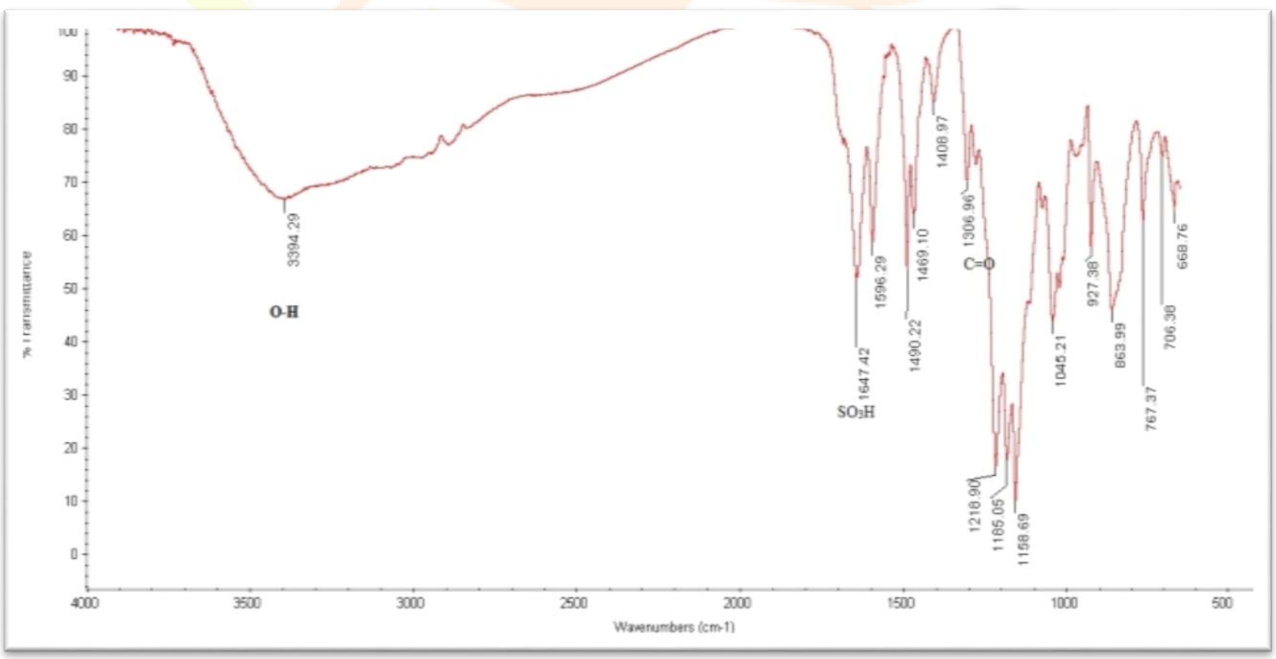


**Figure 3.00. FT-IR Spectrum of Animal hair**

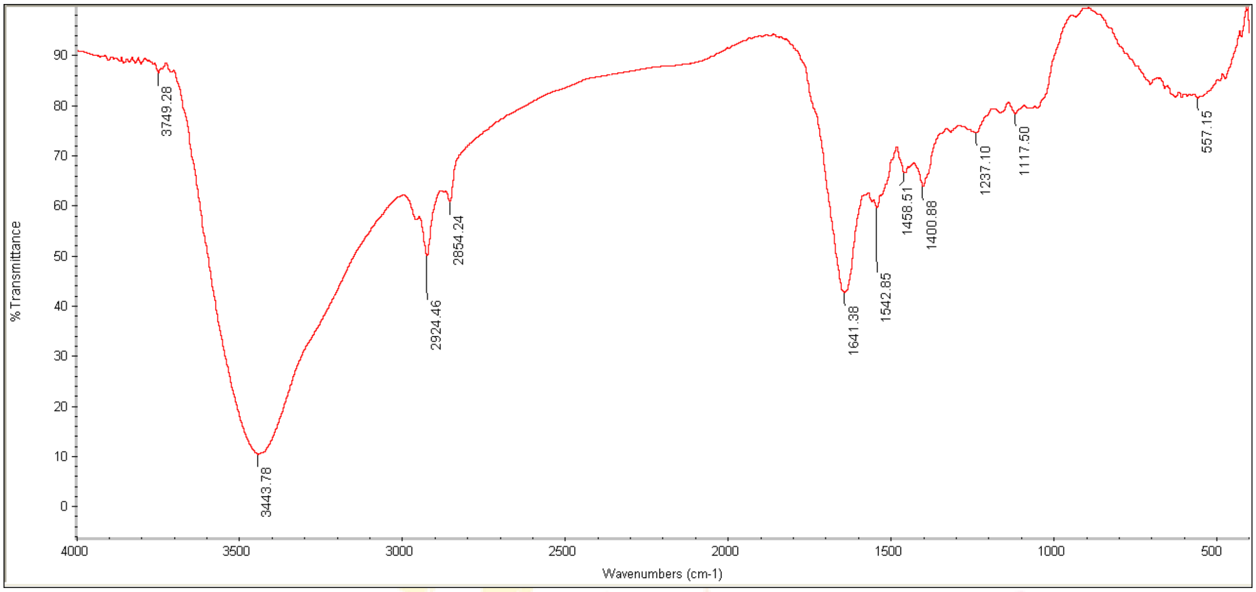


**Figure 3.01. FT-IR Spectrum of Animal hair**

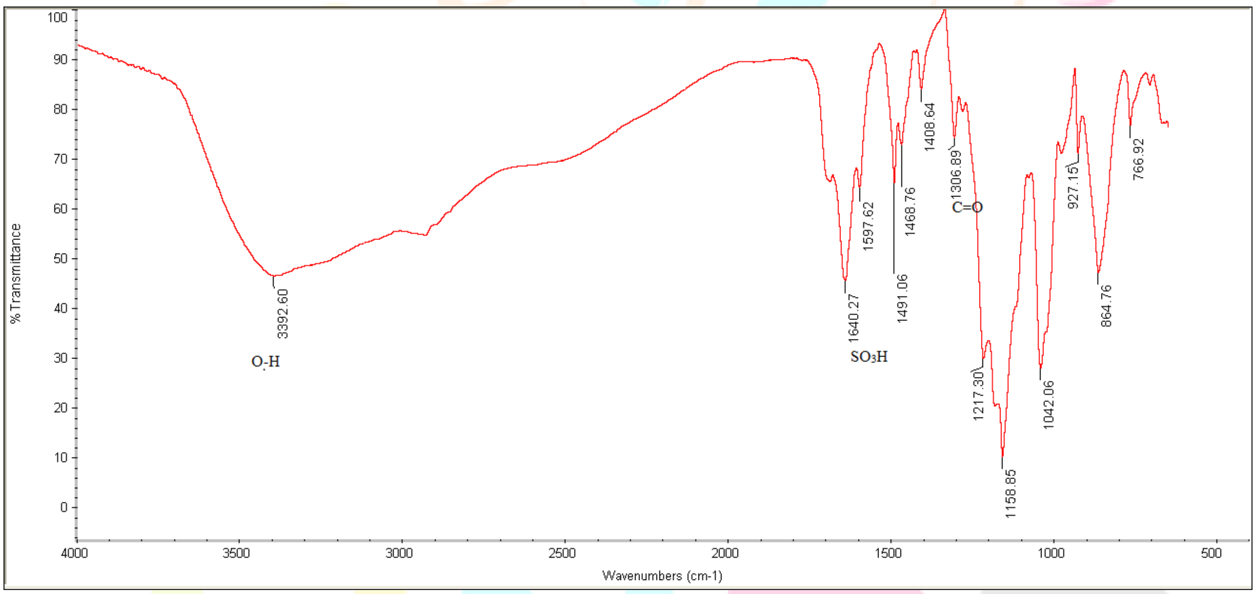


**Figure 3.02. FT-IR Spectrum of 2% Animal hair/SPEEK composite**

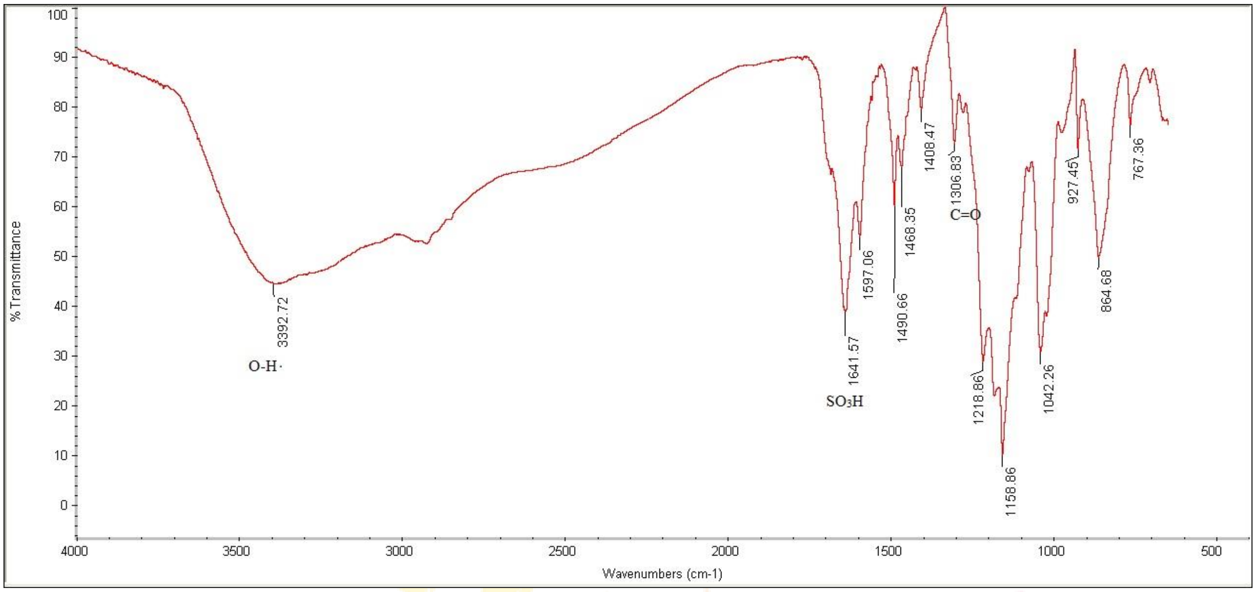


**Figure 3.03. FT-IR Spectrum of 4% Animal hair/SPEEK composite**

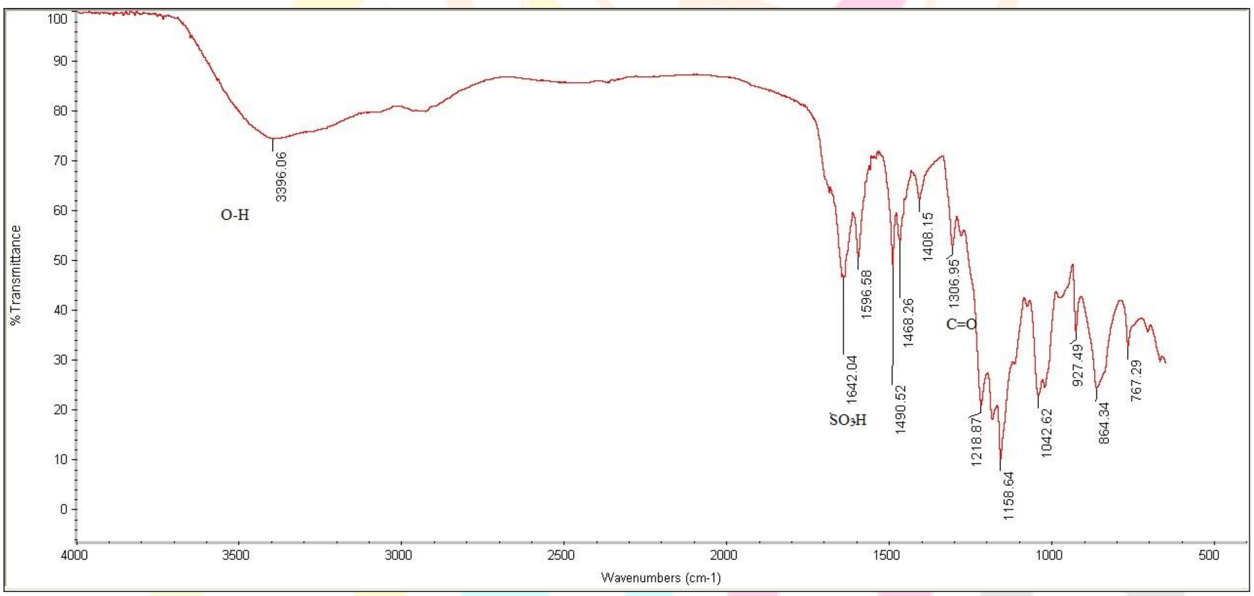


**Figure 3.04. FT-IR Spectrum of 6% Animal hair/SPEEK composite**

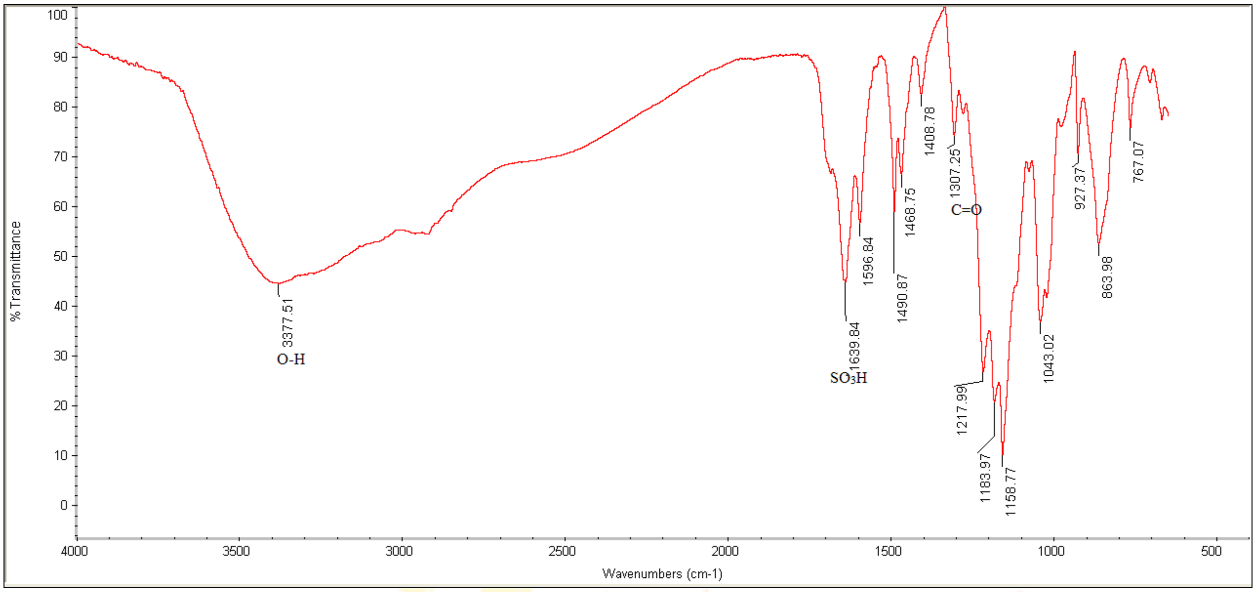


**Figure 3.05 FT-IR Spectrum of 8% Animal hair/SPEEK composite**

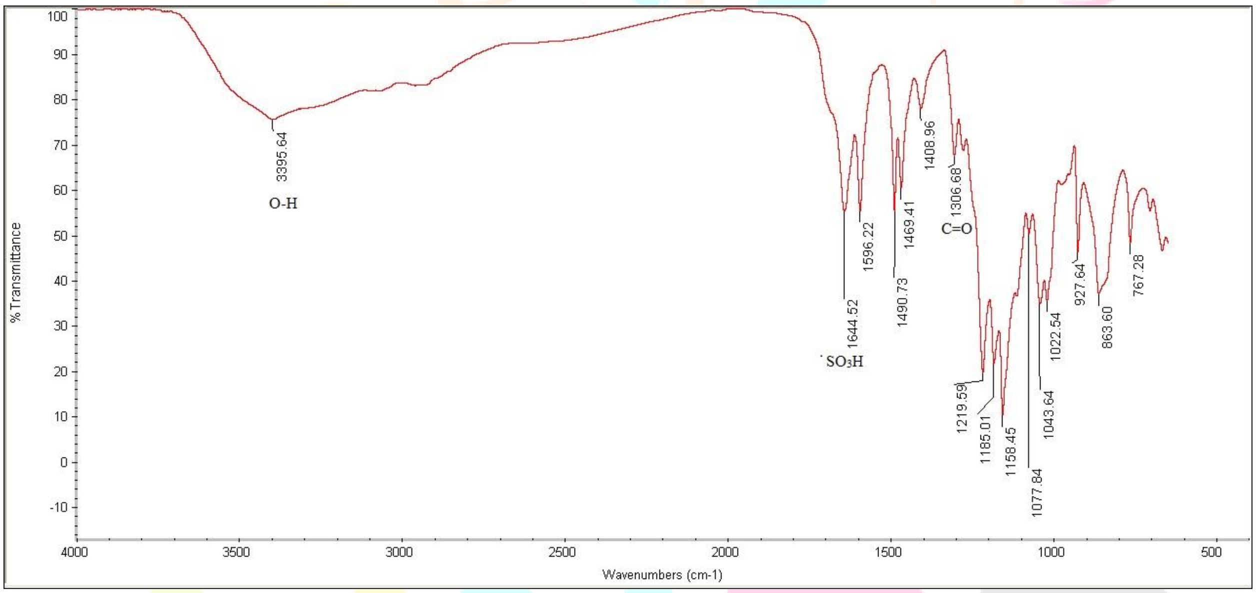


