

# Synthesis and Characterization of Organo -Inorganic Nano composite Membranes for Waste water processes and Bioprocess applications

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## **Abstract**

*Poly ethylene imine (PEI)/Polyether sulfone (PES) and SiO<sub>2</sub> composite membranes were prepared by phase inversion method based on the in situ polymerization process with TEOS/CAL-SIL (Tetra ethyl orthosilicate-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>/calcium orthosilicate-Ca<sub>2</sub>SiO<sub>4</sub>) as a precursor for forming SiO<sub>2</sub> inorganic particles which is also considered as a pore-forming agent. The influence of SiO<sub>2</sub> particles on the morphology and the performance of the composite membrane were investigated by the means of FTIR, SEM, XRD, mechanical strength analysis and pure water flux tests. The results of FTIR shows the presence of silica with their corresponding symmetric and asymmetric vibrations compared with control membrane and shows the amorphous nature of the membranes. The morphology of composite membrane differing from their pure state and shows the formation of silica inorganic particles along with varying pore statistics. The greater degree of homogeneity and the absence of macro phase separation is the result of concurrent formation of inorganic network in polymer matrix.*

**Keywords:** Poly ethylene imine(PEI), Poly ether sulfone(PES), Tetra ethyl ortho silicate (TEOS), Composite membranes, enhanced permeability, calcium orthosilicate(CAL-SIL).

## **INTRODUCTION**

Polymer membranes are widely used in industries to treat waste water especially for separation of organic or inorganic particulates from polluted and toxic aqueous streams. The properties of the polymer matrix such as its stiffness, strength, crystallinity (related to viscosity), tends to alter with the inclusion of the inorganic nanoparticles content. In addition, the interfacial and morphological effects between nanoparticles and polymers influence the performance of the functional materials. The morphology and performance are controlled by varying the casting solvents and are critical in transport of water and other organic molecules across the membrane[1] The inter penetration of silicon-oxygen networks in PVDF membranes proves to

be a responsible candidate for the changing fashion of pure water flux[2].

Poly ether sulfone is an important thermoplastic polymer possessing high glass transition temperature (T<sub>g</sub>) which shows good mechanical, thermo-oxidative and chemical stability along with impressive anti-fouling effect. Because of physio-chemical properties and eco-friendliness, PES finds to be the potential candidate in many industries in the preparation of ultra-filtration and reverse osmosis membranes in spite of some drawbacks such as strict casting conditions and low rejection performance. For improved water permeability and reduced fouling the surface of the membrane has to be engineered towards hydrophilic nature [3]. Polyimides prove to be the suitable agents based on carbonyl group linkage

with water through hydrogen bonding. The research in polymer membrane is still proceeding to improve the performance of the membrane by surface modification[4], blending of various polymers[5,6] with inorganic fillers as additives such as PVP, PEG in cellulose acetate membranes show the change in permeate flux according to the choice of an additive[7] finds suitable method. In addition, preparation of hybrid membranes through in-situ synthesis is another efficient method in which inorganic particles are formed inside the polymer networks at the time of acid hydrolysis and subsequent condensation reaction. [8] Moreover this method seems to be convenient and effective in the formation of inorganic particles and pore formations because of less aggregation of inorganic moieties and no capping or stabilizing agents are required to arrest the size of the particles. It is assumed that the base polymer itself can act as a stabilizing agent and arrest the growth to certain extent. In-situ methods for preparation of composites are favorable because the size control is achieved by the limited availability of precursor and the growth is suppressed by surrounded casting polymer. But in ex-situ preparation of elemental metal and subsequent addition leads to the non-homogeneous and aggregated nature of inorganic particles along with asymmetric pore sizes in membranes [9]. Based on the volume and void fraction of the inorganic nanoparticle fillers, the increment in the relative gas permeability due to the formation of the preferential permeation pathway is reported without sacrificing the selectivity and structure [10].

