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COMPOSITE MEMBRANES WITH CROSS-LINKED MATRIMID SELECTIVE LAYER FOR GAS SEPARATION

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Abstract

In the present work, composite membranes were developed for separation of hydrogen from its mixtures with other gases. The composite membranes were characterized by single gas permeation and scanning electron microscopy. Gas transport properties have been determined for four gases (H_2, CH_4, N_2, CO_2). The influence of cross-linking on transport was measured. H_2/CH_4 selectivity values up to 115 were obtained. The resulting membranes have a selectivity of H_2/CH_4 close to intrinsic selectivity of Matrimid 5218.

Keywords: composite membranes, cross-linking, gas separation, Jeffamine T403, Matrimid

1. Introduction

Due to the fear of the depletion of resources and the growth of environmental awareness more and more researches have set out for seeking alternative energy sources in recent days. Among the alternative energy carriers, hydrogen is preferred because it burns to waste-free water vapour when utilized („clean fuel").

One of the larger applications of composite hydrogen permeable membranes is hydrogen recovery in refineries. A typical application is the recovery of hydrogen from waste gas streams that would otherwise be used as a fuel (Baker, 2002).

Over the past 20 years, there has been an increasing interest for polyimides as membrane materials for gas separation purposes.

Polyimides have proven useful for the formation of gas separation membranes because of their attractive combination properties: high gas permeability as well as high intrinsic permselectivity in comparison to polycarbonate, polysulfone and other materials (Hayes, 1988; Koros et al., 1988; Ohya et al., 1996; Pinnau and Freeman, 2000, Shao et al., 2004).

The gas transport performance of polyimides can be improved by cross-linking modification. Cross-linking of a polymer matrix may influence physical properties and the ability of the material to transport and separate gases. Because cross-linking restricts the mobility of polymer chains by the formation of covalent bonds, it stabilizes the material against thermal and chemical degradations as well as impacting gas transport.

The restriction of the polymer chain mobility can impede gas transport since the diffusion of gas molecules through a polymer involves the cooperative motion of chain segments (Dudley et al., 2001; Liu et al., 2001; Sullivan, 2005; Tin, 2003).

This work presents the development and optimization of Matrimid composite membranes. It's focus is to investigate the influence of the polymer concentration, the type of solvent and non-solvent used, the cross-linking agent and its concentration, the influence of the support, and the speed used for coating. The prepared membranes were evaluated for gas separation.

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2. Experimental

2.1 Materials

The Matrimid 5218 (polyimide of 3, 3', 4, 4'-benzophenonetetracarboxylic dianhidride and diamino-phenylindane) was purchased from Ciba Specialty Chemicals and Huntsman in powder form (http://www.huntsman.com). Matrimid 5218 has an attractive combination of gas permeability and selectivity properties accompanied by excellent mechanical properties, high glass transition temperature (Bateman and Gordon, 1974). It has the structure from Fig.1.

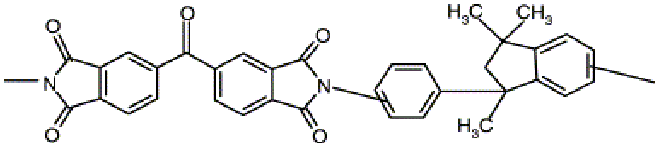
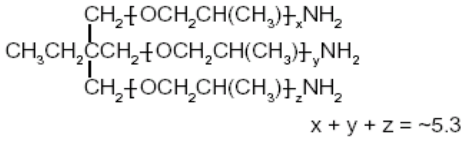


Fig.1. Chemical structure of Matrimid



$$CH_3CH_2\overset{\displaystyle CH_2\left[OCH_2CH(CH_3)\right]_xNH_2}{\underset{\displaystyle CH_2\left[OCH_2CH(CH_3)\right]_zNH_2}{C}}CH_2\left[OCH_2CH(CH_3)\right]_yNH_2$$

$x + y + z = \sim 5.3$

Fig.2. Chemical structure of Jeffamine

Buthylenediamine, chloroform, dichloromethane, toluene, cyclohexane were supplied by Aldrich, and used as received. Polyacrilonitrile (PAN), PAN+γbutirolactone(γBL) and poly(dimethilsiloxane),(PDMS) were used as a support material for composite membranes. The support was prepared at GKSS-Research Center.

