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SULPHONATED POLY ETHER ETHER KETONE /ALL PURPOSE FLOUR (*MAIDA)* COMPOSITE MEMBRANES FOR PEM FUEL CELLS

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Abstract

Composite membranes of All- purpose flour (*Maida*) and S-PEEK (Sulphonated-polyetheretherketone) was prepared using solution casting and solvent evaporation method .The prepared membranes were thus characterized by Fourier transform infra-red (FTIR) to verify sulfonation. Thermo gravimetric analysis (TGA) was carried out to investigate the thermal stability of the sulfonated membranes. Surface morphology and tensile strength were evaluated by scanning electron microscopy (SEM) and UTM, respectively. Sorption experiments were conducted to observe the interaction of sulfonated polymers with water and methanol. The ion exchange capacity (IEC), which is a measure of proton conductivity was evaluated and found to be comparable with the commercially available Nafion^{TM} membranes. The membranes showed sufficient thermal stability also, the water uptakes and swelling ratios of the composite membrane increased with increase in the weight percent of the reinforcement. The membrane was assessed for its potential at different weight percent of All-purpose flour to serve as proton exchange membranes (PEM) in fuel cells and the results were promising.

Keywords: SPEEK, PEMFC, Composite polymer membranes

1. Introduction

The Proton exchange membrane fuel cells (PEMFCs) are among the most promising electrochemical devices for convenient and efficient power generation. The increasing energy requirement and demand is forcing many researchers and scientists to find new energy vectors able to satisfy the demand worldwide. In fact, the rapid growth in global transportation, the increased use of cars and buses, and the higher electricity demand for home

devices such as air conditioning plants, TV, etc., require energy source alternative to the fuel-fed internal combustion engine, as well as new routes for electrical energy production via non-pollutant engines [1].

The most commonly used proton exchange membrane for both PEMFC and DMFC is perfluorinated copolymers such as Nafion, which have high hydrolytic and oxidative stability and excellent proton conductivity [2-6]. However, the perfluorinated polymers have three major drawbacks: very high cost; loss of conductivity at high temperature (>80 ◦C) and low humidity; and high methanol permeability, which hinder their application .The drawbacks of perfluorinated membranes have prompted research into alternative membranes based on hydrocarbon polymer. For example, several aromatic polymer ionomer membranes such as sulfonated polyimide, sulfonated poly(ether sulfone) (SPES), polybenzimidazol (PBI), sulfonated poly(ether ether ketone) (SPEEK) are actively being investigated. Among the various hydrocarbon polymers, poly (ether ether ketone) (PEEK) based membranes were shown to be of considerable promise due to their good thermal stability, appropriate mechanical strength, and high proton conductivity, which increased with their degree of sulfonation (DS). SPEEK polymer is sulfonated polymer to PEEK polymer [7, 8].

According to literature on suitable modification, composite membranes exhibit good conductivities. It is also solvent free and therefore safer, environmental friendlier. Characterization of the composite membrane is done using various tests [9, 14].This work is therefore an attempt to synthesize composite polymer membranes, using a natural fiber such as All purpose flour (*Maida*) in a generally hydrophobic polymer for promoting proton conductivity. This modification makes a huge difference to the membrane's mechanical properties, morphology, and above all the crucial property in the context of fuel cells namely ion exchange capacity.

2. Experimental

2.1 Materials

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

2.2 Synthesis of SPEEK:

PEEK, which is hydrophobic, is sulphonated to convert it into SPEEK (Sulphonatedpolyetheretherketone) which is hydrophilic in nature. Weighted amount of PEEK was weighed and was transferred into a three necked round bottom flask a known quantity of Sulfuric acid was used as the sulphonating agent. The reaction time was determined based on 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).

2.3 Preparation of Composite Membranes:

The required quantity of SPEEK was taken and was dissolved in NMP for an hour mildly heating the mixture at 50^0 C. Then the reinforcement (all-purpose flour *(maida)* 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 all-purpose flour 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 2.1: Composition of Matrix and Reinforcement

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

ION EXCHANGE CAPACITY:

Ion exchange capacity is the method by which the number of milliequivatents of ions per 1 gram of dry polymer are estimated[1]. A known gram 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.

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

SWELLING STUDIES:

This test is to understand the retension properties of the membrane. Weighed amounts of dry membranes of 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:

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

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

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.

FT-IR STUDIES:

FT-IR is an analytical technique, performed by passing infra red radiation through the sample, to identify composition of in 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.

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.

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.

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].

MECHANICAL PROPERTIES TESTING:

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.