**Figure 3.06 FT-IR Spectrum of 10% Animal hair/SPEEK composite**

The FT-IR spectra of S-PEEK and PEEK were compared. The spectrum of PEEK shows trace amounts of water in its matrix as revealed by its O–H stretching vibration. The aromatic ring vibration of various phenyl and carbonyl and other aromatic ring skeletal vibrations were found in the FTIR spectra of PEEK. The FTIR spectrum of S-PEEK, shows an intense broad envelope at 3343 cm-1 which is attributed to the O–H stretching vibration of SO3H which is established during sulphonation of PEEK. The alkyl groups in PEEK are not found in S-PEEK. All the other features are nearly same as that of PEEK[31].

The FT-IR results show that the peaks observed in the animal hair composite membrane and the S-PEEK membrane and Animal hair of varying composition of 2%, 4%,6%, 8%, 10%. There is a shift in the spectra of sulphonic groups in the membrane composites as compared to the S-PEEK membrane (from 1647 to 1639 $cm^{-1}$). The reason for this shift is the interaction of animal hair particles with S-PEEK. All other features are same as compared to S-PEEK.

**B. THERMOGRAVIMETRIC ANALYSIS:**

The thermo gravimetric analyses of S-PEEK and animal hair composites are shown in fig. This is again a multi-step decomposition. The membranes showed the initial weight loss due to moisture content in the temperature region 60-100°C, and the next weight loss was due to decomposition of sulphonic groups in the temperature region 270- 340°C. The decomposition of main chain of PEEK occurs in the range of 600-750°C.

