CO$_2$ SELECTIVE MEMBRANES BASED ON EPOXY SILANE

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The sequestration of CO$_2$ is currently an important task for the modernization of power plants and refineries. For this purpose membrane technology can be a helpful tool. There is an increasing motivation for improving the selectivity of membranes for CO$_2$ separation from the other gases. Composite membranes based on 3-glycidoxypropyl trimethoxysilane (GPTMS) and different diamines containing polyether segments were synthesized by sol-gel processes. The composite membranes were characterized by single and mixed gas permeation, scanning electron microscopy and atomic force microscopy. CO$_2$/N$_2$ selectivity values up to 75 and CO$_2$/CH$_4$ selectivity values up to 20 were measured.

INTRODUCTION

Atmospheric concentration of several greenhouse gases (CO$_2$, CH$_4$, nitrous oxide) have increased by about 2 percent collectively since the industrial revolution began in the middle 19th century. In particular, anthropogenic CO$_2$ emissions have increased dramatically since the beginning of the industrial age, due largely to the burning of fossil fuels, such as coal or natural gas for the production of electricity and petroleum or diesel for transportation. Increasing concentrations of greenhouse gases are likely to accelerate the rate of climate change. Unless significant controls are implemented, a continued rise in the atmospheric concentration of CO$_2$ is projected in the foreseeable future, due to increases in the demand for fossil fuels. Several options exist to abate CO$_2$ emissions from fossil fuel utilization, including increasing the effiency of fossil fuel combustion systems, or replacing fossil fuels with renewable energy sources. These alternatives are very attractive in controling CO$_2$ emmisions in the environment, but each has its limitation.

Membrane separation processes provide several advantages over other conventional separation techniques. First , the membrane process is a viable energy saving alternate for CO$_2$ separation, since it does not require any phase transformation. Second , the necessary process equipment is very simple with no moving parts, compact, relatively easy to operate and control and also easy to scale up.

Membranes constituted only from organic polymers and completely inorganic membranes are generally used in different membrane separation processes. Membranes can profit from advantages of both organic and inorganic segments. Organic components contribute to the formation of defect free inorganic membranes and make it less brittle. On the other side organic membranes can have their chemical and temperature stability improved by an inorganic phase. The posibility of combining properties of organic and inorganic materials started to be explored some years ago.

The incorporation of inorganic materials to improve mechanical properties and thermal stability of polymeric (organic) materials is a very common procedure. Mechanical properties, however, are not always the main goal and the relatively large particles of these fillers may also interfere with other properties such as opacity, conductivity and permeability of different compounds across the final material. In this context, the preparation of hybrid organic-inorganic materials using the sol

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gel processes has been a subject of growing interest. Using the sol-gel process it is possible to grow the inorganic phase into an organic polymer matrix, with a very fine dispersion of the inorganic phase even at the molecular level[1-4]. There are several methods of hybrid preparation. One of the most simple one is to grow an inorganic network in a solution already containing the organic polymer or to prepare new polymers with covalent bonds between organic and inorganic segments. The precursor can be then submitted to hydrolysis and condensation in the presence of water and acid catalyst. The inorganic content of the polymer can be in some preparation increased by adding tetraethoxysilane (TEOS) to the reaction medium[5-7].

EXPERIMENTAL

1. Materials

3-glycidoxypropyltrimethoxysilane (GPTMS) was purchased from Gelest and used without further purification. The diamines poly(propylene glycol)-block-poly(ethylene glycol)-block- poly(propylene glycol)bis (2-aminopropyl ether) PAPE (MW=600g/mol and 2000g/mol),TEOS and poly(ethylene glycol) (PEG) were supplied by Aldrich and used as received. Tetrahydrofuran (THF) was purchased from Merk and used as received.

2. Preparation of composite membranes

2.1. GPTMS-PAPE membrane

The amine and epoxy were mixed for 24 hours at room temperature in THF. The solution was cast on asymmetric porous supports of polyacrylonitrile.

2.2. GPTMS-PAPE-PEG membrane

The amine, epoxy and poly(ethyleneglycol) were mixed 24 hours at room temperature in THF. The solution was cast on asymmetric porous supports of polyacrylonitrile.