Organo functional transition metal alkoxides such as TEOS/CAL-SIL liquid is usually taken as a common precursor to form silica inorganic networks due to safe, low cost, easy handling, slow and controllable reaction during condensation [11]. The formation of silica nanoparticles

depends on the concentration of TEOS/CAL-SIL, reaction temperature, feed rate and catalyst such as ammonia [12]. TEOS/CAL-SIL is also used in silicone polymers as a cross linking agent and coatings for various materials. W.Chen et.al has reported the in-situ generation of silica nanoparticles in cellulose acetate membranes treated with different coagulation baths to enrich the permeability based on the increment in pore size and skin layer density. The addition of Poly ethylene imine (PEI) and TEOS/CAL-SIL aimed at improving the hydrophilicity, mechanical strength and permeability of the PES membrane. The formation of silica nanoparticles inside the membrane would act as an inorganic filler material whereas the surface nanoparticles on the membrane play as an adsorbent of contaminants owing to their high reactivity contributed by their increase surface to volume ratio.

The main objective of this work is to investigate the effect of silica inorganic particles on PES and PES/PEI blend membranes in terms of pore statistics, morphological changes, pure water flux, nature of hydrophilicity etc. PES, PES/SiO<sub>2</sub> and PES/PEI/SiO<sub>2</sub> membranes were prepared by phase inversion method. The functional elements present were characterized by FTIR spectrometer, the crystallinity of membranes was analyzed by X-ray diffractometer and morphology by scanning electron microscope.

## **Experimental**

### ***Materials and methods***

PES/PEI, The polymers procured from Solvay process, India, was used without any further treatment. Analytical grade N, N'- dimethylformamide (DMF) and sodium lauryl sulfate (SLS) were obtained from Qualigens Fine Chemicals, Glaxo India Ltd., India. TEOS and CAL-SIL (Sigma Aldrich), PEI (average Mw 25 kD). De ionized and distilled water was

used for the preparation of feed solution and for the gelation bath preparation.

### **Membrane preparation**

PES, TEOS/CAL-SIL PEI and the solvent DMF were taken in different compositions mentioned in Table 1. For other compositions the ratio between the reactants are varied and the total weight percentages should not exceed hundred. PES and DMF was taken in a double neck round bottom flask and stirred with Teflon and the temperature of the solution is maintained at 50°C. After 5 minutes, TEOS/CAL-SIL was added drop wise and the solution kept stirring until a homogenous mixture had obtained. After attainment of homogeneity, the solution was permitted to cool and casted on a glass plate using a film applicator with the thickness of 500µm. After 30 seconds of casting time, the glass plate was immersed on the coagulation bath contains water and sodium lauryl sulphate mixture for phase separation to occur. After 24 hours the membranes were washed with water and transferred to a bath containing diluted formaldehyde. The membranes were dried and cut into small pieces for characterization.

### **Characterization**

#### **Elemental analysis**

The chemical elements (characterized by functional group) present in the PES/TEOS/CAL-SIL/PEI membrane was done by FTIR (Perkin Elmer make, Model: Spectrum RXI) between the wave number range 400 and 4000cm<sup>-1</sup>.

#### **X-Ray diffraction**

Properties of membrane crystallinity were analyzed by X-ray diffractometer (D/Max ultima III, Rigaku corporation, Japan) equipped with monochromatic Cu Ka radiation ( $\lambda = 0.154$  nm) operated at 40 mA and 40 kV from 58 to 808.

#### **Morphological studies**

The morphological characterization of all the blend membranes were studied using scanning electron microscopy (SEM) (Hitachi S-3000H). The membranes were cut into pieces of varied sizes and dried in room temperature and sputter coated with gold. The top surface and cross-sectional view of the membranes were observed by SEM under very high vacuum at 25 kV and at different magnifications