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. Result and Discussion

3.1 FTIR analysis:

The FT-IR spectrum of PEEK is shown in the Figure below

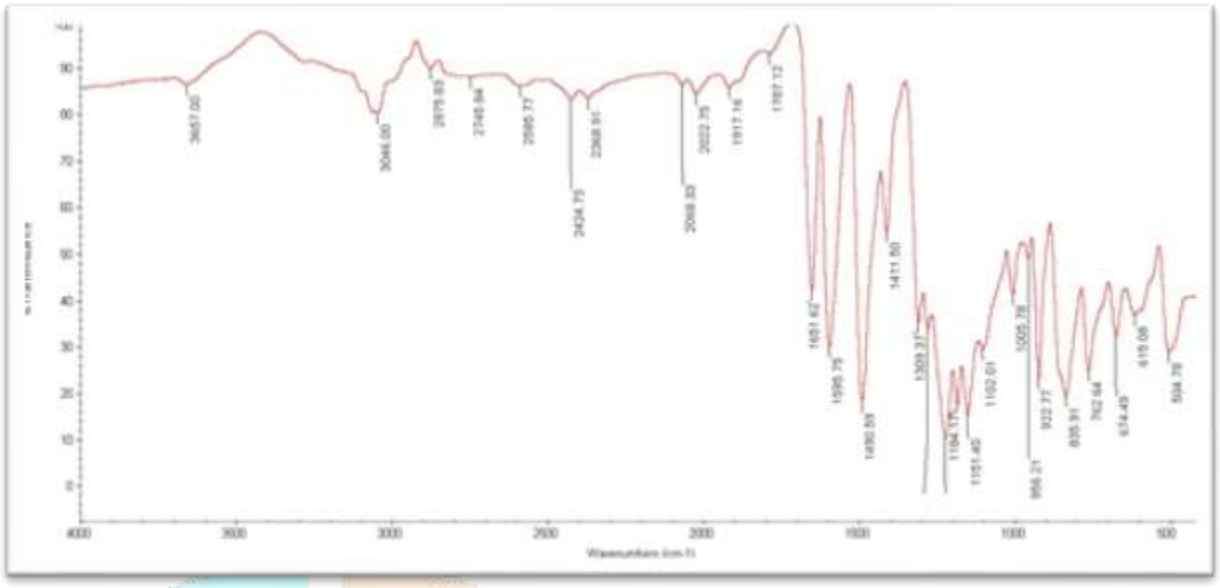

Figure 3.1. FT-IR Spectrum of PEEK

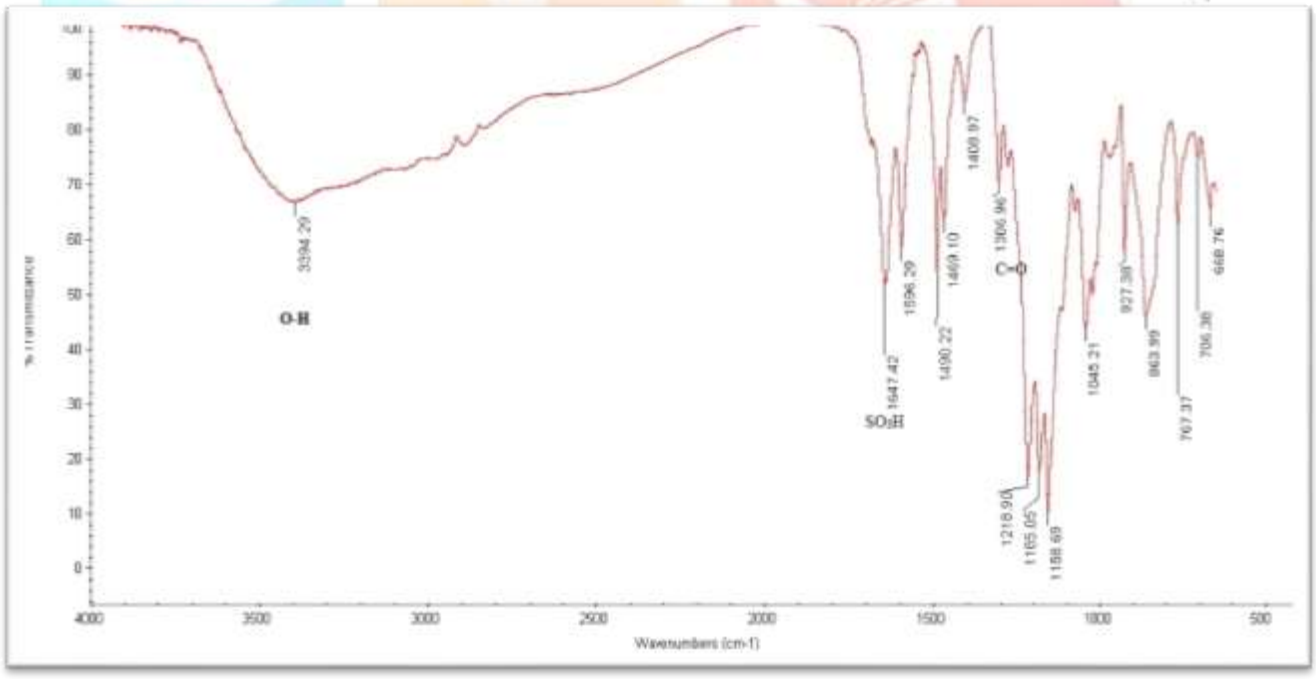

Figure 3.2 FT-IR Spectrum of SPEEK

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 SPEEK, shows an intense broad envelope at 3343 cm^{-1} which is attributed to the O–H stretching vibration of SO_3H which is established during sulphonation of PEEK. The alkyl groups in PEEK are not found in SPEEK. All the other features are nearly same as that of PEEK[2].

The FT-IR spectrum of SPEEK-*Maida* is shown below for different composition.