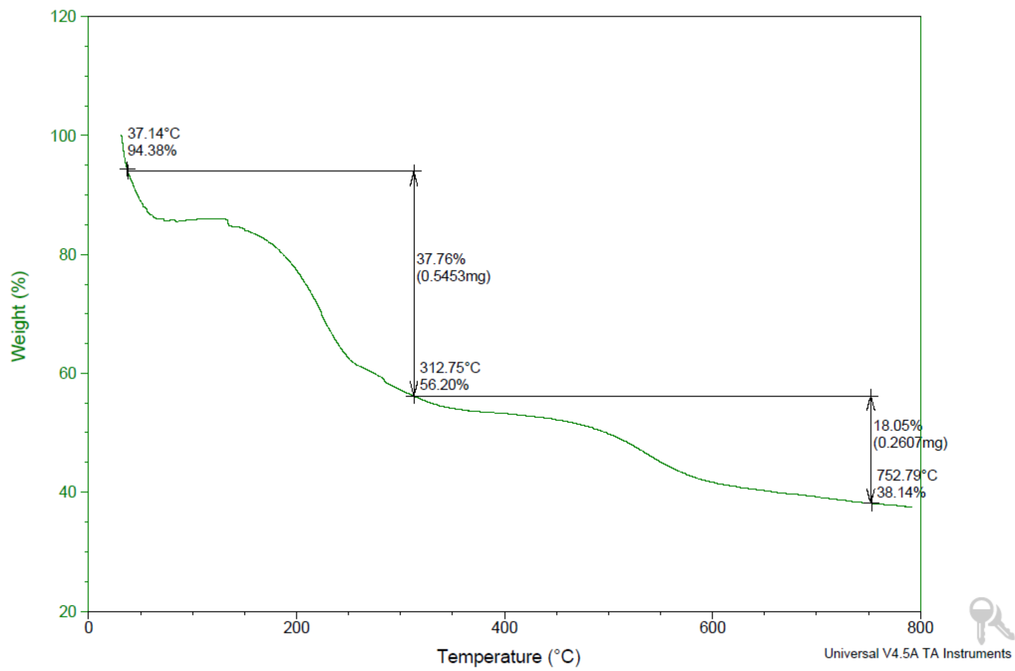


**Figure 3.07 TGA Spectra of 2% Animal hair/SPEEK composite**

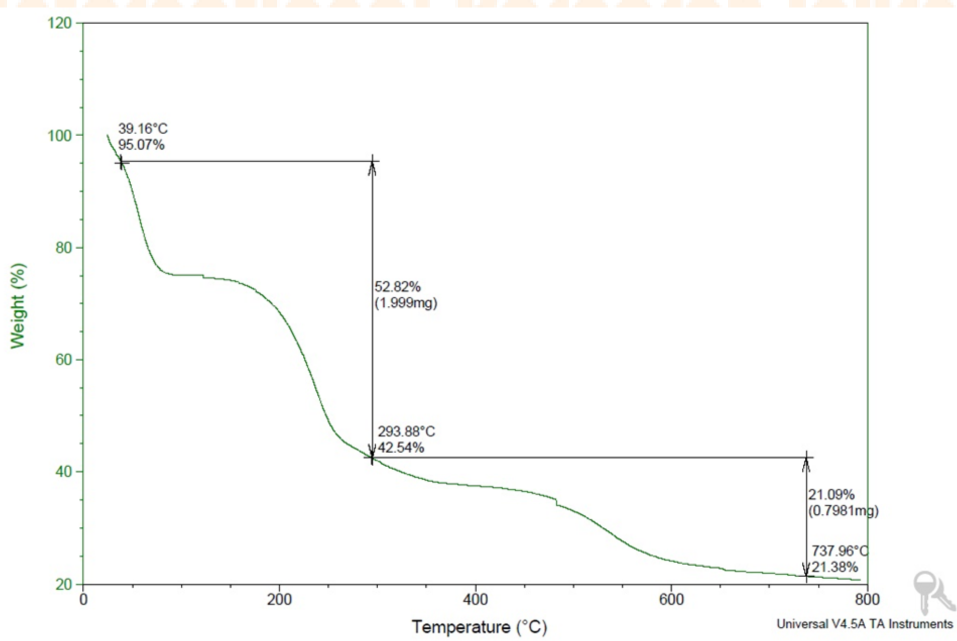


**Figure 3.08 TGA Spectra of 4% Animal hair/SPEEK composite**

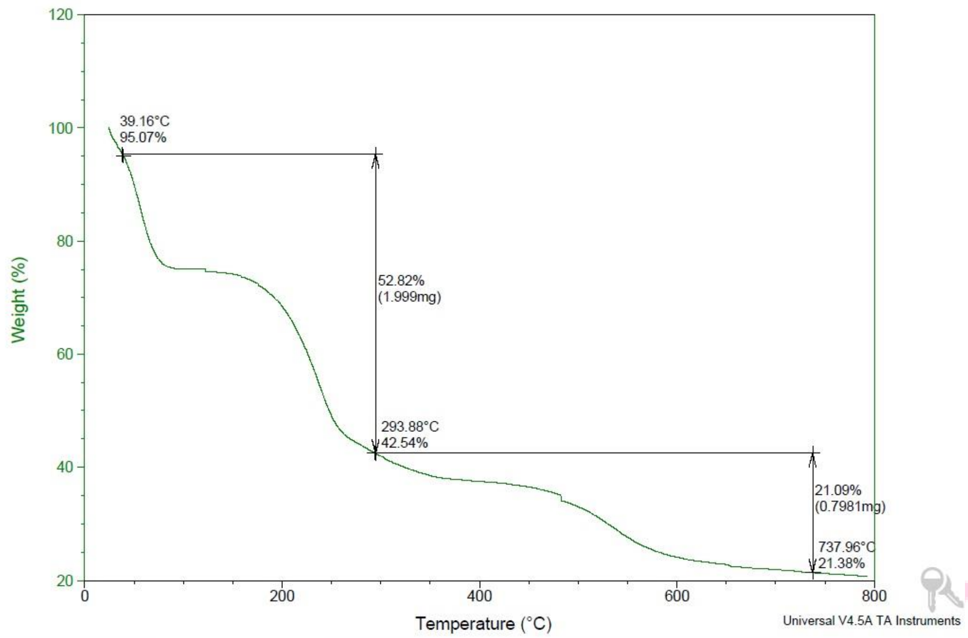


**Figure 3.09 TGA Spectra of 6% Animal hair/SPEEK composite**

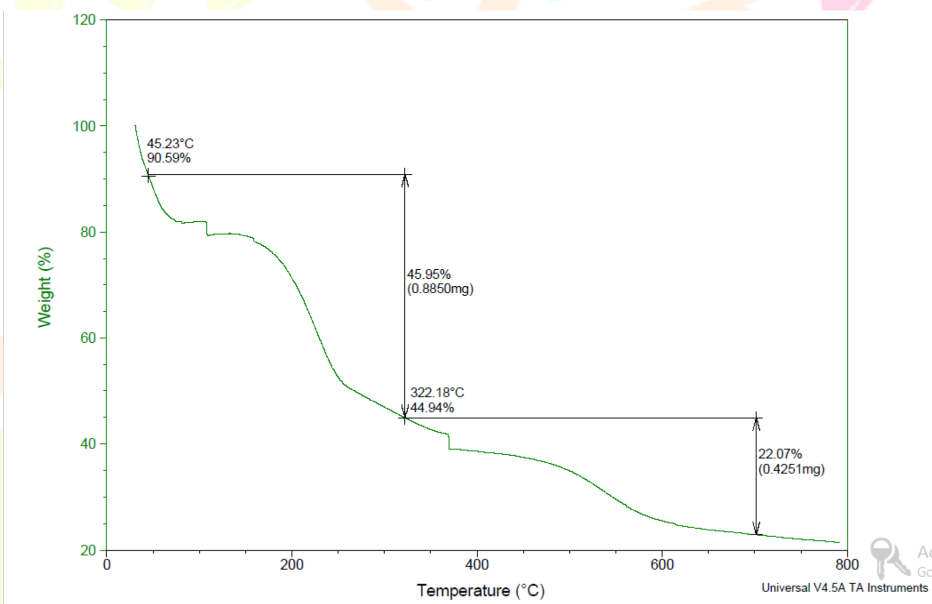


**Figure 3.10 TGA Spectra of 8% Animal hair/SPEEK composite**

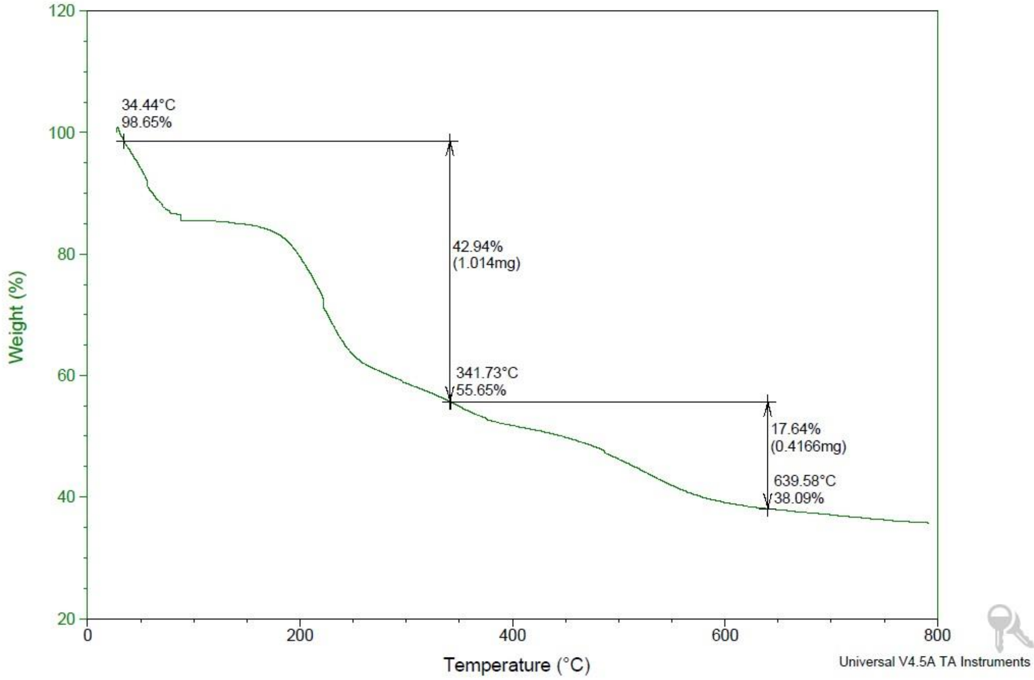


**Figure 3.11 TGA Spectra of 2% Animal hair/SPEEK composite**

**C.SEM Analysis:**

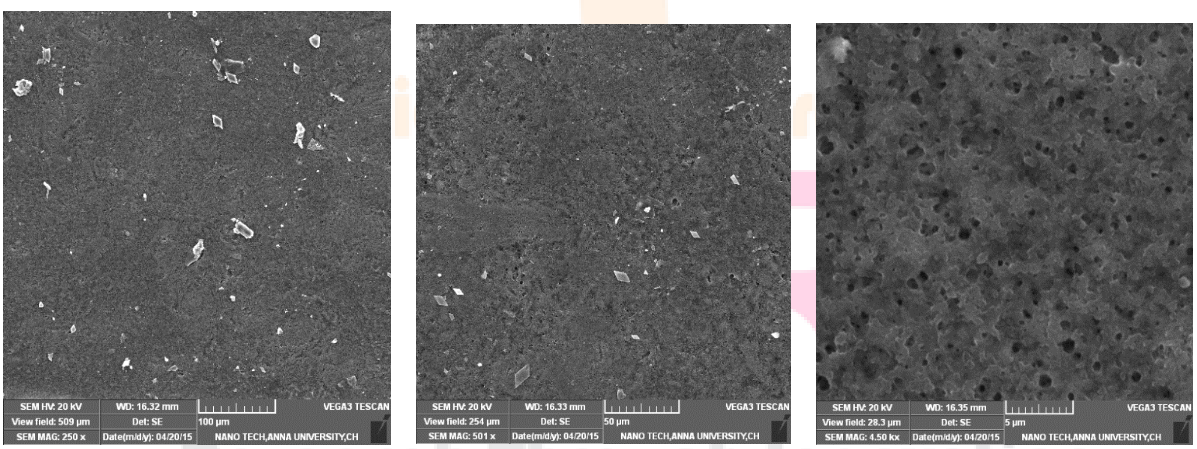