2.3. GPTMS-PAPE silica membrane prepared by sol-gel processes

The amine and epoxy were mixed for 24 hours at room temperature in THF and then TEOS and HCl 0,15 M were added in stoichiometric amounts and mixed for 24 hours more at ambient temperature, followed by 2 hours at 80^0C. The solution was cast on asymmetric porous supports of polyacrylonitrile. For all types of membranes the support was prepared at GKSS-Research Center. The supports were previously coated with a 0,3% PEBAX 4011 solution in butanol. This layer of PEBAX had only the purpose of partially closing the pores of PAN support, avoiding that the organic-inorganic solution flows into the pores. The membranes were dried for 2 h, and further was cast another solution 1% PDMS in isooctane. The membranes prepared were further dried in a vacuum oven at 60^0C for 24 h. Membranes with thickness of 70-100µm were obtained.

3. Gas permeability and selectivity

The gas permeability measurments of composite membranes were carried out with a commercially available test cell using pure gases. The basic principle is a simple pressure measurement which is independent in type of gas. The whole measurement is automatically controlled by a computer including the filling, refilling and evacuation processes. The dependence of permeability from temperature and swelling could be measured in one step. One important design feature is the quality control of each measurement by an automatically registration of the measuring steps by means of a data report. A schematic representation of the system used is illustrated in Fig 1. By changing the headparts the membrane area can be varied from 2cm² until 40 cm². By variation of the permeate volume it is possible to measure permeance from 10^{-6} up to 100 Nm³/m².h.bar. In our case the effective membrane area was 34,2 cm². Single gas permeation data were determined at 30^0C, 300 mbar feed pressure up to 2 bar.
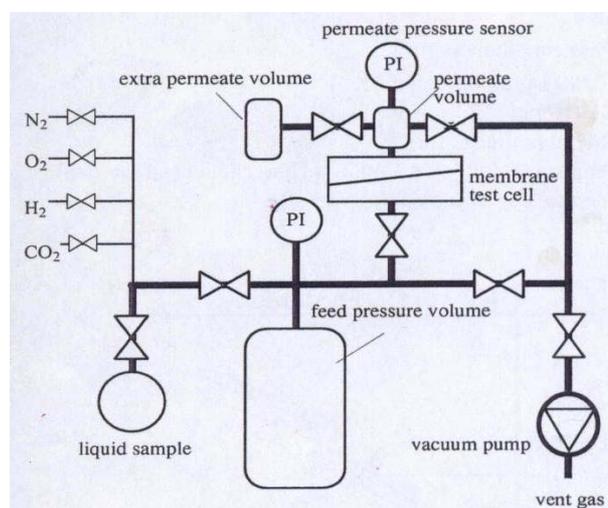

Fig.1 – Principle of a pressure increase measurement system.

Mixed gas permeation properties of membranes were determined with a feed containing 25% vol. CO_2 and 75% N_2 ; 40% vol CO_2 and 60 % vol CH_4 at 20^0C using the apparatus schematically shown in Fig.2.Before each measurement, the membrane was kept dry under vacuum. The mixed gas system, with combination of permeation cell and GC, allows straighforward determination of gas permeabilities. The GC used was a MTI Refinery Gas Analyzer. Before permeation testing GC was calibrated by one set of Messer gas mixture of CO_2 and N_2 or CO_2 and CH_4 with known composition to obtain the GC peak area as a function of gas mole fraction.

4. Morphological investigation

4.1. Scanning electron microscopy

The samples were fractured in liquid nitrogen and coated with Au/Pd by sputtering and observed in a field emission scanning electron microscope Leo Gemini 1550 VP.