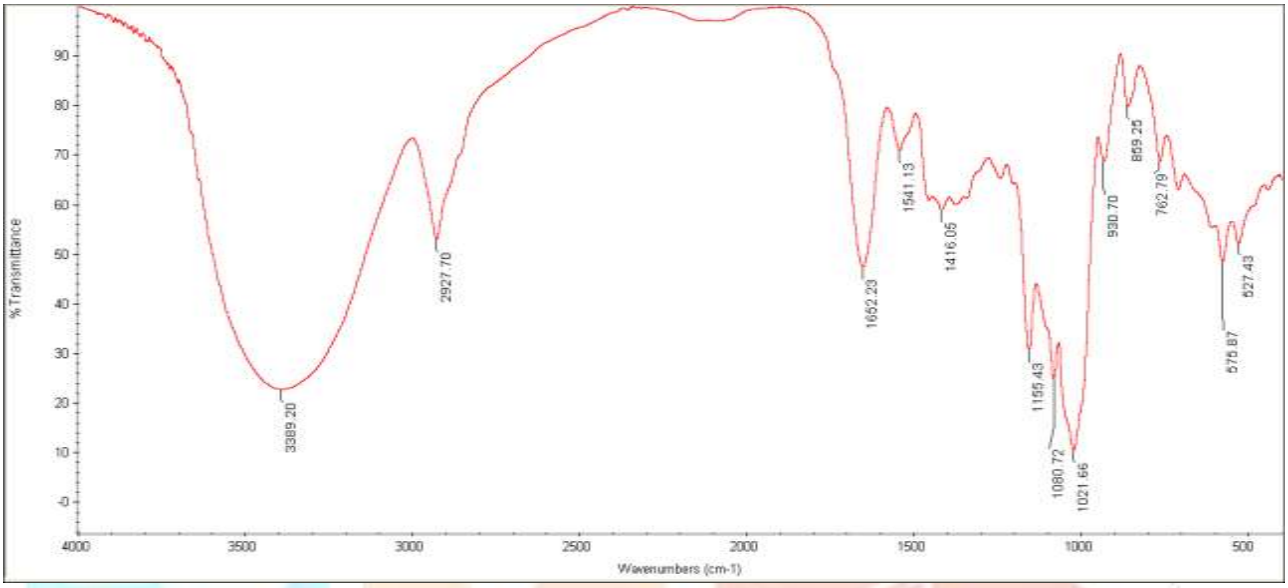

Figure 3.3. FT-IR spectrum of *Maida*

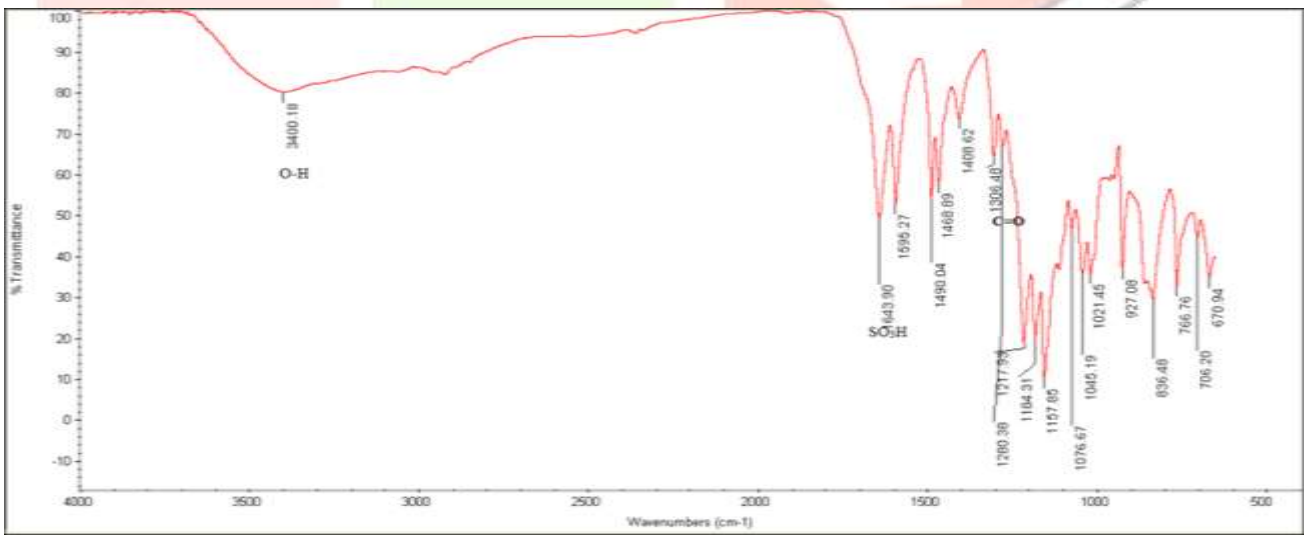

Figure 3.4. FT-IR Spectrum of 2% *maida* composition

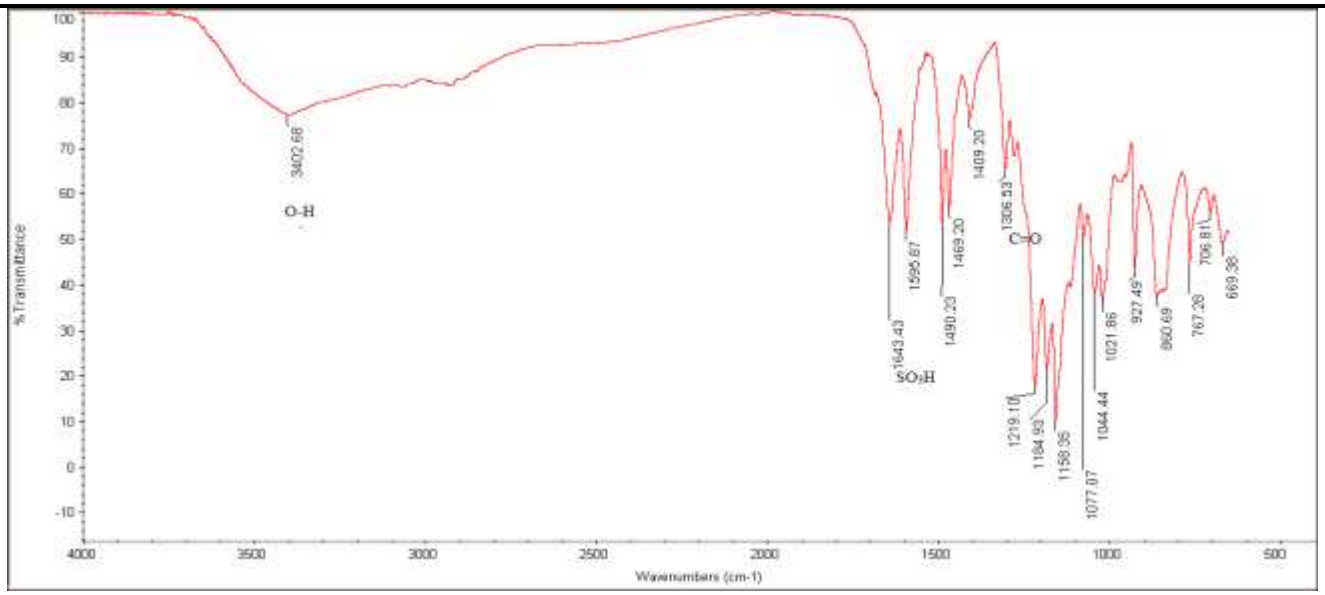

Figure 3.5. FT-IR Spectrum of 4% *maida* composition

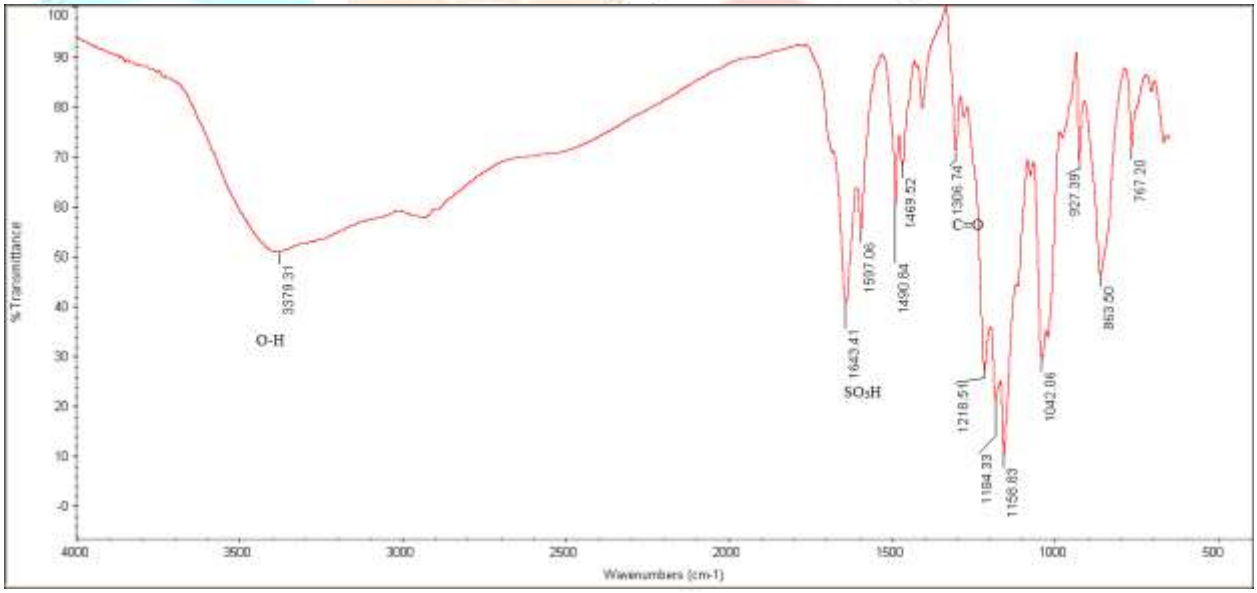

Figure 3.6. FT-IR Spectrum of 6% *maida* composition

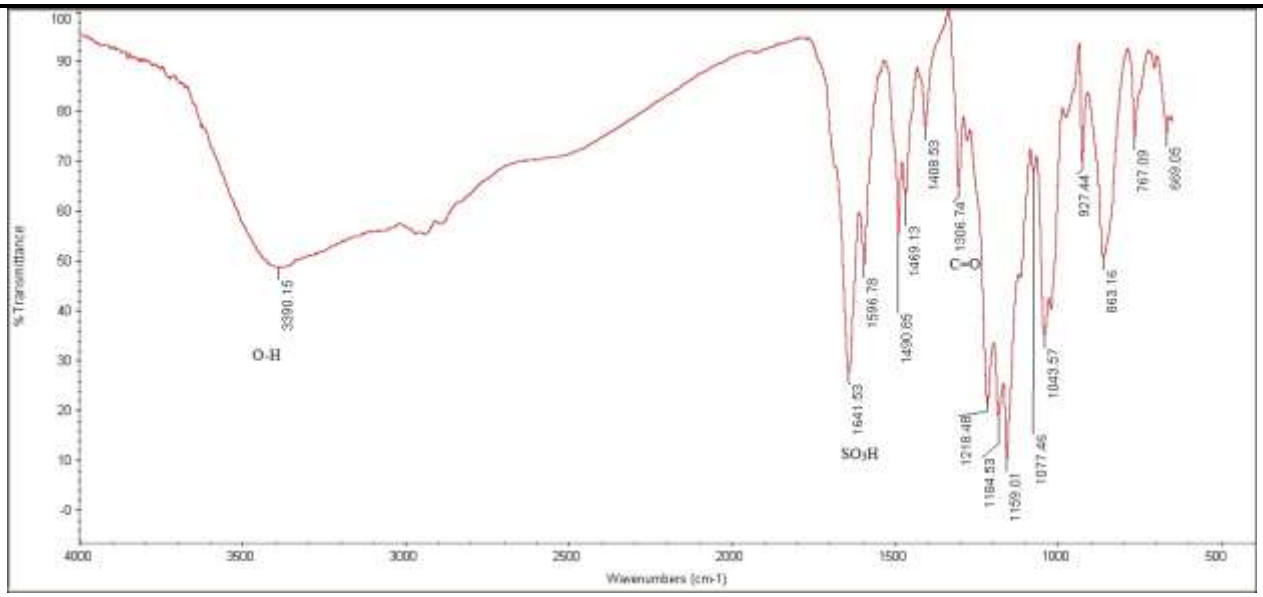