**Figure 3.12 SEM Images of 2% Animal hair /SPEEK**

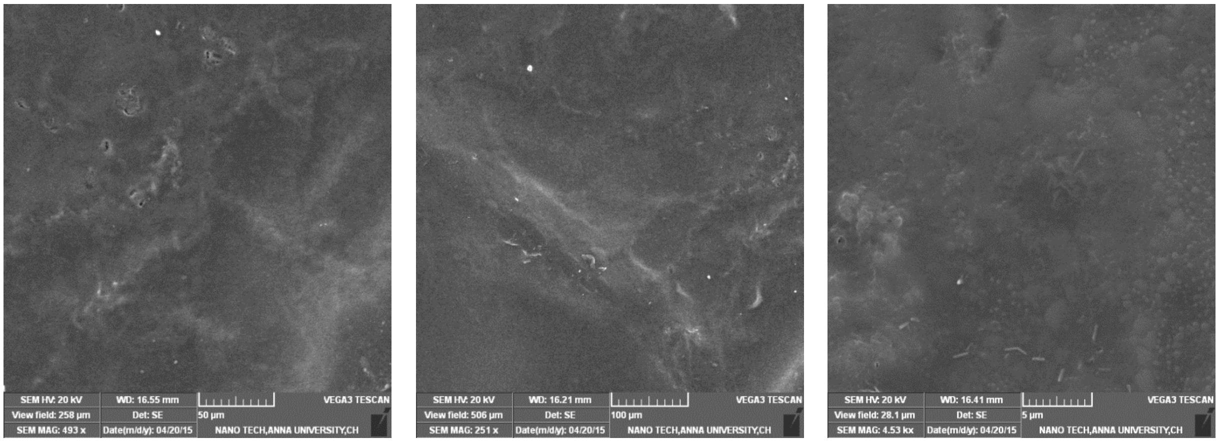


**Figure 3.13 SEM Images of 4% Animal hair /SPEEK**

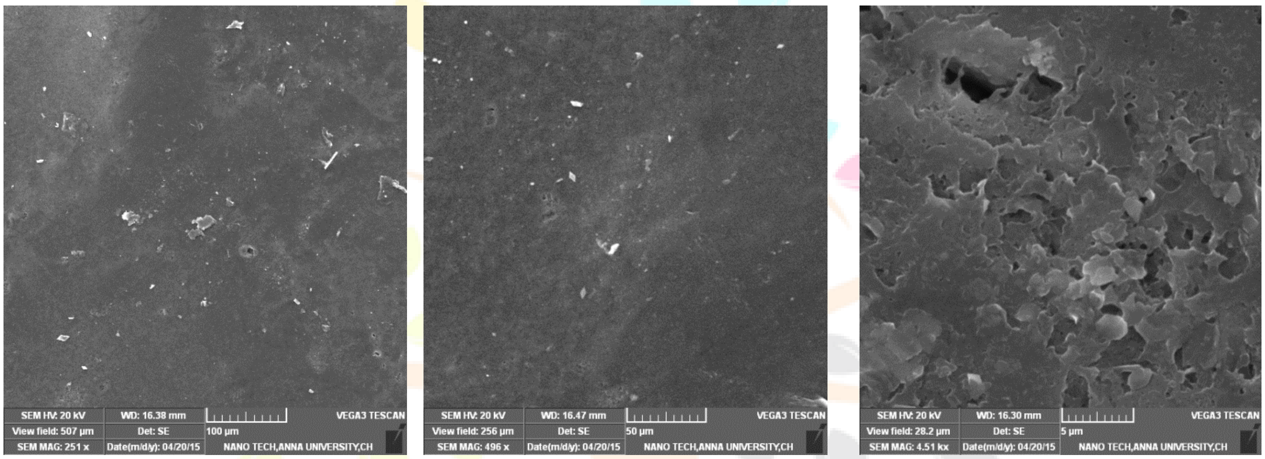


**Figure 3.14 SEM Images of 6% Animal Hair/SPEEK**

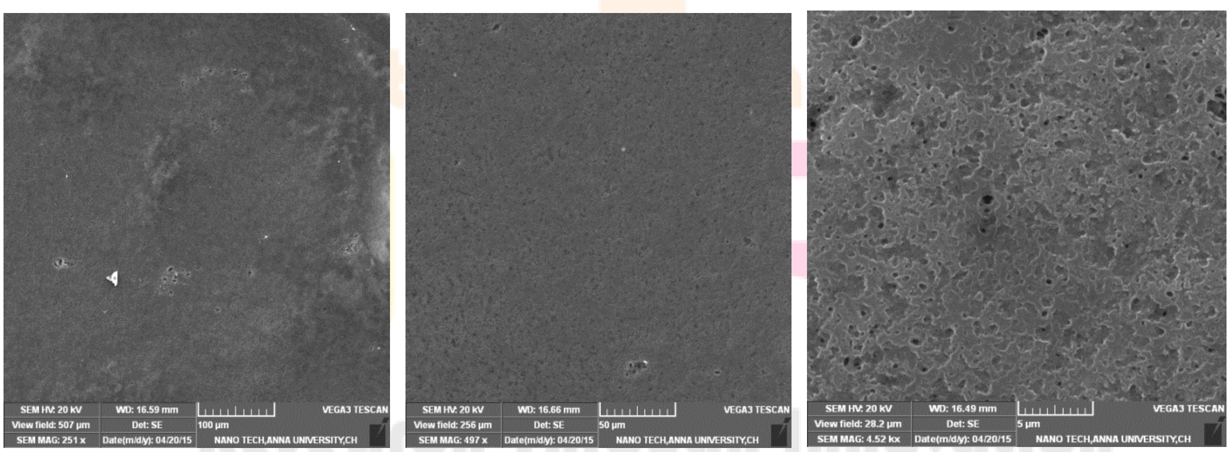


**Figure 3.15 SEM Images of 8% Animal hair/SPEEK**

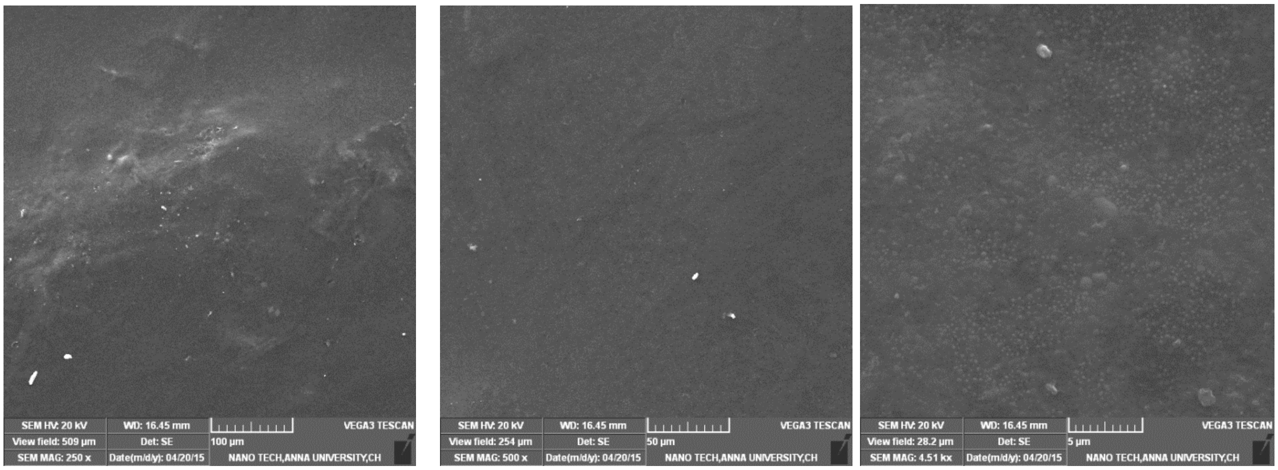

**Figure 3.16 SEM Images of 10% Animal hair/SPEEK**

The above SEM images have magnification 5, 50, 100µm. The SEM image looks dense, clear and homogenous indicating a very good compatibility between the animal hair and SPEEK. Even at higher magnifications, the blend membranes showed no fissures which may be due to the high boiling point of the solvent used for the casting purpose. The evaporation of NMP solvent (boiling point 203°C) was performed at 90°C indicating a very slow process of evaporation.

On the other hand, in certain cases fissures were observed at higher magnification. The reason attributed to this may be due to faster rate of evaporation in these cases. The composite membranes appear to be pores-free even at higher magnification in most of the cases.