### **Results and discussion**

#### **FTIR Analysis**

Molecular structures of compounds were analyzed by Fourier transform infra-red spectrometer in the region of 400-4000cm<sup>-1</sup>. Tetra ethyl ortho silicate and Poly ethylene imine were introduced with varying proportions which are basically responsible for the differing properties composite membranes with respect to the virgin membrane. The formation of ethanol and silica networks and their functional group's various modes of vibration are observed from FTIR. From the figure [1&2] the presence of peaks at 840 and 957 cm<sup>-1</sup> refers to the symmetric stretching of Si-O-Si groups and stretching of Si-OH groups respectively and there is no prominent peak corresponds to pure membrane (A). The formation of the above peaks is due to the hydrolysis and subsequent poly condensation reactions which were catalyzed by sodium lauryl sulfate in the coagulation bath during phase inversion process. Strong absorption peak at 1471 and 1573 cm<sup>-1</sup> are associated with the C-H<sub>2</sub> and N-H bending vibration respectively. The broad -OH peaks observed at around 3430 cm<sup>-1</sup> indicated a major contribution from Si-OH or -OH groups of TEOS/CAL-SIL. The characteristic bands at 694cm<sup>-1</sup> (-NH wagging vibration), 1628 cm<sup>-1</sup> (NH<sub>2</sub>-scissoring vibration and C-H stretching vibration), 2314cm<sup>-1</sup> and 2113 cm<sup>-1</sup> (NH<sup>+</sup> asymmetric stretching vibration) for the addition of poly ethylene imine can be

seen with respect to pure membrane (A) where those peaks are absent.

### **Contact angle**

The changes occurred in the nature of the hydrophilicity and the membrane surface properties are determined by measuring the contact angle between the water drop and the membrane surface. The dynamic contact angle observation is suitable for micro porous membranes and it is evident that the decreasing trend in contact angle with respect to the percentage of TEOS/CAL-SIL addition. From the graphical figure 3, 4 and Table 2, the mean water contact angle for pure (A=51.9°) and composite membranes are B=48.1°; J=43.3°; K=45.4° respectively. Decreasing contact angle refers to changing trend towards hydrophilic nature. This is due to the formation of hydroxyl groups on the membrane surface due to hydrolysis and condensation of TEOS/CAL-SIL during casting and penetration of water in to the membrane. But for L=56.2°, the increase in water contact angle may result in the formation of large scale network with respect to maximum TEOS/CAL-SIL content during condensation of Si-OH group which prevents -OH groups on the membrane surface. [14]. Fig. 1 shows that increased TEOS/CAL-SIL or PEI concentrations led to increased water permeate fluxes, although this trend cease when the quantity of the nano-sized Al<sub>2</sub>O<sub>3</sub> particles reached a certain level as reported [17.]

### **XRD analysis**

The XRD patterns for pure PES and PES/TEOS/CAL-SIL composite membranes with different compositions are shown in figure.5 .It can be observed that the peak for pure PES membranes and composite membranes are almost identical (2θ=18.06° -18.5°) and there is no prominent difference occurred due to the amorphous nature of silica particles.. The formation happens only at the high

temperature treatment (1000°-1300°C) in vacuum air oven which results in ordered silica particles. If there is a formation of silica Nano crystalline material, corresponding peaks can be observed at a definite angle. Since the formation is based on the insitu synthesis in polymer networks, the resultant composite membranes shows identical to the control membrane. Suppose if we had added the synthesized silica particles to the membranes, definitely it would have shown the extra peaks corresponding to their characteristics. Similar work based on the addition of TiO<sub>2</sub> with PES has been reported with the prominent XRD peaks [13].

### **Scanning electron microscope analysis**

For specific applications, the surface of the membrane i.e. the 'skin' part plays a key role. The surface morphology and the cross section of the membrane were carried out by scanning electron microscope after sputter coated with gold. Images of top and cross sections of the dried samples were taken in high vacuum operating conditions. Fig. 6 shows the SEM images for the surfaces and cross-section of hybrid PES-SiO<sub>2</sub> membranes containing 5-20wt. % SiO<sub>2</sub> in the membrane-forming materials were presented. From the figure, it is observed that the pore size and the pore distribution increases with respect to the amount of TEOS/CAL-SIL added or based on the formation of silica which act as a pore forming agent which leaches out of the membrane in coagulation bath after casting was clearly seen. (Fig 6.A) shows the virgin membrane doesn't contain any silica particles along with less pore structure but other membrane morphology shows the presence of silica particles with high porosity. The existence of silica particles with varying sizes and distribution and shows no particle aggregation due to the sol-gel technique of formation of silica particles [15]. The higher cross linking

density [16] of inorganic and organic networks within them leads to the compactness of the membrane. Fig. 4.B shows the size of the silica in between 100-500nm where as in 4.D the pore size itself varies between 1 $\mu$ m-2 $\mu$ m. In Fig 4.H, there exist a spherical silica particles which are non-uniformly distributed and the size between 200-600nm and the pore size ranges between 800-1000nm. The uneven distribution of pores may result from dissolving nature of PEI gel. In Fig 4.I and J, the highest amount of PEI addition is resulted a channel like pores (may be due to the water dissolving nature of PEI) which appears to be a crack on the surface.