Figure 3.7. FT-IR Spectrum of 8% *maida* composition

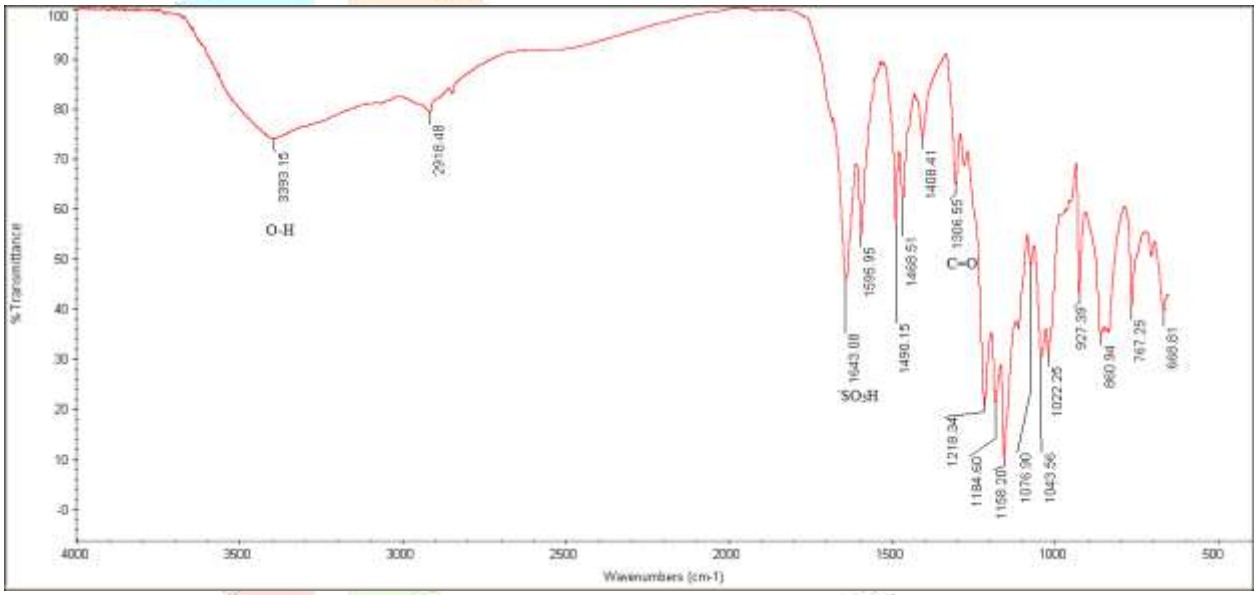

Figure 3.8. FT-IR Spectrum of 10% *maida* composition

The above figures show the FT-IR images of PEEK, S-PEEK, All purpose flour(Maida) and composites 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 1643 cm^{-1}) . The reason for this shift is the interaction of maida particles with S-PEEK. All other features are same as compared to S-PEEK.