**D.X-Ray Diffraction Studies:**

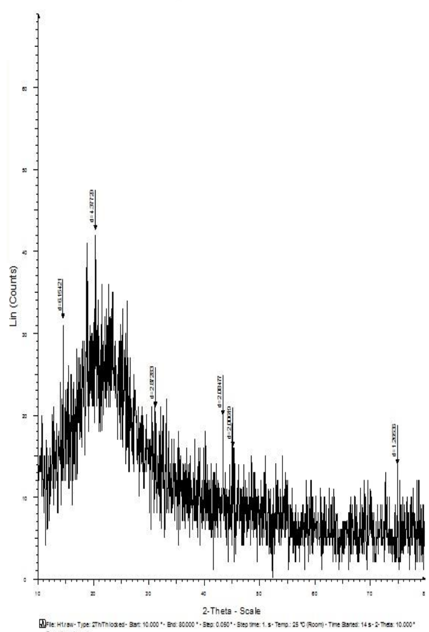

**Figure 3.17 XRD spectra of 2% Animal hair/ SPEEK composite**

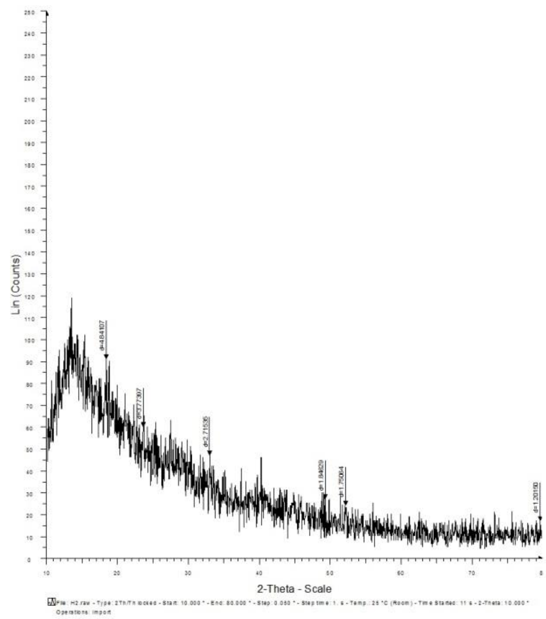


**Figure 3.18 XRD spectra of 4% Animal hair/ SPEEK composite**

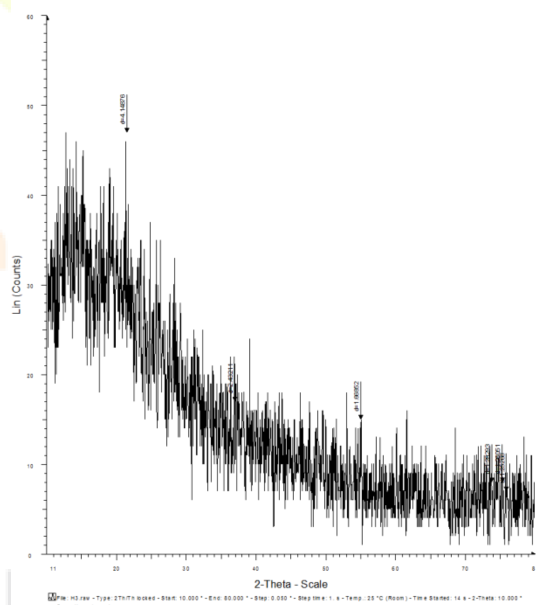


**Figure 3.19 XRD spectra of 6% Animal hair/ SPEEK composite**

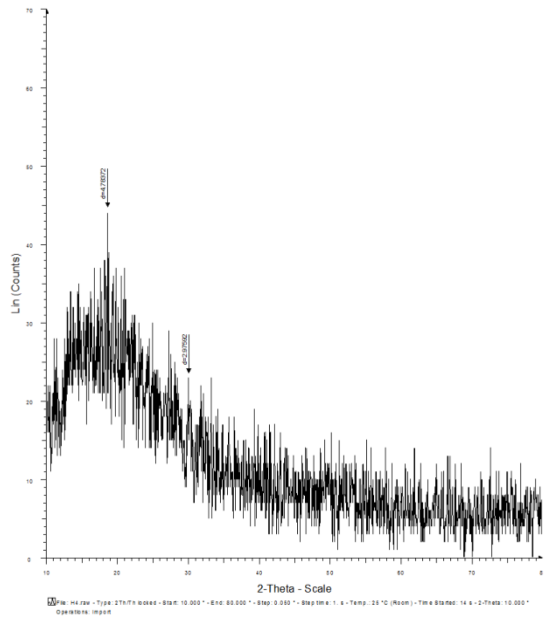


**Figure 3.20 XRD spectra of 8% Animal hair/ SPEEK composite**

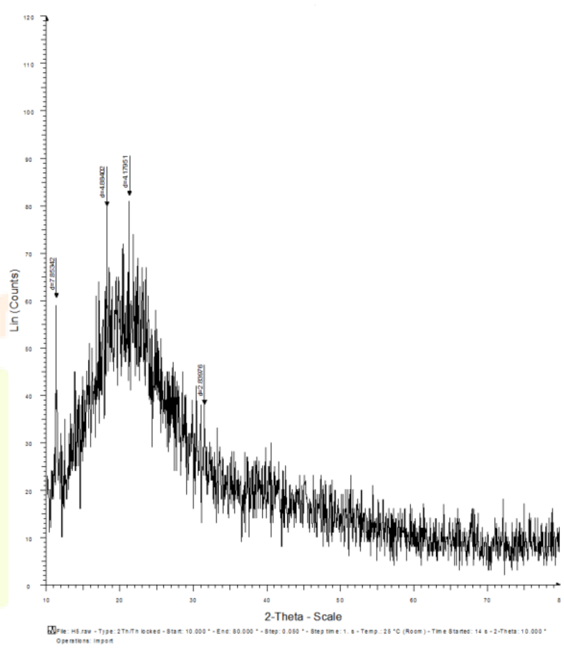


**Figure 3.21 XRD spectra of 10% Animal hair/ SPEEK composite**

Figure 3.37-3.45 shows the XRD images of the SPEEK , and various percentage of composites containing Animal Hair. There is a prominent peek observed in all composites containing animal hair around $25^0$. There is a shift in the peeks in S-PEEK and all animal hair containing composite from $15^0$ due to the interaction between the reinforcement and the matrix.

**E. Ion Exchange Capacity:**

Ion-exchange capacity (IEC) indicates the amount of the ion exchangeable groups present in a polymer matrix which are responsible for proton transfer, and thus is an indirect and reliable approximation of the proton conductivity [32]. Figure 1 shows the relationship between ion-exchange capacity (IEC) and the various compositions of Animal hair-SPEEK composites at room temperature. It can be observed that IEC decreases from 0.14 to 0.105 mequi. The results reveal that IEC decreases as the weight content of composite composition (%) increases. Decreasing IEC is due to the decreased –SO3H groups with a higher degree of cross linking that consumed part of the ion-exchange groups.

The amount of SO3H groups is responsible for the ion exchange and the water uptake in the sulfonated membranes [33]. Due to the repulsive forces between the condensed sulfonic acid groups at a higher degree of crosslinking, the water uptake tends to reach a saturated level and hence slowing the increase of IEC[33].