4.2 Atomic force microscopy

The structure of the membrane surfaces was observed using the tapping mode of the VEECO NANOSCOPE 4 Atomic Force Microscope. Measurements were carried out with a Phosphorus (n) doped Si probes (VEECO) having natural oscillating frequency of 300 kHz.
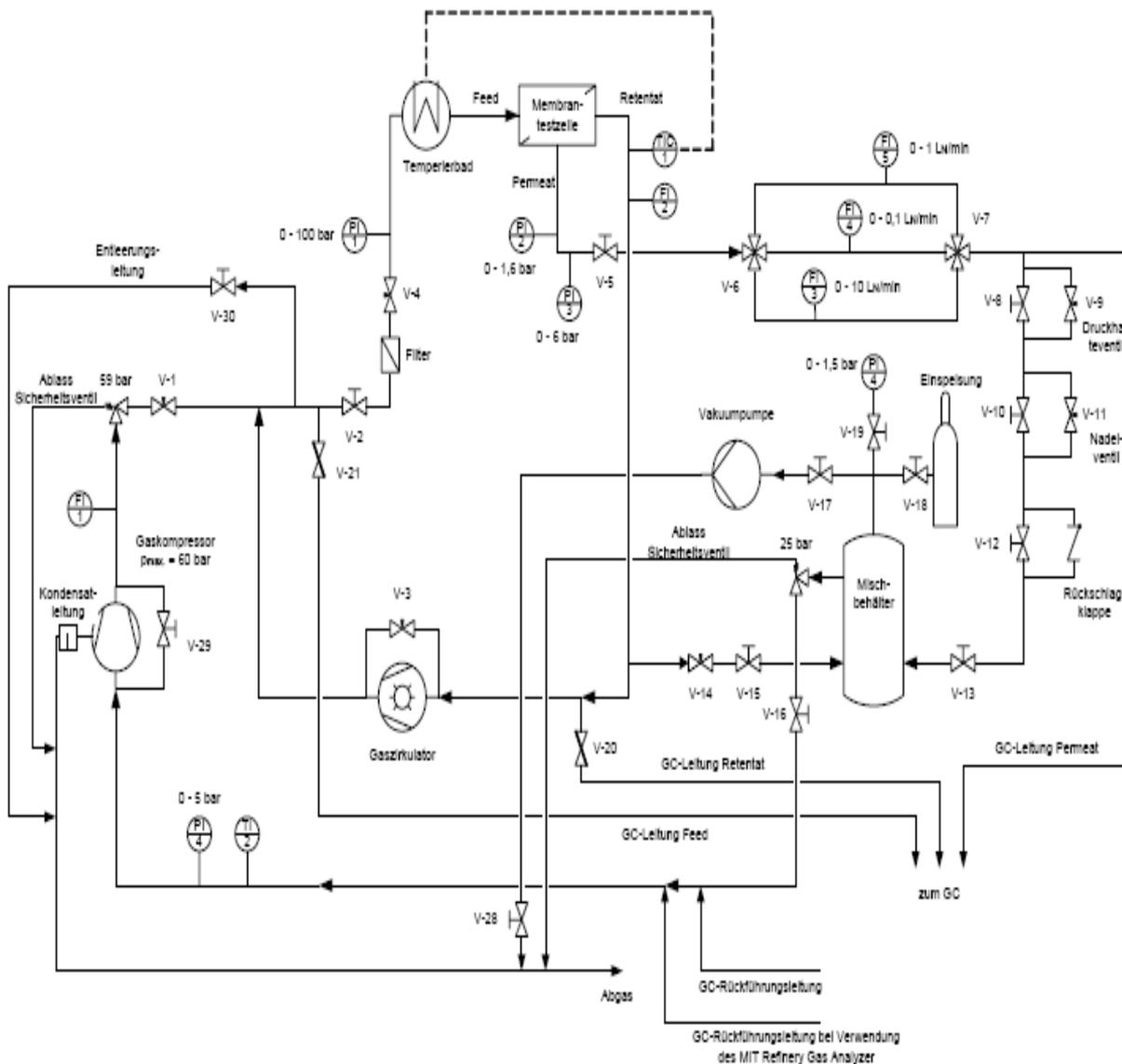
Fig. 2 – Scheme of mixture gas permeation apparatus.

RESULTS AND DISCUSSION

1. Permeation transport of simple gas

The membranes were prepared with PAPE having different molecular weights. The results presented in Fig 3 suggest that the molecular weight may have a significant influence on the gas permeation properties. To collaborate to this hypothesis, there is the work of Sforca et al[1]. which reported the influence of PAPE molecular weight on its gas permeation properties. It was observed that CO_2/ N_2 selectivity increases with increasing molecular weight. When comparing membranes prepared with PAPE 600 and those prepared with PAPE 2000, the latter are more crystalline and probably because of this higher crystallinity, they are less permeable to H_2, N_2, O_2 and CH_4. The higher polyether content make the membrane much more selective to CO_2 in the mixtures CO_2/N_2 or CO_2/CH_4.

It was also observed that CO_2/ N_2 selectivity increases with increasing of GPTMS content for both types of membranes (membranes prepared with PAPE 600 and membranes prepared with PAPE 2000), as shown in Fig 4 and Fig 5. It could be seen that with increasing of GPTMS content the permeability decreased.

The unique property of polar ether oxygens for CO_2 separation has attracted much interest. Generally, polar groups in a polymer matrix improve polymer chain packing efficiency and

promote chain crystallization. This is the case of PEG. We can see from the Fig 6 that the selectivity for CO_2/N_2 shows an increase when the membranes are prepared using PEG. Factors that seem to have an effect on the permeabilities are PEG segment lenght, the amount of rigid segment that is dissolved and the morphology of the rigid segments[8]. CO_2/N_2 selectivity values are quite good when compared to values reported in the literature for other polymeric materials [9].