### CONCLUSION

In this investigation PES and PEI is chosen as a base polymers to prepare membrane and it has been used with solvents DMF. Dry/wet immersion method and wet immersion method were employed to prepare membranes. The influence of SiO<sub>2</sub> particles on the morphology and the performance of the composite membrane were investigated and reported. Membrane characterization like pure water flux and membrane hydraulic resistance had been done. The characterization of prepared membranes illustrates that the pure water flux and mechanical strength was increased while the membrane hydraulic resistance was decreased as increased SiO<sub>2</sub> particle concentration on the prepared membranes. The membranes were used in the application of toxic heavy metal ion removal. Heavy metal ions like Ni (II), Cu(II) and Cr(III) were separated by using the prepared membranes. The results of the above mentioned methods were discussed and reported.

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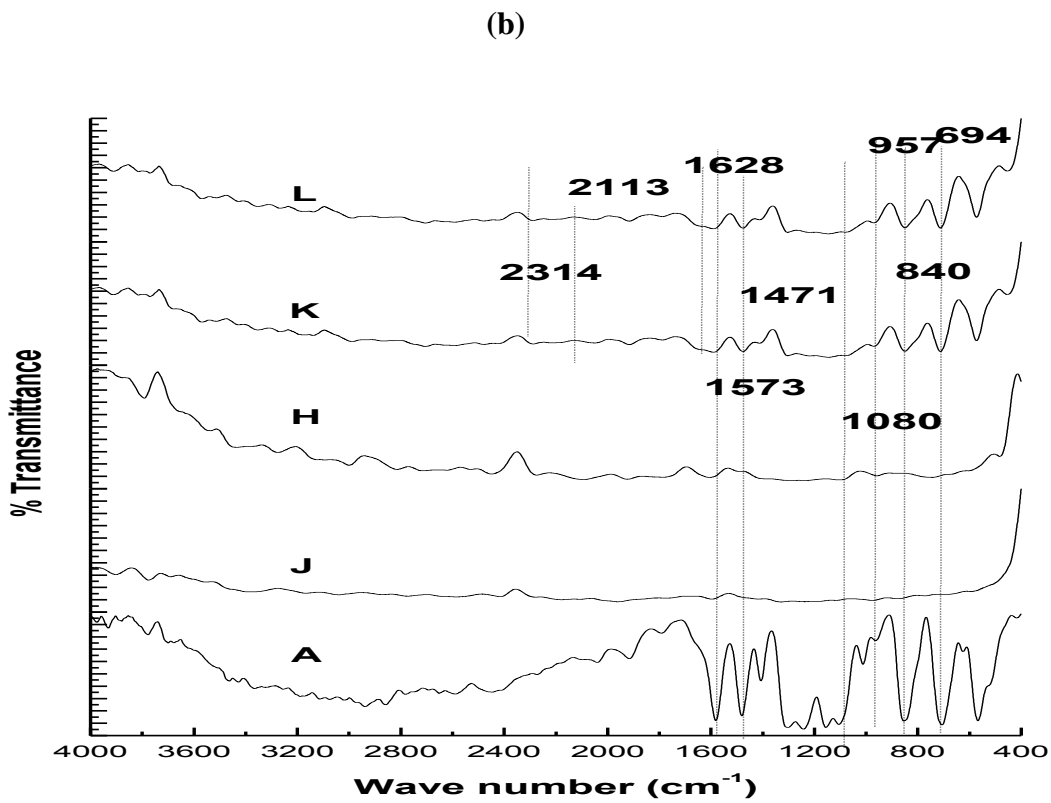
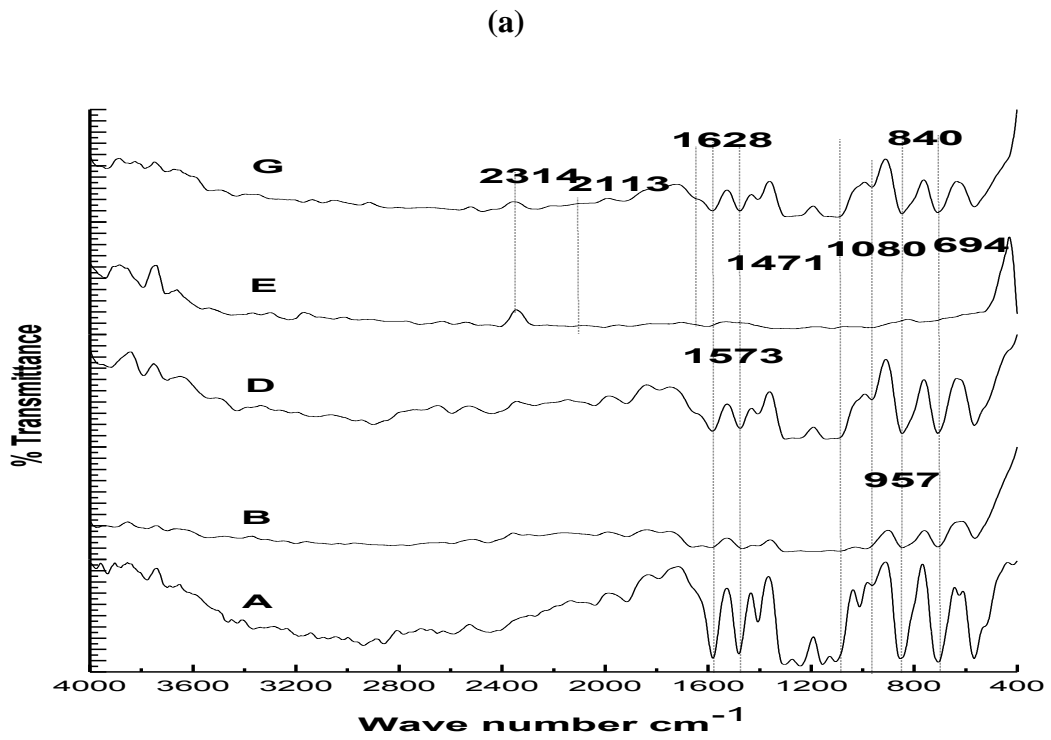
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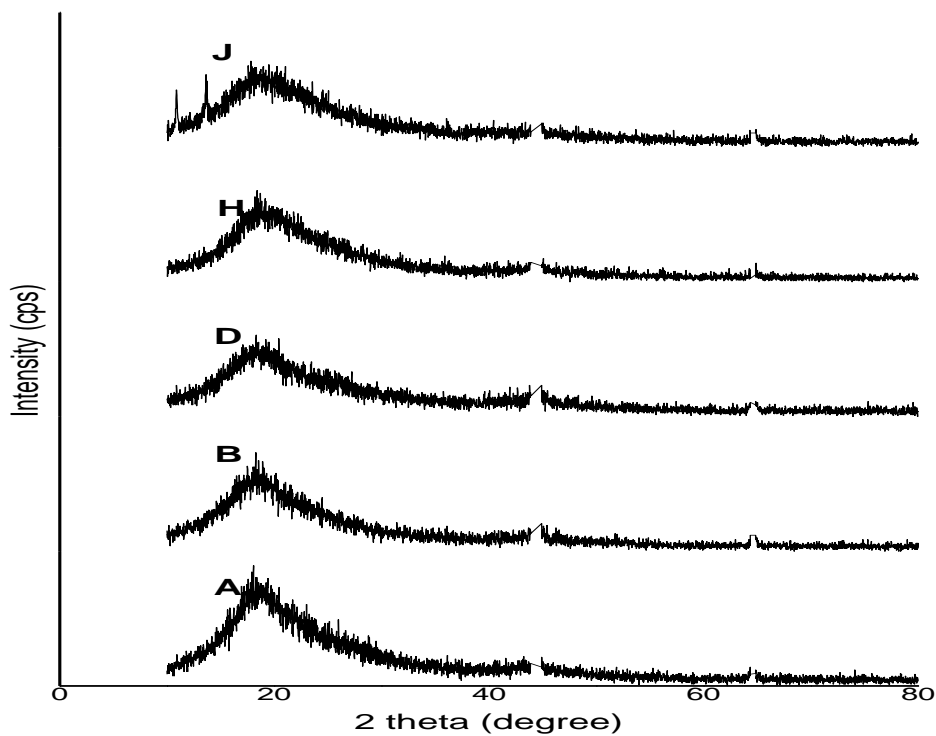
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**Table 1: Membrane Compositions**