3.2 Thermo gravimetric Analysis:

The TGA spectra of SPEEK is shown in Figure 3.15

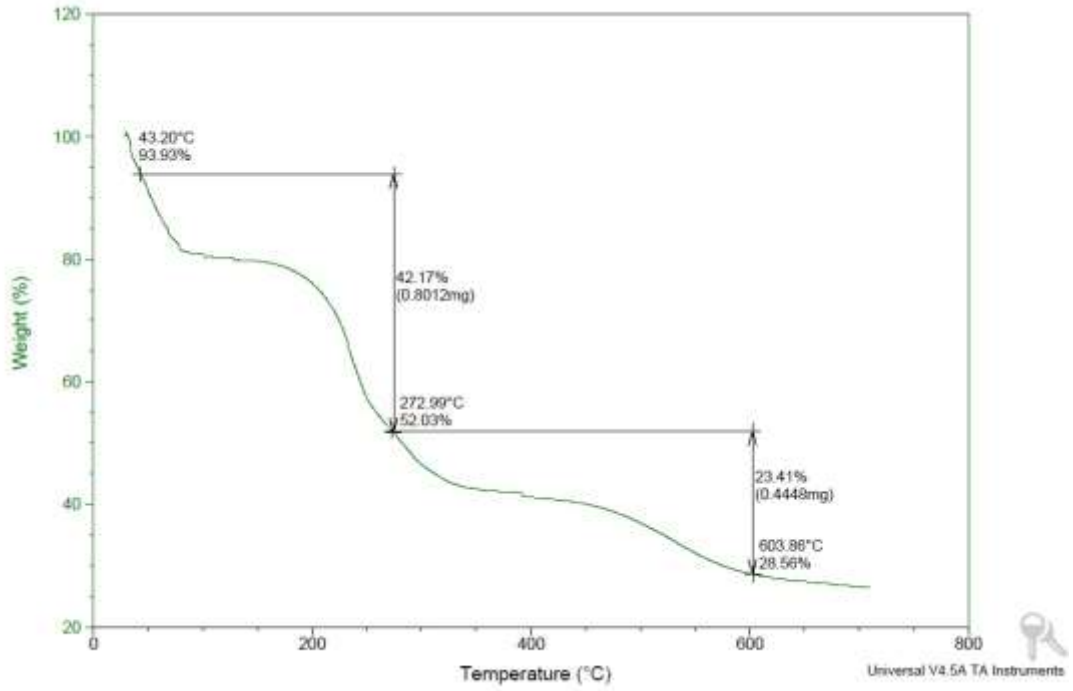

Figure 3.15 TGA Spectra of SPEEK

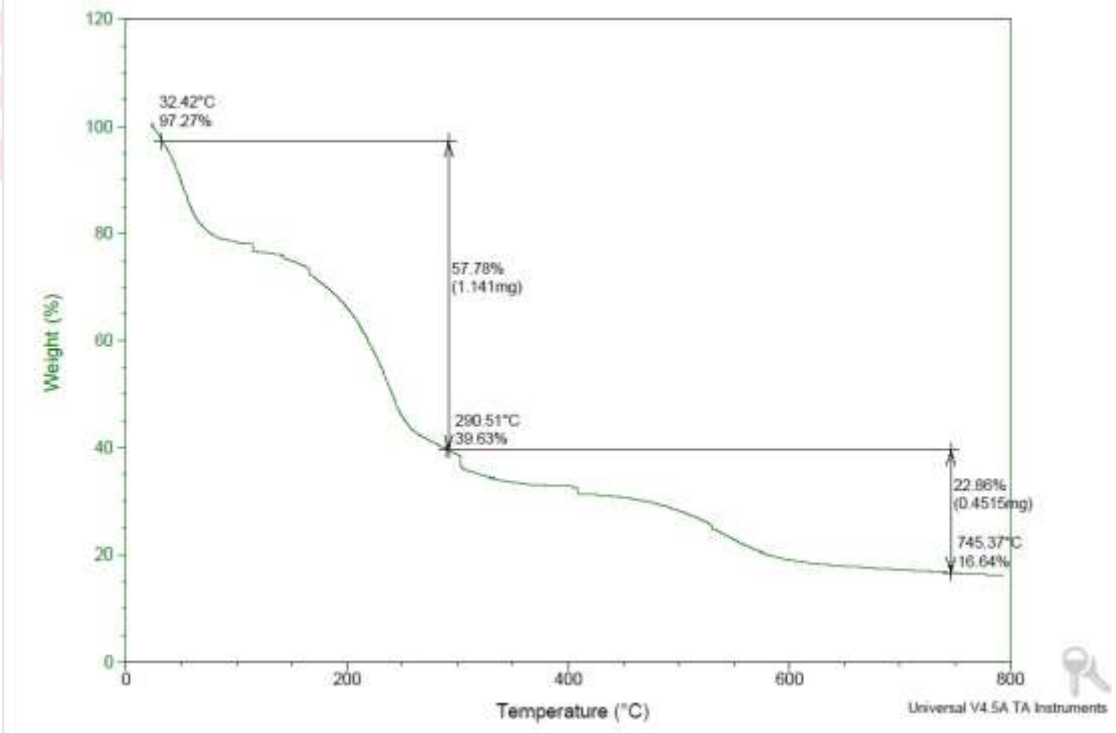

Figure 3.16 TGA Spectra of 2% maida/SPEEK Composite

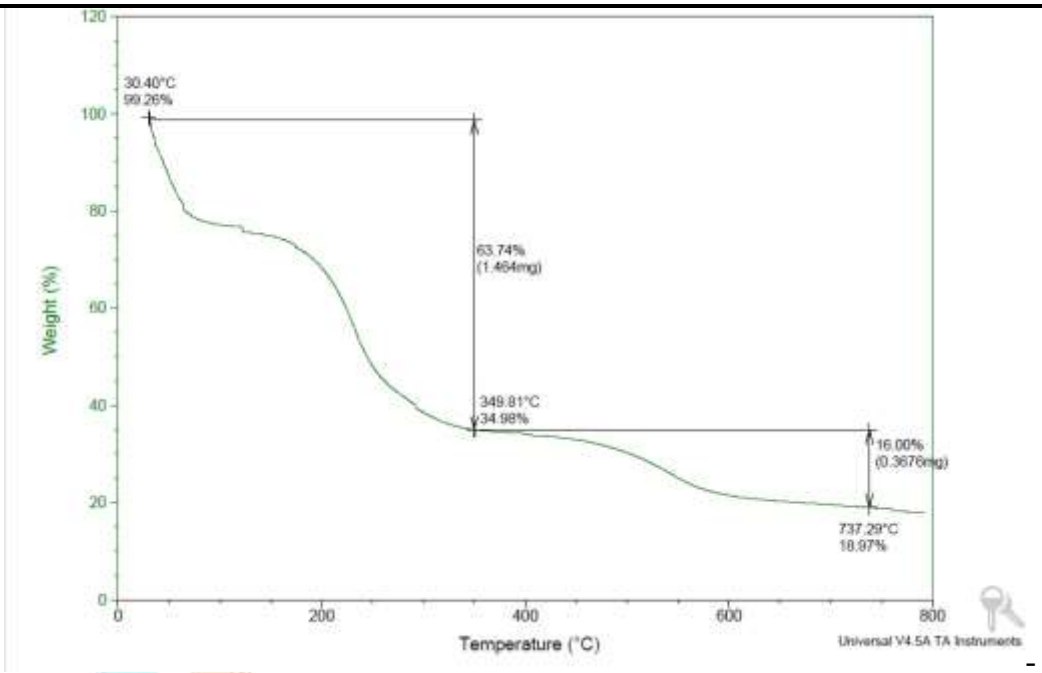

Figure 3.17 TGA Spectra of 4% maida/SPEEK Composite

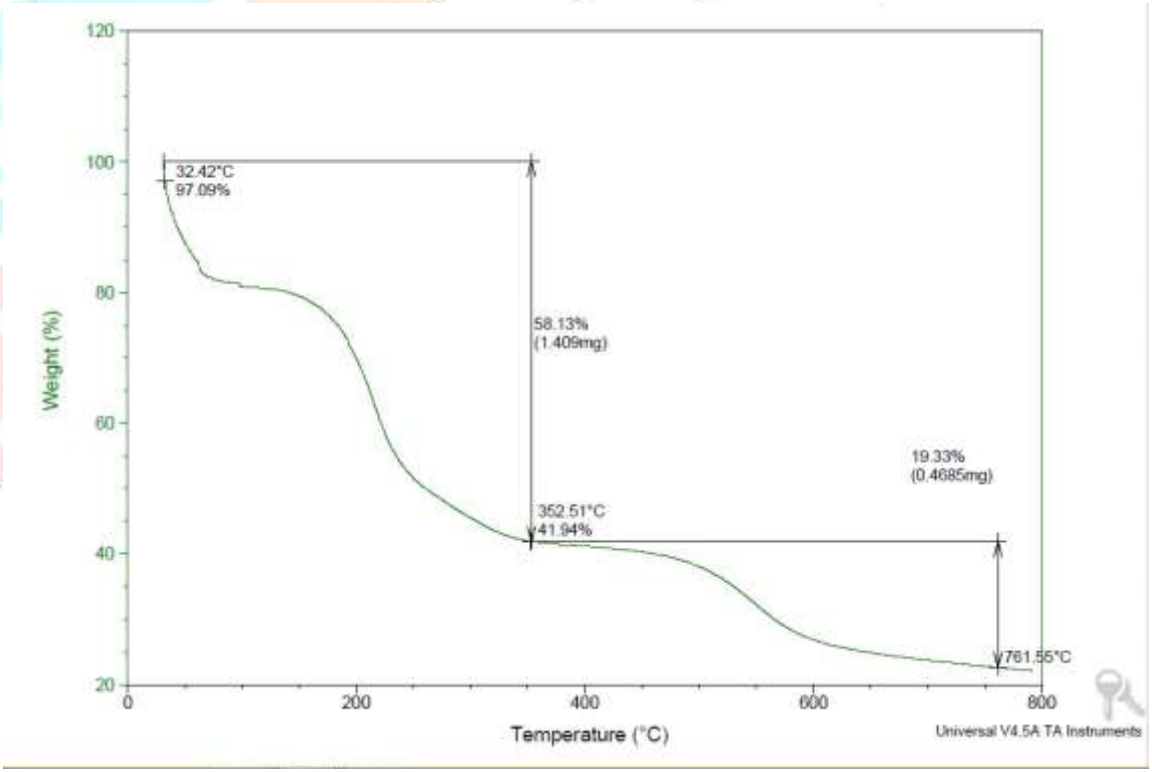

Figure 3.18 TGA Spectra of 6% maida/SPEEK Composite

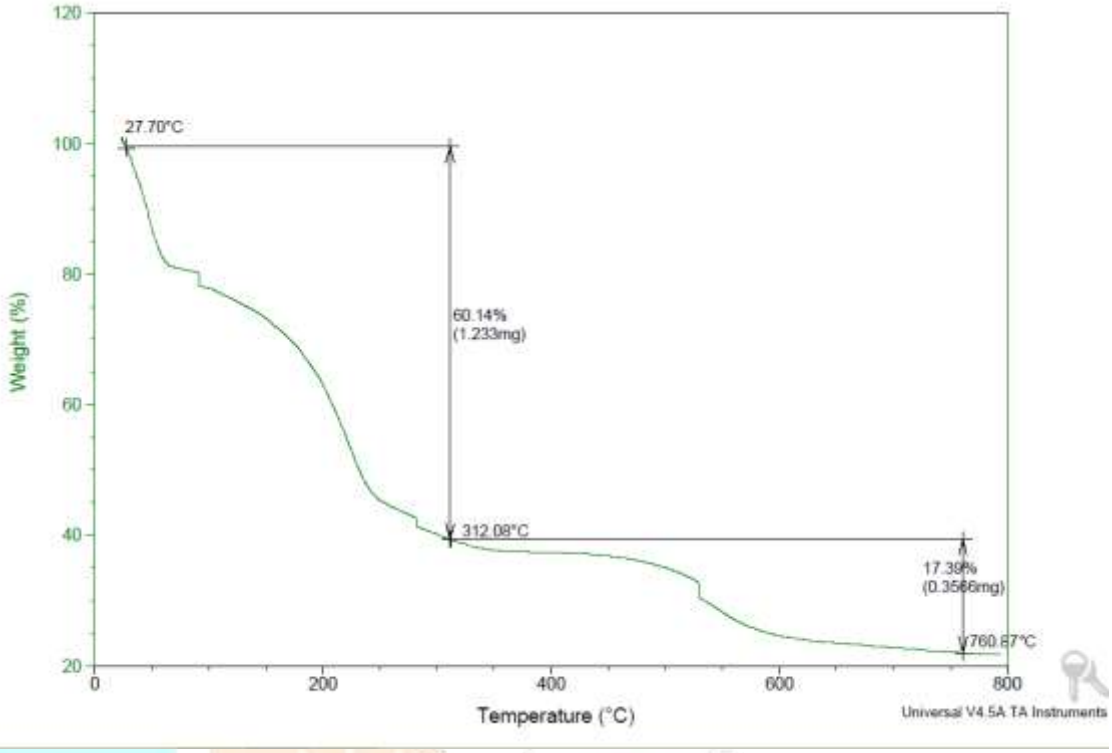

Figure 3.19 TGA Spectra of 8% maida/SPEEK Composite