The presence of polyether segments and amino groups in the organic-inorganic network made the membranes particularly permeable for CO_2[10-16]. Now taking in account the TEOS content in the membrane, TEOS may take part in the formation of the network by adding more Si-O-Si segments to it or may build an independent inorganic network which would be embedded in the PAPE/GPTMS network without necessarily being covalently bonded to it. TEOS seems to decrease the available free volume for diffusion in the organic-inorganic polymer matrix. The transport of CO_2 is not considerably changed with the addition of TEOS (Fig 7).
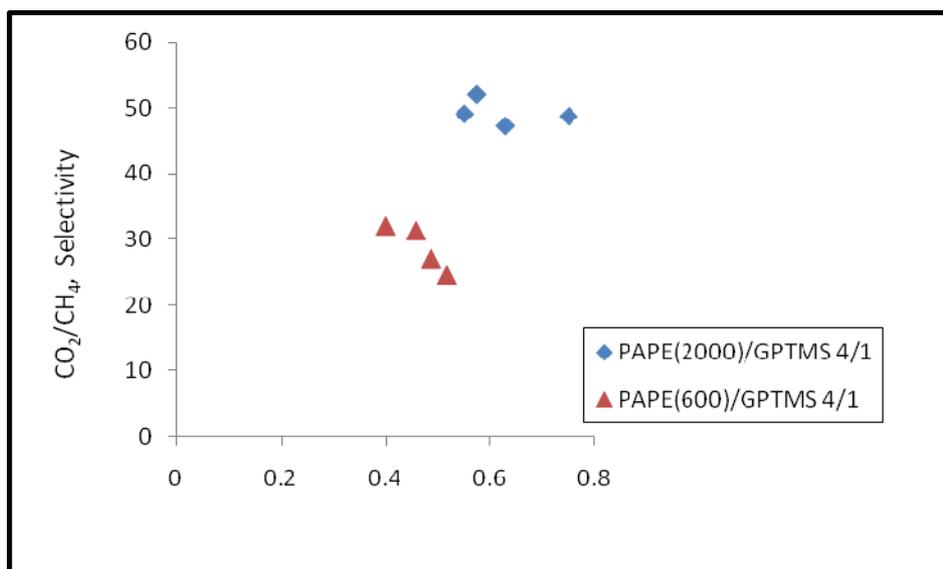

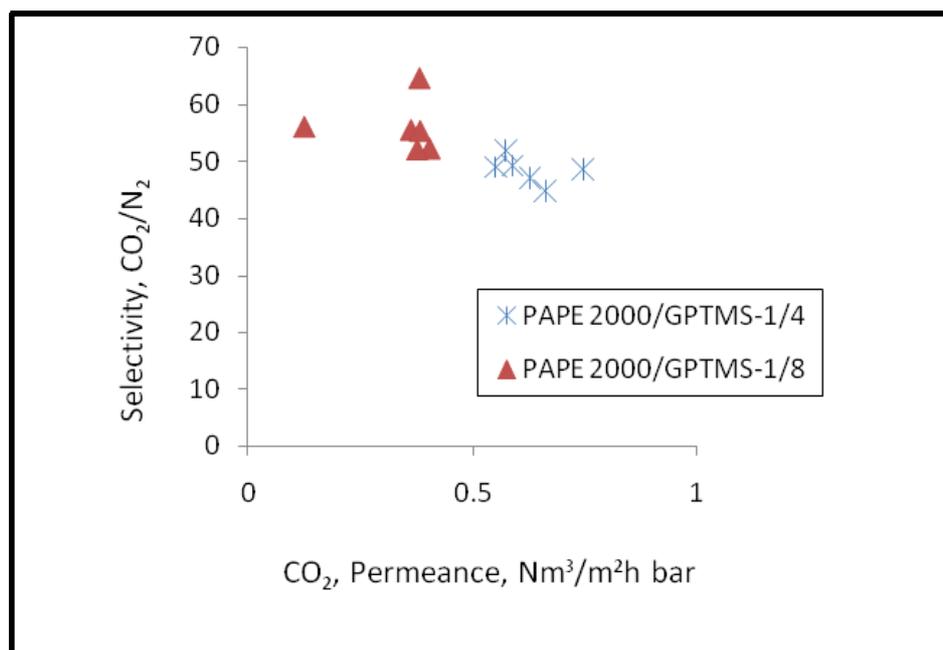Fig. 3 – Effect of molecular weight on selectivity.