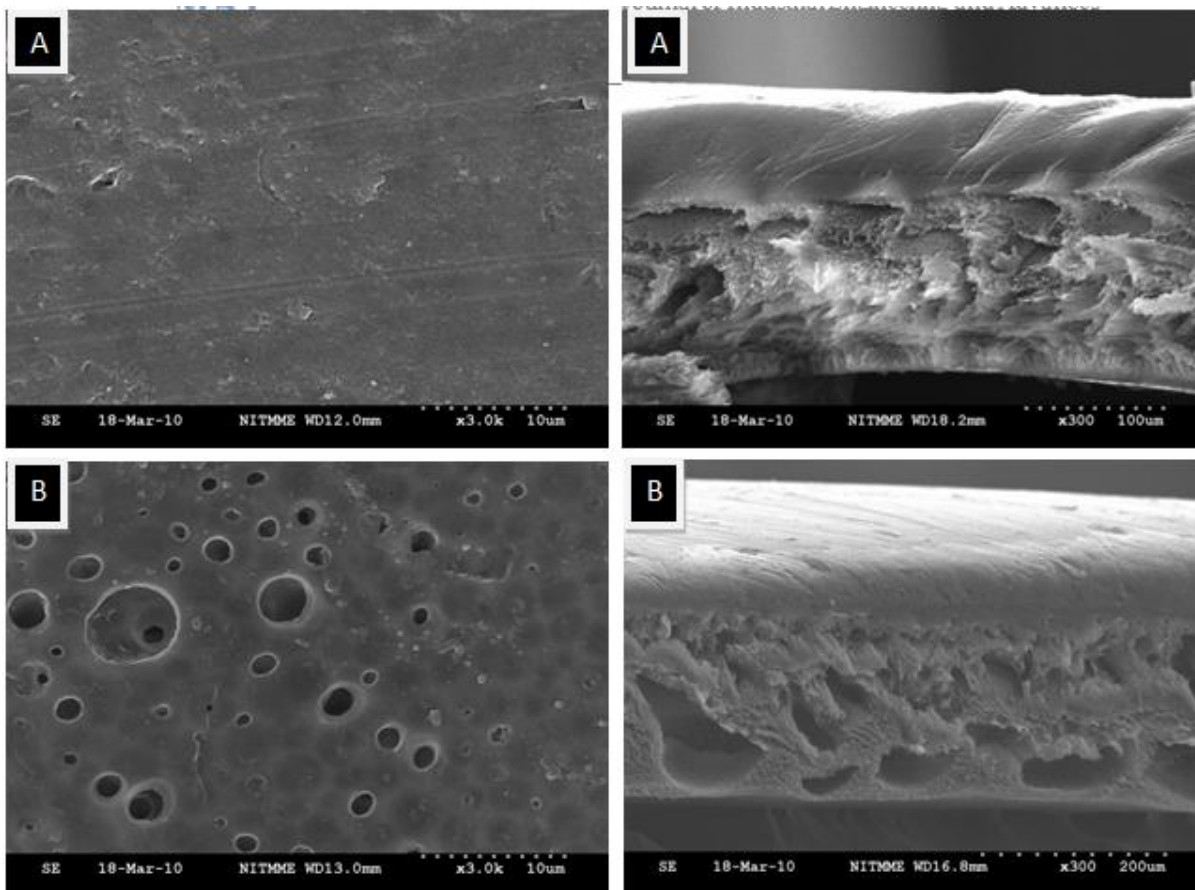
Membrane Type	Composition			
	Polymer (wt. %)			
	PES (wt. %)	PEI(gm.)	TEOS/CAL-SIL (wt. %)	DMF (wt. %)
A	17.5	0	0	82.5
B	17.5	0	5	77.5
C	17.5	0	7.5	75
D	17.5	0	10	72.5
E	17.5	0.375	5	77.5
F	17.5	0.65	7.5	75
G	17.5	1	10	72.5
H	17.5	0	10	60
I	17.5	0	15	65
J	17.5	0	20	60
K	17.5	0.5	15	65
L	17.5	0.75	20	60