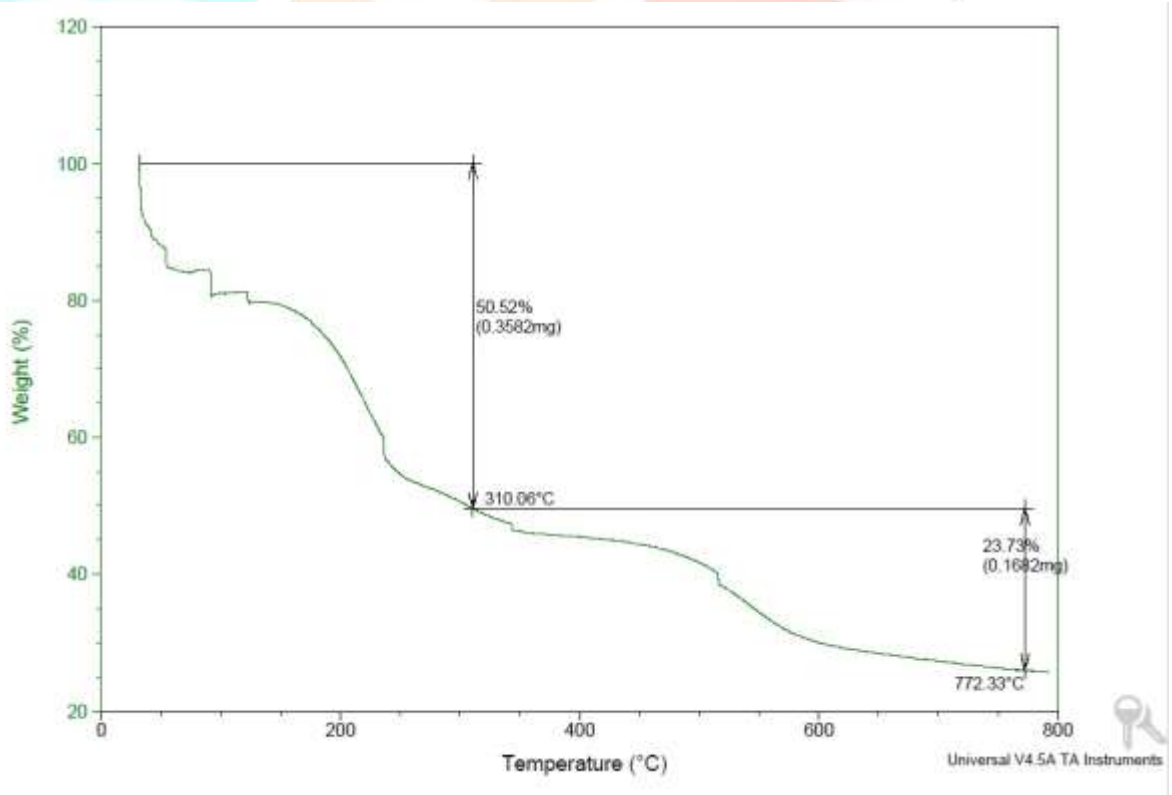

Figure 3.19 TGA Spectra of 10% maida/SPEEK Composite

Figure 3.16-3.19 shows the results of thermo gravimetric analysis of S-PEEK and Maida composites of different compositions. It is 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- 355°C. The decomposition of main chain of PEEK occurs in the range of 600-750°C.

3.3 SEM Analysis

SEM images of SPEEK at three different magnifications namely 5 , 50 ,100 (from left to right) are shown below