Fig. 4 – Effect of GPTMS content on selectivity (membranes were prepared with PAPE 2000).
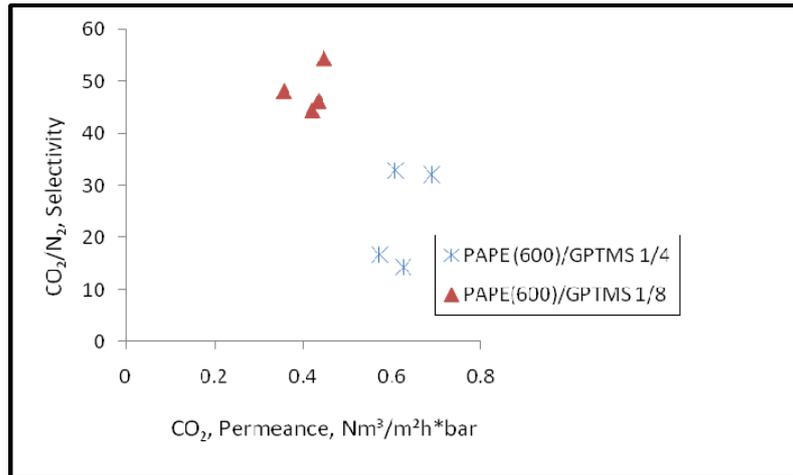
Fig. 5 – Effect of GPTMS content on selectivity (membranes were prepared with PAPE 600).
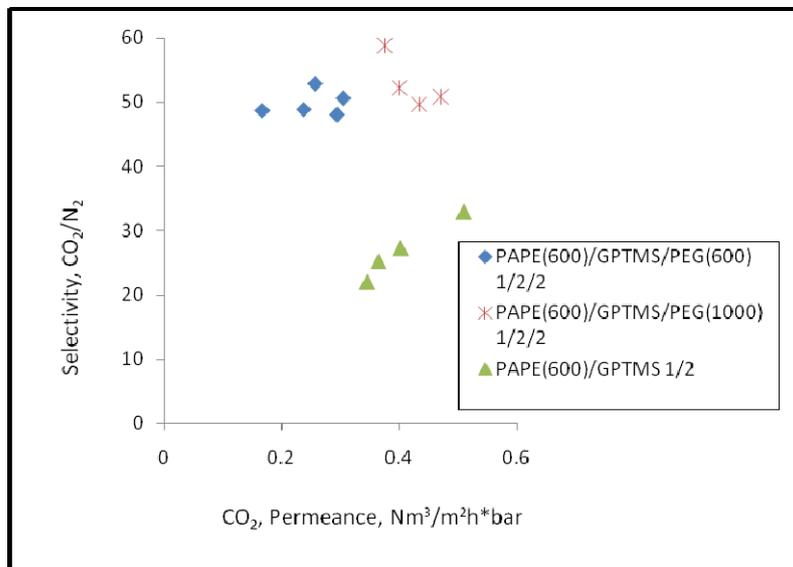

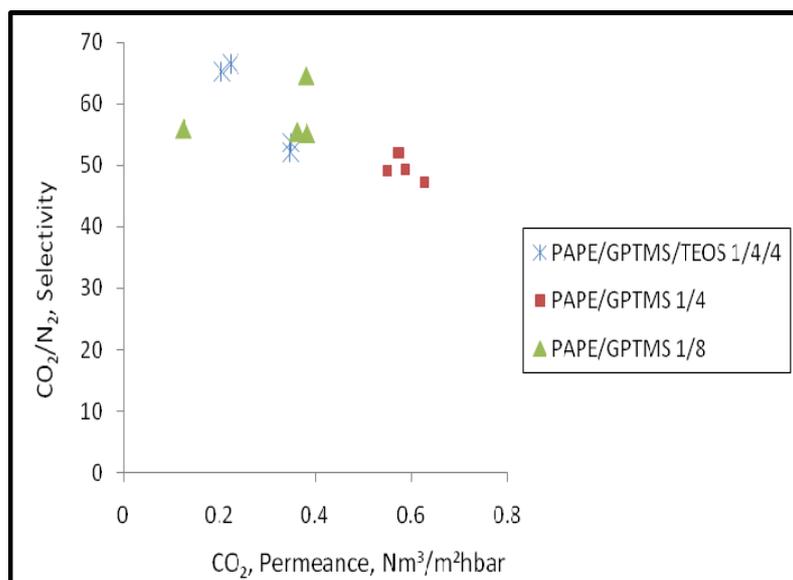
Fig. 6 – Effect of PEG content on selectivity.