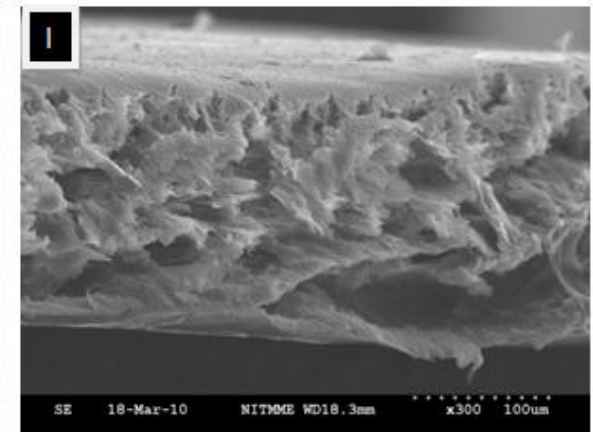
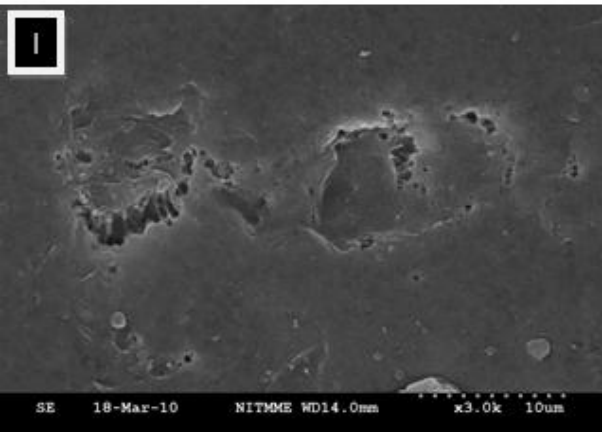
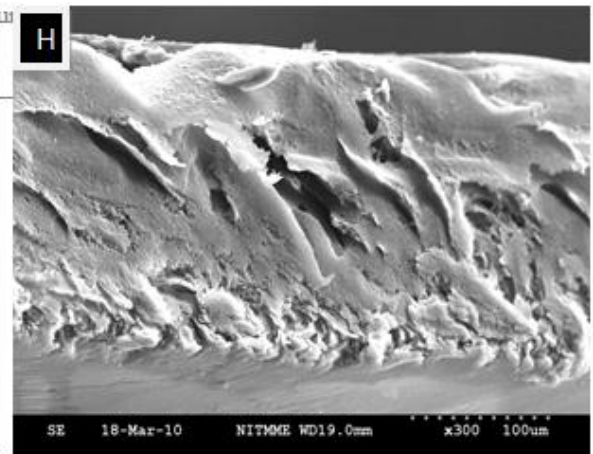
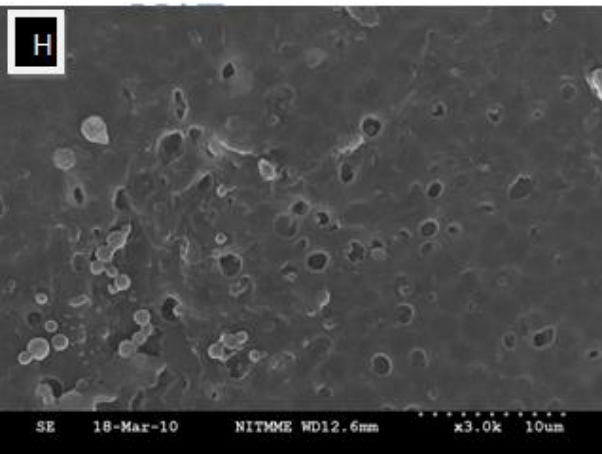
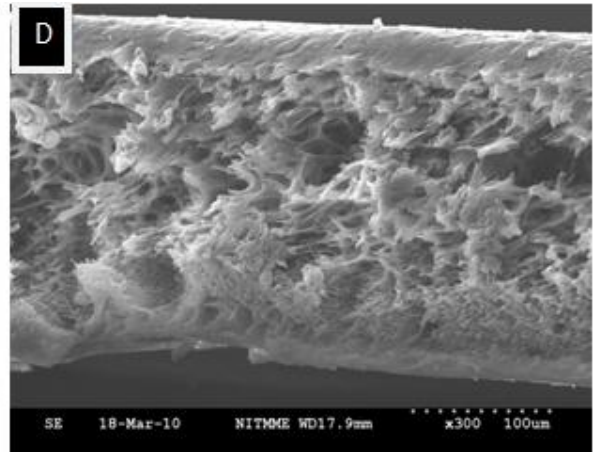
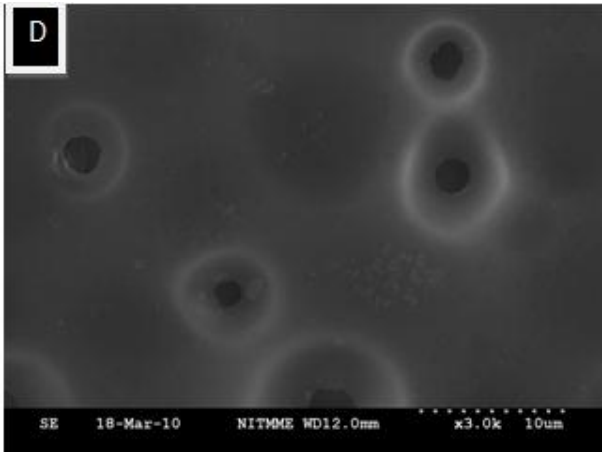
*Fig. 1. FTIR spectra of pure and composite membranes*