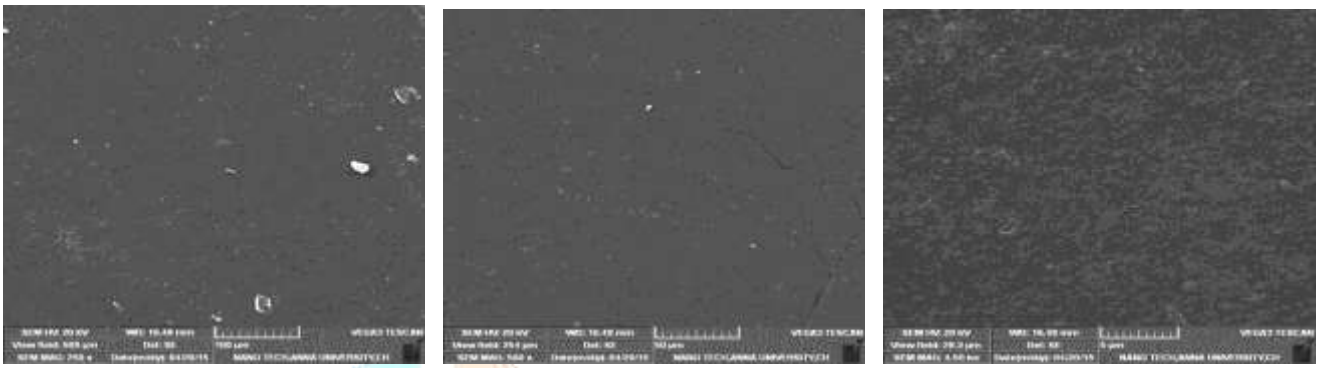

Figure 3.26 SEM images of SPEEK

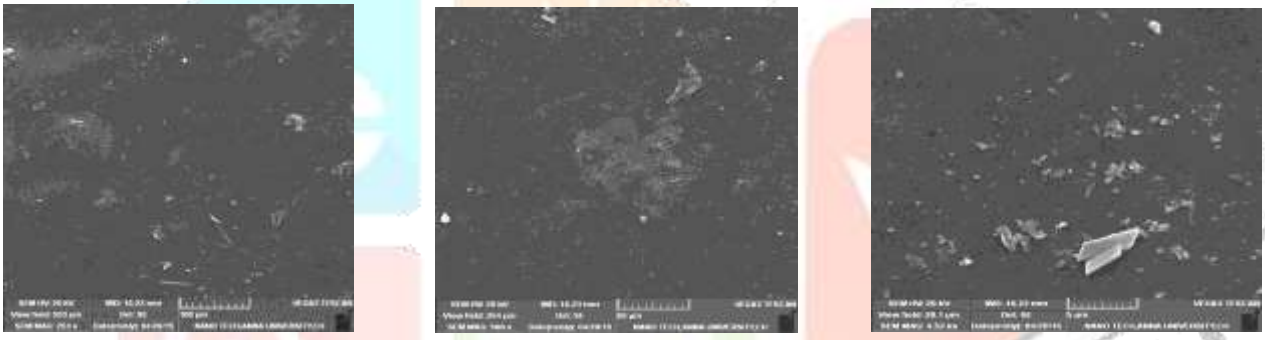

Figure 3.27 SEM Images of 2% Maida/SPEEK

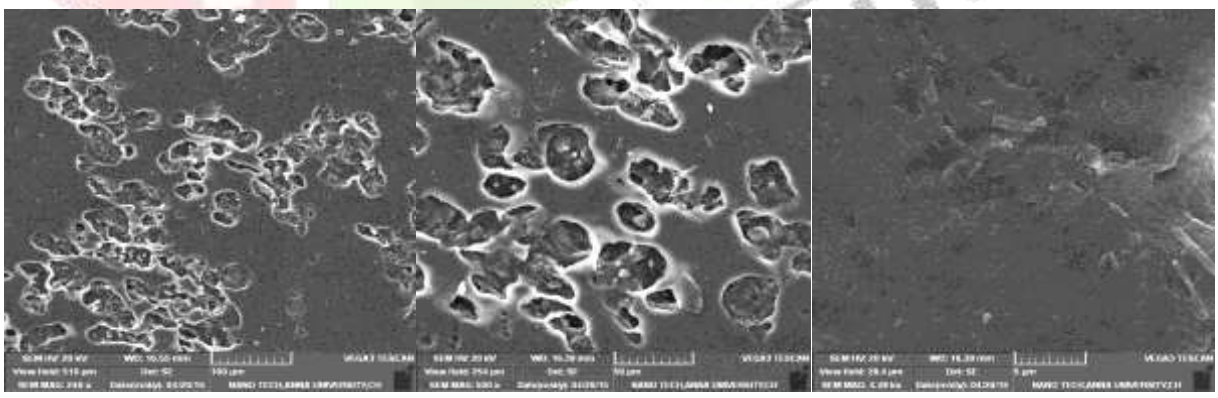

Figure 3.28 SEM Images of 4% Maida/SPEEK

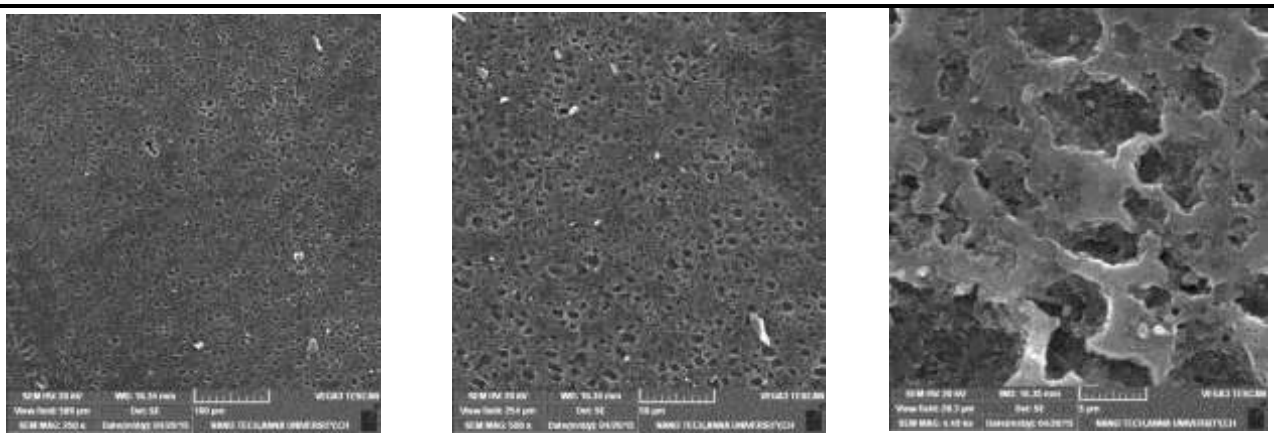

Figure 3.29 SEM Images of 6% Maida/SPEEK

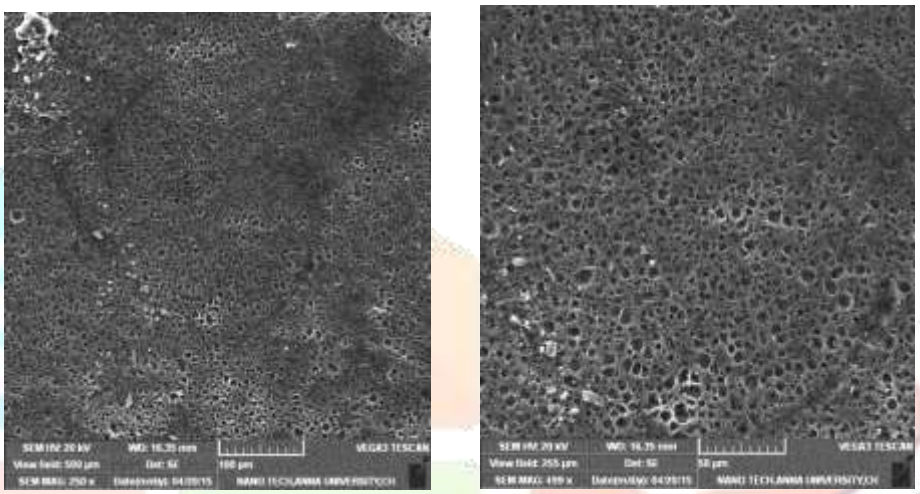

Figure 3.30 SEM Images of 8% Maida/SPEEK :

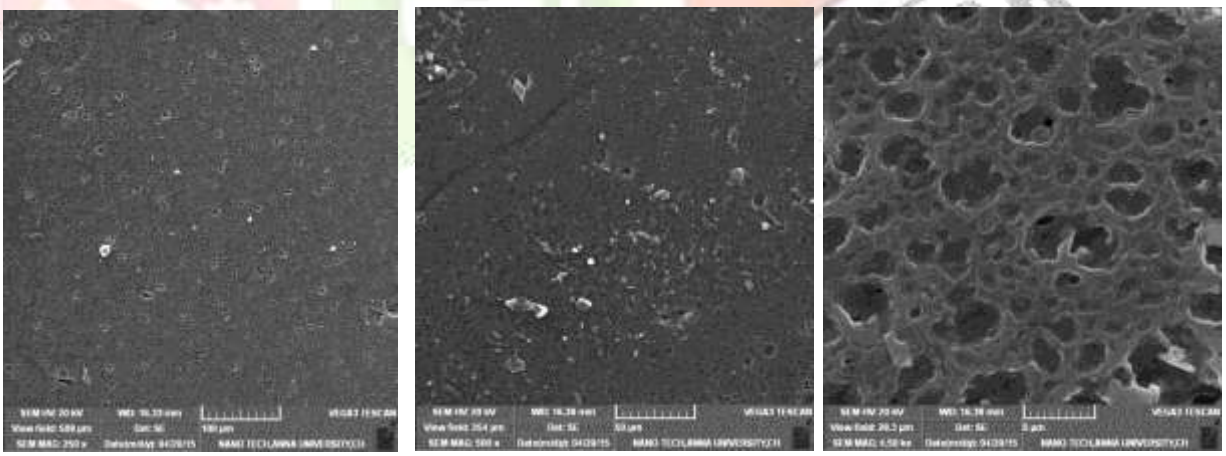

Figure 3.31 SEM Images of 10% Maida/SPEEK

The above SEM images have magnification 5, 50, 100µm. The SEM image looks dense, clear and homogenous indicating a very good compatibility between the *Maida* 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.

3.4 X-Ray Diffraction Studies:

The XRD spectra of the various blends are shown in Figure . It includes blends of SPEEK with (a) 2% *maida*, (b) 4% maida (c) 6% maida, (d) 8% maida and (e) 10% maida