Fig. 7 – Effect of composition on selectivity.

2. Permeation transport of mixed gas

The variation of the permeability between the pure gas and mixed gas has always been observed because the transport of a component in the mixture of gases is significantly affected by presence of other components.[17-19] This discrepancy is believed to arise from the effect of penetrants competition, gas phase non- ideality, plasticization phenomena and gas polarisation [17-19]. For these reasons, mixed gas permeation measurements were conducted and pure gas permeation tests for CO_2, N_2 and CH_4 were carried out for comparison. Table 1 and Table 2 summarised the performance of different membranes for both mixed gas and pure gas measurements. Measurements with mixed gas indeed showed a slight decrease of selectivity, but the values are still quite high compared to other available membranes as shown also in Fig 8.

However, surprisingly, the selectivity CO_2/N_2 obtained in the mixed gas tests for the samples prepared with PEG was greater than those of pure gas tests. It may arise from the fact that the PEG presence reduces chains mobility and the interstitial space among chains, which may have different effects on diffusivity.

3. Morphology

Fig 9 shows the AFM micrographs of PAPE/ GPTMS/ PEG membrane, PAPE/GPTMS/TEOS membrane, and GPTMS/TEOS membrane. It can be seen the lamellar structure for all types of membranes,

AFM images show that there is a difference in the morphology of the membranes. For the membranes prepared with TEOS it was observed that silica particles were unhomogeneously dispersed in PAPE/GPTMS/TEOS membrane.

CONCLUSIONS

The organic-inorganic hibrids based on GPTMS and PAPE were prepared using the sol gel process. The membranes were specially interesting for gas separation. Due to the presence of polyether segments and amino groups the transport of CO_2 was prevailed. The hybrid membranes exhibited higher selectivities than those of GPTMS/ PAPE. The selectivity also increased when PEG was used for membrane preparation. CO_2/N_2 selectivity values up to 75 and CO_2/CH_4 selectivity values up to 20 were measured. Measurements with mixed gas feed is very important since CO_2 might swell the membrane and affect selectivity. Measurements with mixed gas indeed showed a slight decrease of selectivity, but the values are still quite high compared to the other available membranes.

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Table 1

A comparison of transport performance for membranes between mixed gas and pure gas measurements
(mixed gas 40%CO_2 60%CH_4)

Membrane	Mixed gas(40%CO_2 60%CH_4)		Pure gas	
	Pressure(bar)	αCO_2/CH_4	Pressure(bar)	αCO_2/CH_4
GPTMS/PAPE(2000)/PEG(1000)2/1/2	8	15,33	0,3-2	15,42
GPTMS/PAPE(2000)/PEG(1000)2/1/2	8	18,035	0,3-2	19,29
GPTMS/PAPE(600)/PEG(1000)2/1/2	8	16	0,3-2	18,05
GPTMS/PAPE(600)/PEG(1000)2/1/2	8	13,15	0,3-2	16,89

Table 2

A comparison of transport performance for membranes between mixed gas and pure gas measurments (mixed gas 25%CO_2 75%N_2)