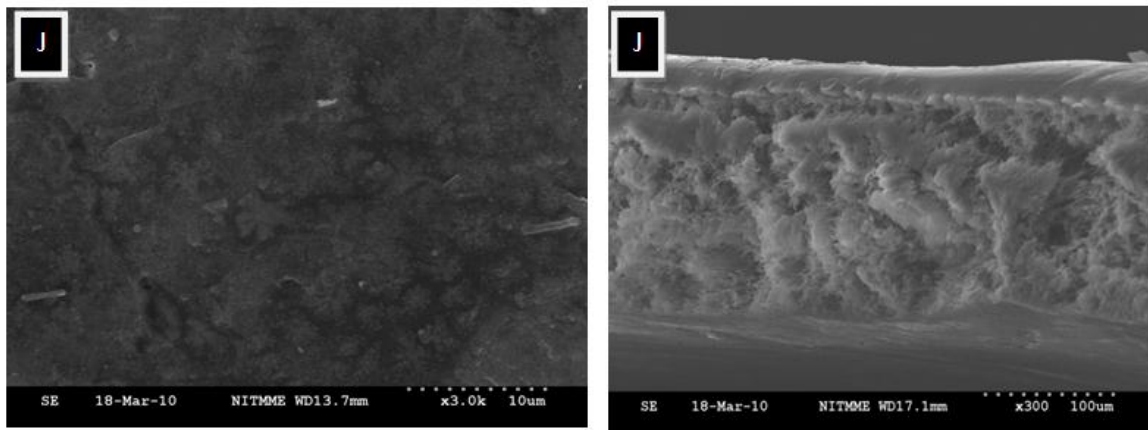


*Fig.2. X-ray diffraction patterns of PES and PES/PEI-TEOS/CAL-SIL composite membrane.*









*Fig.3. Membrane Morphology and cross sections*