2.2 Preparation of composite membrane

2.2.1 Matrimid membrane

A 0.5 (w/w) of polymer solution was prepared by dissolving Matrimid powder in solvent (chloroform, dichloromethane). The casting solution was filtered using a 20 μm metal mesh filter.

2.2.2 Matrimid cross-linked membrane

A solution of 5 % Matrimid, solvent and cross-linked agent was prepared and mixed for 24 hours at 24^0C. With this solution, solutions with different concentrations of Matrimid (0.25 %, 0.5%, 1%) were prepared. The casting solutions were filtered using a 20 μm metal mesh filter.

Membranes were prepared on PAN and PDMS support by hand or on PAN and PAN+γBL support in a pilot scale membrane casting machine. Further it was cast another solution 1% PDMS in isooctane.

The deposition of PDMS layer on the surface of Matrimid has a drastic effect on selectivity. PDMS blocks the defects of the selective layer. The gas flow through the PDMS blocked pores becomes then negligible compared to the quantity of gas penetrated through the total surface of the membrane and membrane's selectivity turns to be controlled by the properties of the selective layer material (Shishatskiy et al., 2006). For coating different speeds were used.

2.3 Gas permeability and selectivity

The membranes were tested for gas permeation using the semi-automatic apparatus based on the barometric method. The set up allows to program of the testing sequence up to 8 individual gases at a feed pressure up to 1.3 bar within the temperature range 20-80^0C. In the current study membranes were tested at 30°C in the range of feed pressures 0.3 – 2 bar using the measurement cell with the active membrane area of 34.2 cm^2. The selectivity (α) was obtained calculating the ratio between permeability values for different gases.

2.4. Scanning electron microscopy

The morphology of the prepared membranes was analyzed by Scanning Electron Microscopy (SEM). Samples were immersed in isopropanol and fractured in liquid nitrogen, coated with Au/Pd by sputtering and observed in a field emmision scanning electron microscope Leo Gemini1550 VP.

3. Result and discussion

The chemical mechanism of the cross-linking may be described as follows: the amino groups in buthylenediamine or Jeffamine react with imide groups of Matrimid to form amide groups, and thus the cross-linked is formed. The reaction and the final product structure should be that depicted in Figs. 3 and 4.

3.1 Permeation transport of simple gas

The results presented in Table 1 suggest that the crosslinking may have a significant influence on gas permeation properties.

Table 1. Gas transport properties for membranes prepared without and with cross-linking agent (Jeffamine)

Solution	***H_2 Permeance, m^3/m^2h*bar***	***α (H_2/CH_4)***
0.5% Matrimid în $CHCl_3$	0.1562	86.71
	0.1478	82.28
	0.164	83.13
	0.1686	81.78
2% Jeffamine to Matrimid, 0.5%$CHCl_3$	0.2781	88.74
	0.2842	82.00
	0.289	85.57
	0.247	92.65

The improvement of H_2/CH_4 selectivity was mainly resulted by the reduced chain mobility and increased the packing density of the polymer chains after cross-linking.

Table 2 show the permeance and selectivity values measured for membranes with butilenediamine and Jeffamine like cross-linking agent. For membranes preparation solutions of 1% Jeffamine to 1% Matrimid in CH_2Cl_2 and 0.1% $(CH_2)_4(NH_2)_2$ to 1% matrimid in CH_2Cl_2. were used. PAN dry support was used as support.

Consequently, Jeffamine will ensure a more advanced degree of cross-linking, which in turn will determine a more intense passing a smaller molecules, such as hydrogen, leading to a better selectivity of membranes. Therefore, Jeffamine was chosen as a cross-linking agent for further experiments. Some influence of the casting solvent on the permeation properties has been reported in the literature. As it can be seen in Fig. 5, the cast film of Matrimid from chloroform has higher permeability coefficients than the film cast from dichloromethane.