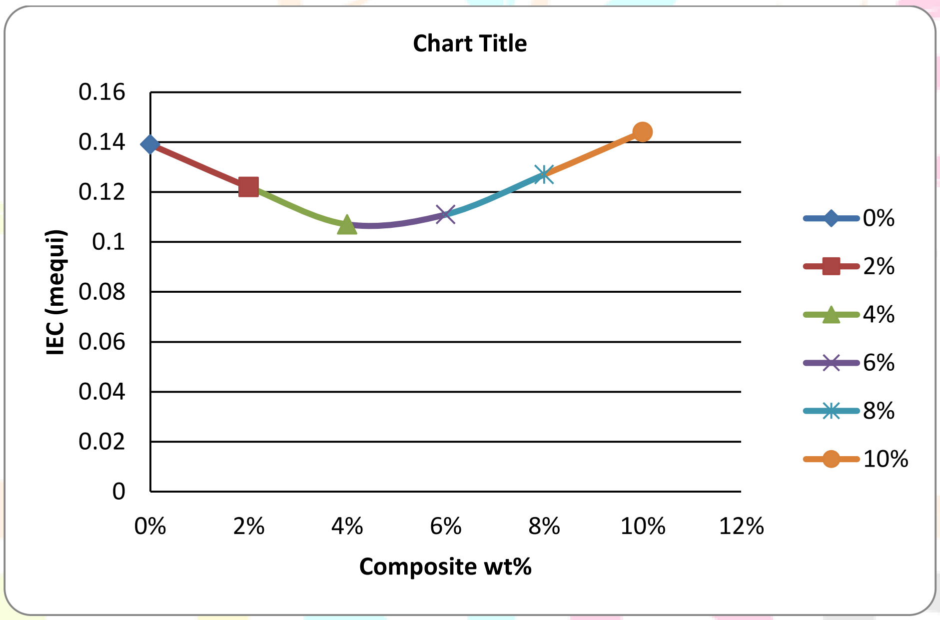


**Figure 3.22 IEC of Animal hair-SPEEK Composite**

**F.DURABILITY STUDIES:**

In the durability study, the time taken for the physical disintegration of the various blend membranes was studied. It is evident from the figure that there is a gradual increase in the withstanding ability of the blends with increase in the concentration of animal hair. An increase in the durability of the blend membranes suggests that the individual constituent polymeric materials in the blends are compatible with each other.

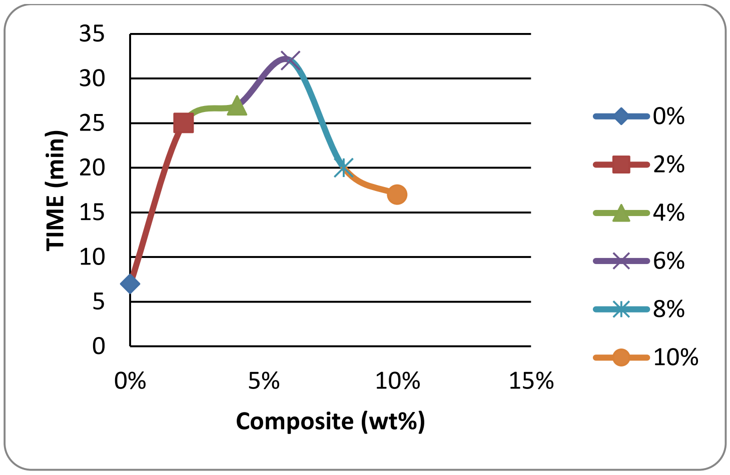


**Figure 3.23 Durability test for Animal hair/SPEEK composite**

But it can be observed that there is a sudden decrease after 6% animal hair-SPEEK composite. Decreasing in durability with increase in composite composition can be attributed to the fact that the continuous linkage between reinforcement and SPEEK is disrupted.

## G. Mechanical Properties

The tensile strength as well as the percentage elongation of SPEEK and Animal hair/SPEEK are given in Table below.

**Table 3.1 Material properties of SPEEK-Animal Hair membrane**

| S.No | *Animal hair* Composition (wt %) | Tensile Strength (MPa) | Percentage Elongation (%) |
|---|---|---|---|
| 1 | 0 | 31.6 | 55.2 |
| 2 | 4 | 35.5 | 53.4 |
| 3 | 8 | 39.9 | 51.8 |

There is an increase in the tensile strength with increase in the content of animal hair. It is due to the very good compatibility among the constituents, thus making the membrane stiffer. As a result, an increase in the tensile property is observed. On the other hand, the percentage elongation decreases with increasing content of animal hair. Once again, as the membranes are getting more and stiffer with the addition of animal hair, the membranes break without much elongation.

## H.SOLVENT ABSORPTION STUDIES:

**Table 3.2 Water and methanol uptake for SPEEK/Animal hair composite**

For an excellent proton conducting ability, the membranes should have some appreciable water absorbing property. The absorbed water molecule acts like a canal for the passage of protons and the proton conductivity is largely dependent on the connectivity of the hydrated domains which in turn increases the mobility of ions. But excessive swelling in water results in a loss of mechanical and dimensional stability. The water uptake of the S-PEEK is totally dependent upon the sulphonation; hence S-PEEK and their blends are preferred.

Both water and methanol absorptions increase with increase in the content of reinforcement. Animal Hair is known to hold a very large amount of water.

| SNo. | Water Absorption (%) | Methanol Absorption (%) |
|---|---|---|
| SPEEK | 5.76 | 6.44 |
| 2% | 9.85 | 7.04 |
| 4% | 10.38 | 9.1 |
| 6% | 10.5 | 10.2 |
| 8% | 11.62 | 11.13 |
| 10% | 12.9 | 13.1 |



## I. PROTON CONDUCTIVITY STUDIES:

**Table 3.3 Proton Conductivity of the Composites with variation in Animal hair content**

| S. No. | % Composition of Animal Hair | Proton Conductivity x $10^{-3}$ S/cm |
|---|---|---|

| | | |
|---|---|---|
| 1 | 0 | 4.81 |
| 2 | 2 | 5.10 |
| 3 | 4 | 5.54 |
| 4 | 6 | 5.93 |
| 5 | 8 | 6.21 |
| 6 | 10 | 6.32 |

Similar to the earlier case, with increase in the concentration of Animal Hair, there is an increase in the proton conducting ability. This could once again be attributed to the water holding capacity of the animal hair.

**4. CONCLUSION:**

Our group had prepared a series of SPEEK-Animal Hair composites of varying the composite composition. The IEC values were found in the order of $10^{-3}$ S/cm. The FTIR and XRD showed interaction between the particles and SEM images show a good distribution of reinforcement in the polymer matrix. The membranes were found to be thermally stable by TGA analysis upto $270^{0}$C which is excellent for the operation of PEMFC. Thus Animal hair –SPEEK composite can be used in the making of membranes for PEMFC.

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