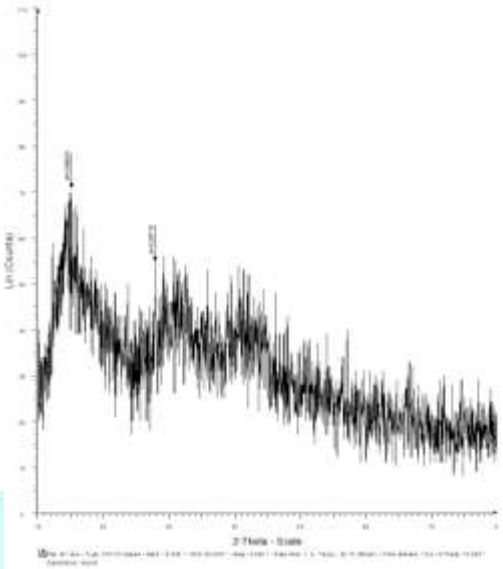

Figure 3.37 XRD spectra of SPEEK

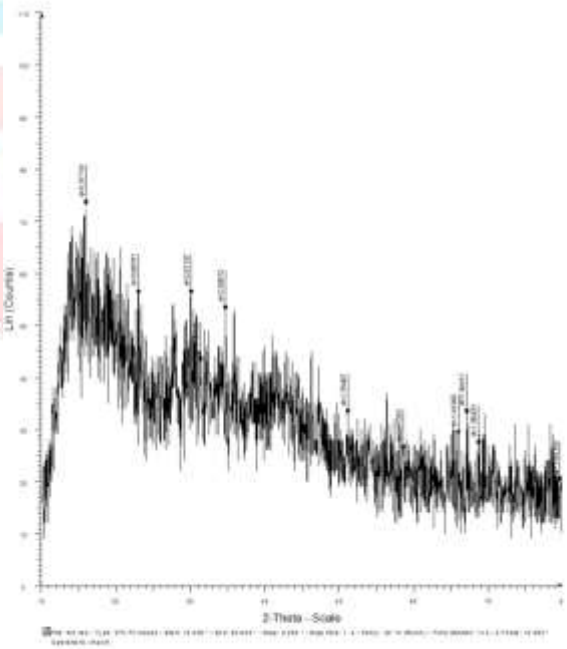

Figure 3.38 XRD spectra of 2% maida/SPEEK composite

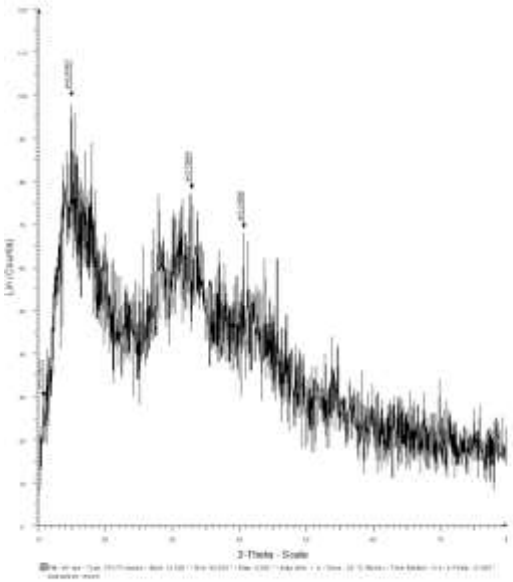

Figure 3.39 XRD spectra of 6% maida/SPEEK composite

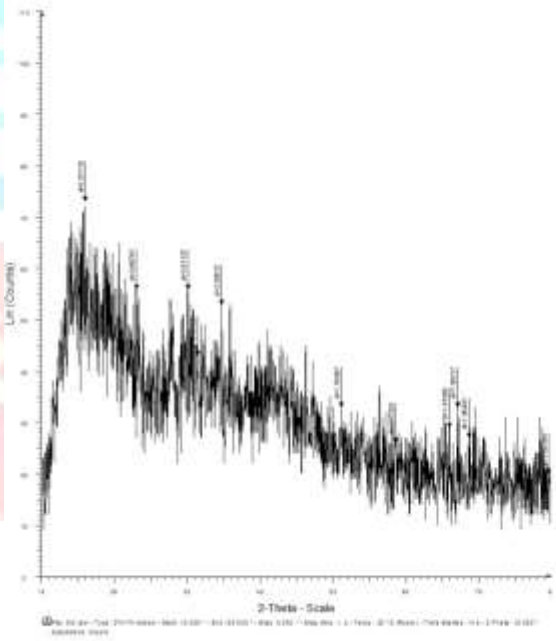

Figure 3.39 XRD spectra of 8% maida/SPEEK composite

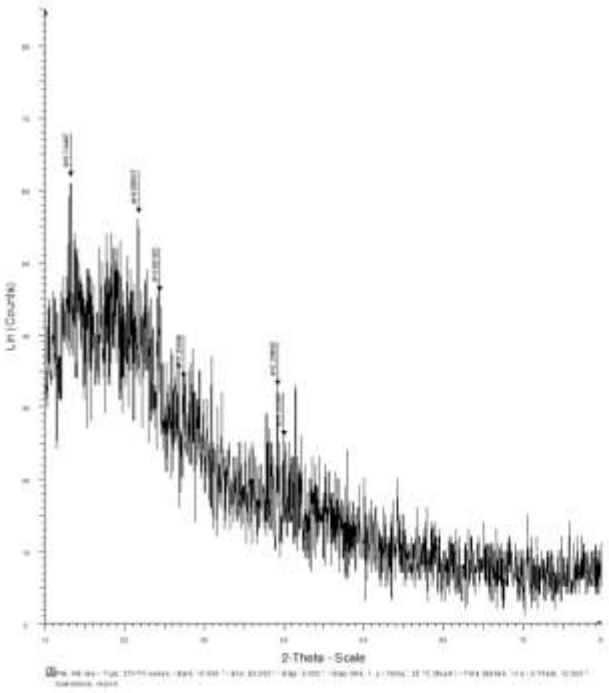

Figure 3.40 XRD spectra of 10% maida/SPEEK composite

Figure 3.37-3.45 shows the XRD images of the SPEEK , and various percentage of composites containing *Maida.* There is a prominent peak around 15 ^{0} in all the images and there is another peek around 35^0 in all composites containing *Maida* as a reinforcement. This is possibly due to the interaction between SPEEK and *Maida*.

3.5 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 [16]. Figure 1 shows the relationship between ion-exchange capacity (IEC) and the various compositions of Maida-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 [17]. 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[17].

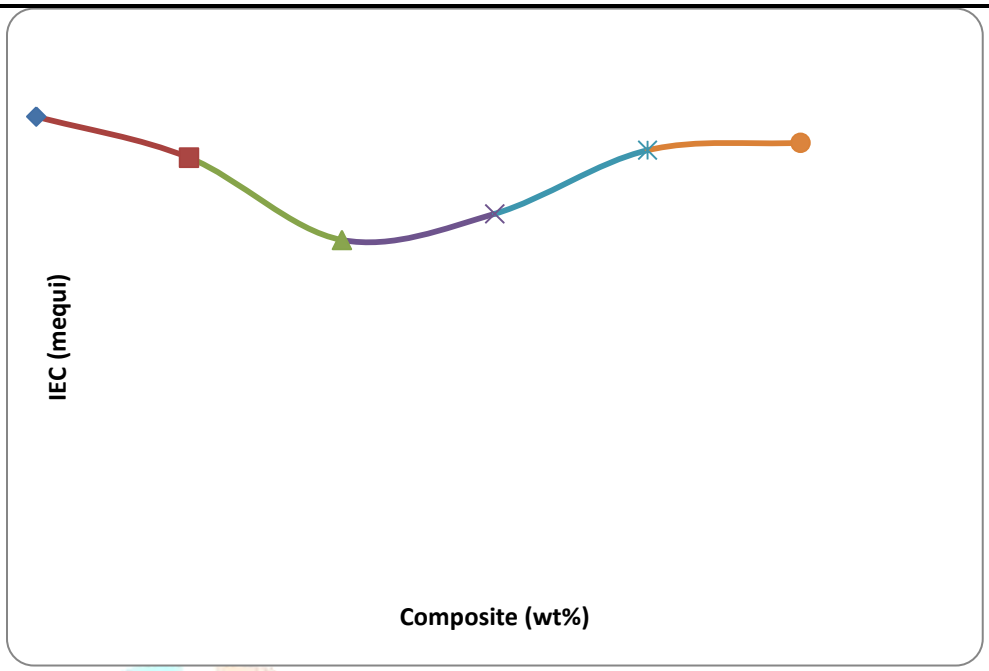

Figure 3.46 IEC of Maida-SPEEK Composite

3.6 Accelerated Stability tests:

The durability study was performed using a solution of water containing 3% H2O2 and 4 ppm FAS and the results are shown below in the figure for Maida –SPEEK.

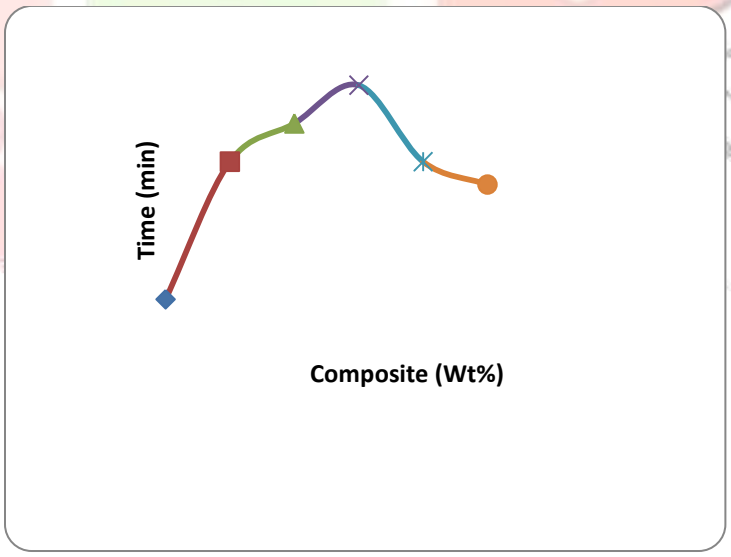

Figure 3.48 Durability test for Maida/SPEEK composite

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 *Maida*. An increase in the durability of the blend membranes suggests that the individual constituent polymeric materials in the blends are compatible with each other.

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

3.7 Mechanical Properties

The tensile strength as well as the percentage elongation of SPEEK as well as the Maida/SPEEK and Animal hair/SPEEK are given in Table below. There is a decrease in the tensile strength with increase in the content of maida. One possible reason for this kind of behaviour in the mechanical properties may be due to the compatibility among the constituents, thus making the membrane less stiff. As a result, a decrease in the tensile property was observed. On the other hand, the percentage elongation increases with increasing content of maida which means the membranes break after much elongation.

Table 3.2 Material properties of SPEEK-Maida membrane

S.No	*Maida* Composition (wt %)	Tensile Strength (MPa)	Percentage Elongation (%)
1	0	31.6	55.2
2	4	26.6	90.4
3	8	25.6	121.8

3.8 Solvent absorption studies:

The results of water and methanol absorption of the composite membranes are given in Table

Table 3.4 Water and methanol uptake for SPEEK/Maida composite

SNo.	Water Absorption (%)	Methanol Absorption (%)
SPEEK	5.76	6.44
2%	9.89	5.7
4%	16.74	5.92
6%	21.13	6.8
8%	27.67	7.77
10%	30.14	9.2

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 SPEEK is totally dependent upon the sulponation, hence SPEEK and their blends are preferred.

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

3.9 Proton Conductivity Test:

The proton conductivities of the various composite membranes are given the table below.

Table 3.6 Proton Conductivity of the Composites with variation in *Maida* content

S. No.	% Composition of All Purpose Flour	Proton Conductivity x 10^{-3} S/cm
1	0	4.81
2	2	5.43
3	4	6.09
4	6	6.57
5	8	7.4
6	10	7.6

With increase in the concentration of All Purpose Flour, there is an increase in the proton conducting ability. This kind of attitude may be the result of the following factor.

Though there is a decrease in the net amount of sulphonic acid grouping the water absorption capacity of the composite membranes increased with increasing concentration of All Purpose Flour. It is well known that the inorganic content is capable of holding a good amount of moisture. Thus the presence of additional amount of water facilitates proton conduction

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