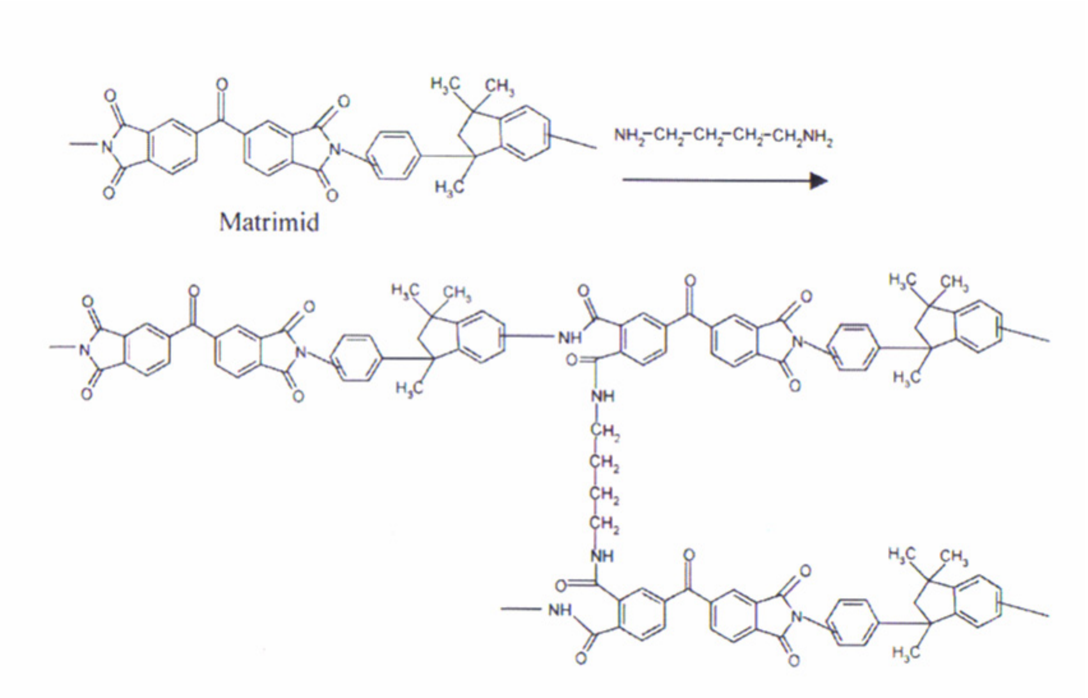


Fig.3. Mechanism of chemical cross-linking of Matrimid with buthylenediamine

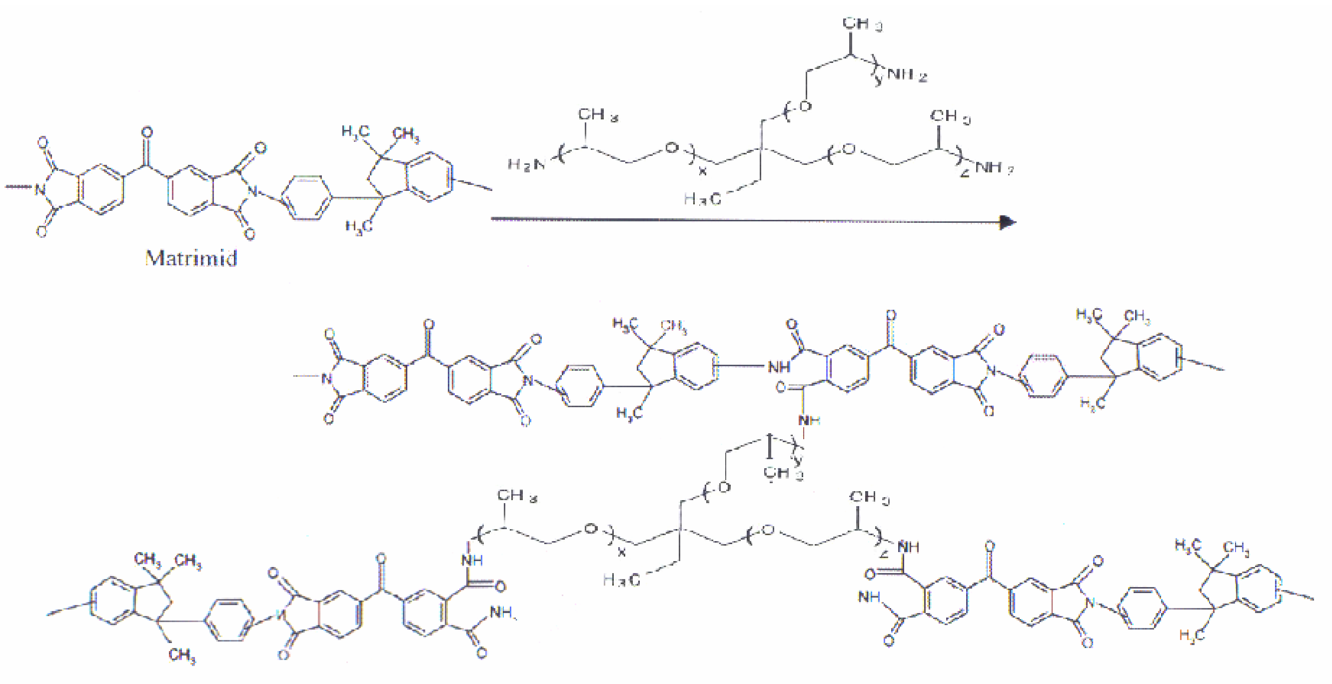


Fig. 4. Mechanism of chemical cross-linking of Matrimid with Jeffamine

This can be explained by the volatility of chloroform. The drying of the solution cast films is faster if chloroform is used instead of dichloromethane. It is possible that due to this fast drying process a large free volume arises in the dry film. It was also found that the permeability increases with increasing free volume.

Table 2. Permeance and selectivity of membranes prepared from Jeffamine (buthylenediamine)/Matrimid/ dichloromethane (manually prepared)

Sample	*H_2 Permeance, m^3/m^2h*bar*	*A (H_2/CH_4)*
with Jeffamine	0.0029	76.46
with Jeffamine	0.0593	74.25
with buthylenediamine	0.0590	45.59
with buthylenediamine	0.0454	57.20

It is well known that the flux is dependent on selective skin thickness. Therefore, to decrease the thickness it can be use a non-solvent for dry phase separation and asymmetric structure formation. As non-solvents, cyclohexane, buthanol, and toluene were tested.

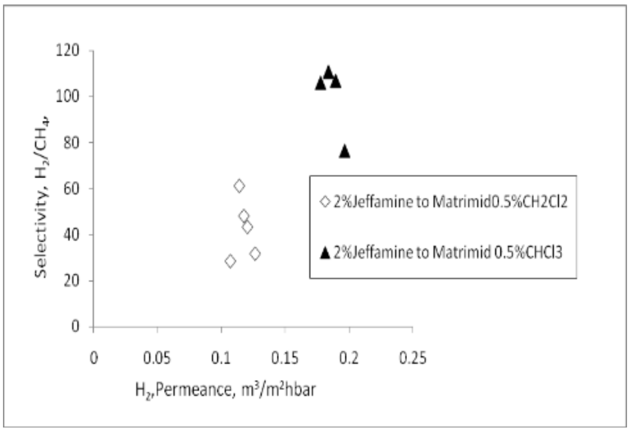