Membrane	Mixed gas(25%CO_2 75%N_2)		Pure gas	
	Pressure(bar)	αCO_2/N_2	Pressure(bar)	αCO_2/N_2
GPTMS/PAPE(2000) 4/1	8	38,026	0,3-2	52,06
GPTMS/PAPE(2000)/TEOS 4/1/4	8	33,11	0,3-2	66,51
GPTMS/PAPE(600)/PEG(600)2/1/2	8	59,46	0,3-2	52,81
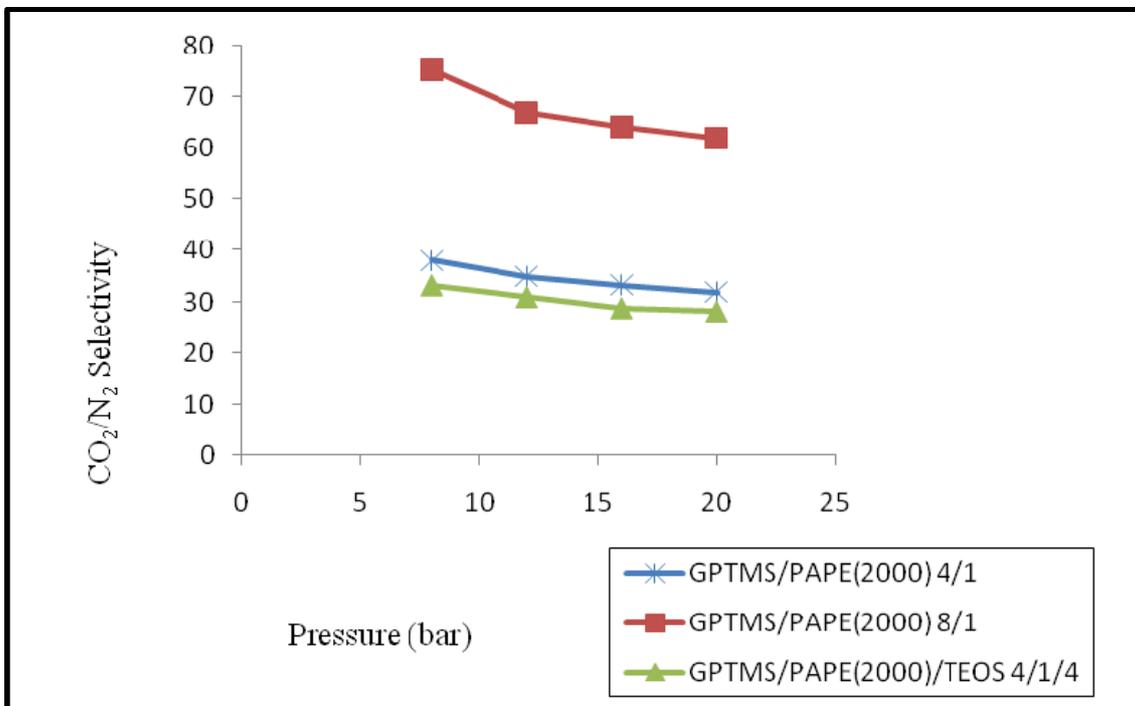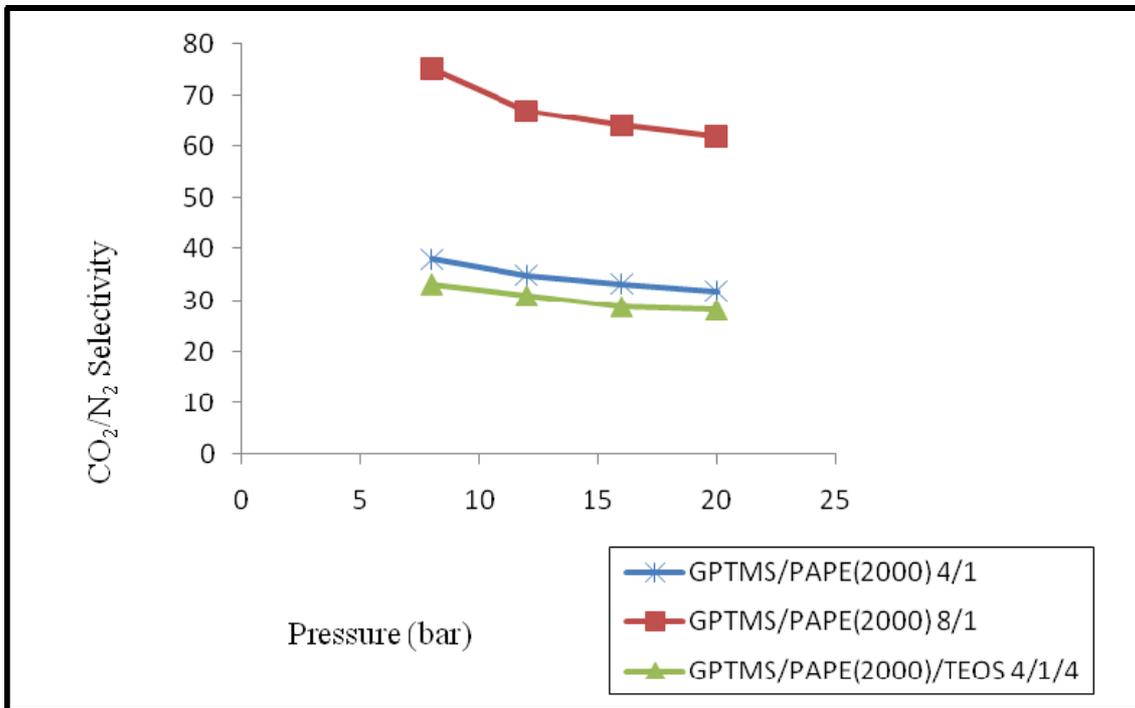
Fig. 8 – Measurements with mixed feed gas (40/60CO_2/CH_4 and 25/75 CO_2/N_2).