Fig. 5. Gas transport properties for membranes prepared with CH_2Cl_2 and for membranes prepared with $CHCl_3$

Knowing the position of the cloud point line in the phase diagram of Matrimid/$CHCl_3$/non-solvent, several casting solution were prepared with the Matrimid 5218 concentration 0.35 to 2% and concentration of non-solvent 0.2 to 10 % wt. For exemplification, Fig.6 presents the phase diagram of Matrimid/ $CHCl_3$/Bu-OH system. The obtained membranes exhibit reasonable permeances and selectivities (Table 3).

Different kinds of support were tested for membrane preparations. PAN and PDMS supports were tried out for the membranes manually prepared. For non-coated samples, the results are more or less comparable, but after the deposition of the PDMS layer it can be seen that for the membranes prepared on PAN support the selectivity increases about 4 times whereas for the membranes prepared on PDMS support the selectivity doesn't increase significantly (Table 4).

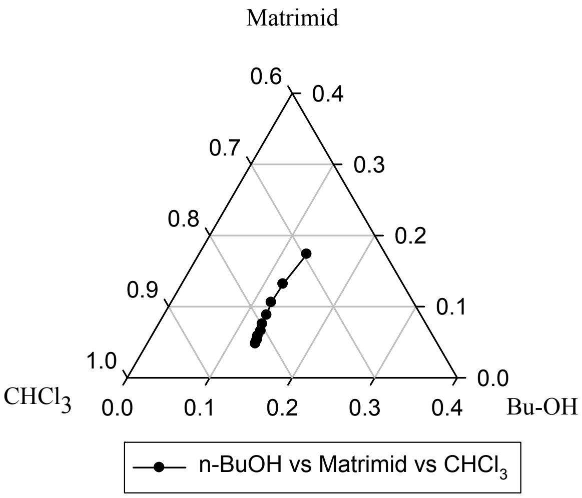


Fig. 6. Phase diagram of Matrimid/ $CHCl_3$/Bu-OH

Table 3. Gas transport properties of Matrimid membranes prepared with non-solvent