a)PAPE 600/GPTMS/ PEG 1000 1/2/2   b) PAPE(2000)/GPTMS/ TEOS 1/4/8

c)PAPE(2000)/ GPTMS 1/4   d) PAPE(2000)/GPTMS/TEOS 1/4/4
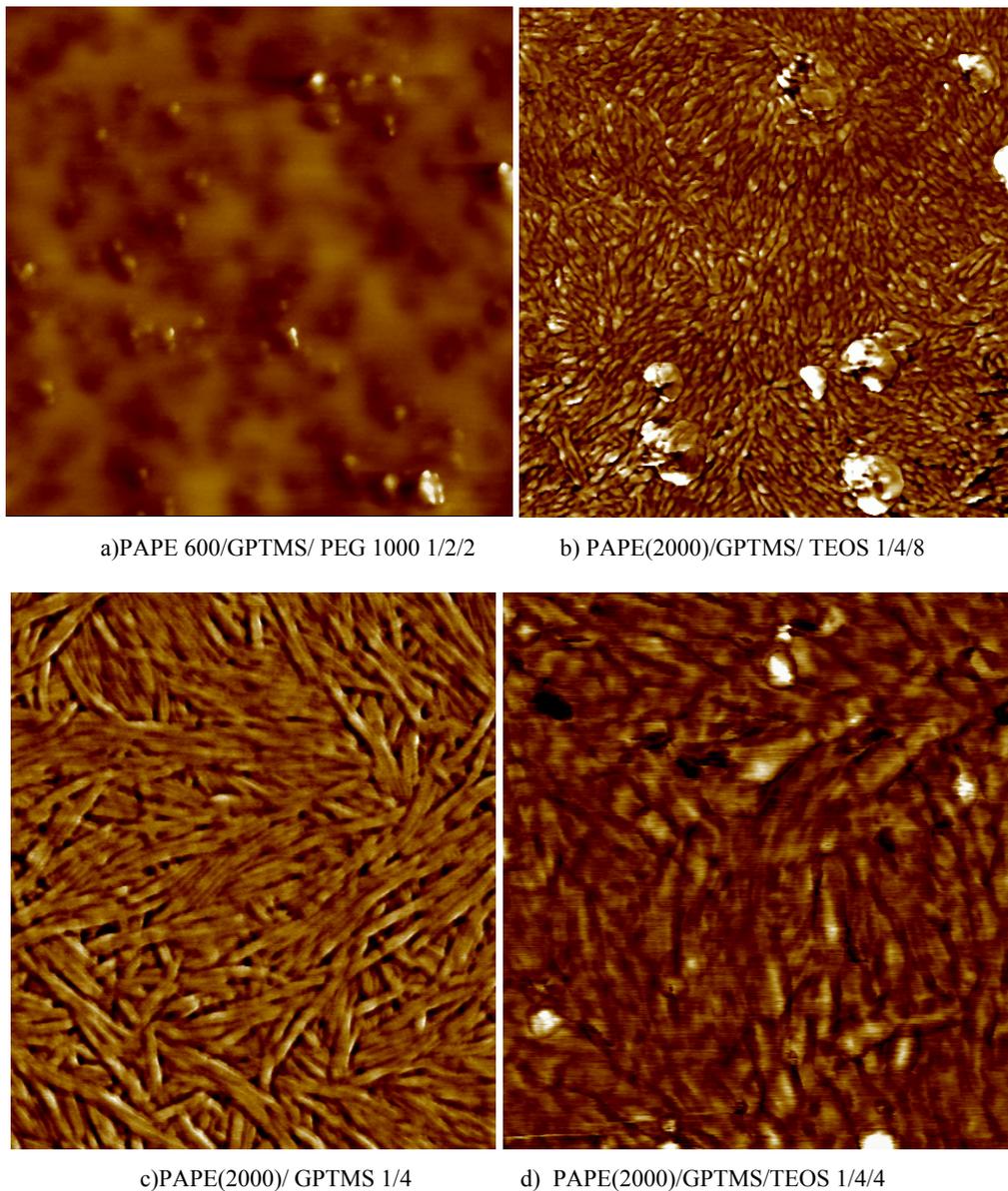
Fig. 9 – AFM micrographs.

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