Membrane	*H_2 Permeance, m^3/m^2h*bar*	*α (H_2/CH_4)*
2% Jeffamine to 0.5% Matrimid in $CHCl_3$+0.5% Cyclohexane	0.1918	83.84
2% Jeffamine to 0.5% Matrimid in $CHCl_3$+0.5% Toluene	0.2036	73.00
2% Jeffamine to 0.5% Matrimid in $CHCl_3$+0.5% Buthanol	0.2531	82.11

For the membranes prepared on lab scale machine, PAN and PAN+γBL supports were tested. From Table 5, it can be observed that the selectivity is higher when PAN+γBL support is used, but the flux is higher in the case of PAN support.

Table 4. Gas transport properties for membranes manually prepared using different types of support

Membrane	*H_2 Permeance, m^3/m^2h*bar*	*α (H_2/CH_4)*
1% Jeffamine to 1% Matrimid in CH_2Cl_2 (PAN support, non-coated with PDMS)	0.0758	22.37
1% Jeffamine to 1% Matrimid in CH_2Cl_2(PDMS support, non-coated with PDMS)	0.1268	22.24
1% Jeffamine to 1% Matrimid in CH_2Cl_2 (PAN support, coated with PDMS)	0.0593	74.25
1% Jeffamine to 1% Matrimid in CH_2Cl_2 (PDMS support, coated with PDMS)	0.1130	30.11

In order to see if the membranes are reproducible, the same samples were tested at different intervals: after two days, after one week and after two months. The obtained membranes using

PAN and γBL dry support exhibit very interesting results in comparison to membranes prepared on PAN and γBL wet support.

Table 5. Gas transport properties for membranes prepared in a pilot scale membrane casting machine using different types of support

Membrane	*H_2 Permeance, m^3/m^2h*bar*	*α (H_2/CH_4)*
2% Jeffamine to 0.5% Matrimid in $CHCl_3$ (PAN support, coated with PDMS)	0.1404	90.94
	0.1854	92.19
2% Jeffamine to 0.5% Matrimid in $CHCl_3$ (PAN+γBL support, coated with PDMS)	0.0723	112.32
	0.0727	109.57

It can be seen from the Fig. 7 that the selectivity of membranes prepared on wet support is decreasing and the selectivity of membranes prepared on dry support is increasing unexpectedly (Fig. 8).

This could be explained because of the different structure of membranes prepared on wet support in comparison to the membranes prepared on dry support as can be seen from the SEM photomicrographs.

3.2 Morphology

Fig. 9 shows the SEM photomicrographs of cross-sections of Matrimid membranes prepared with different solutions and different supports. The morphology investigation of membranes by electron microscopy demonstrates a well developed open porosity. By using wet support for membrane preparation (Fig. 9c, 9d) it can be observed that a microcrystalline structure is formed.

By using dichloromethane as a solvent, a microcrystalline structure is formed in both cases: for wet and also for dry support (Fig. 9b, 9d). Utilizing a dry support leads to a structure with more closed pores as compared to wet support. These different structures obviously explain the higher selectivity noted when utilizing dry support.

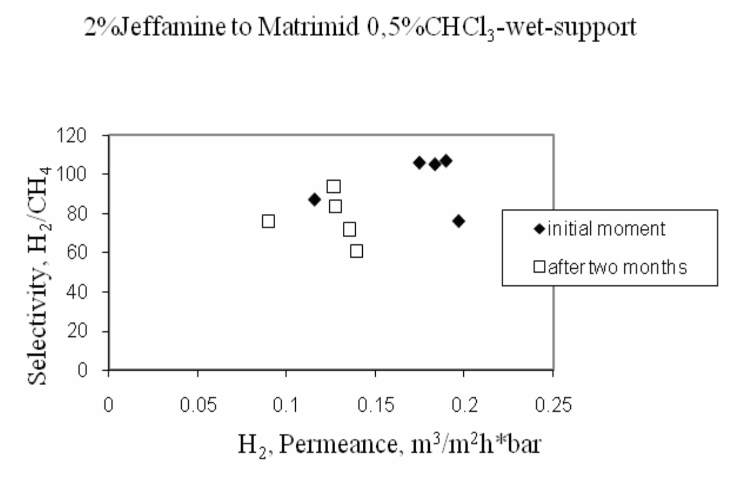


Fig 7. Gas transport properties for membranes prepared on wet support measured after two months

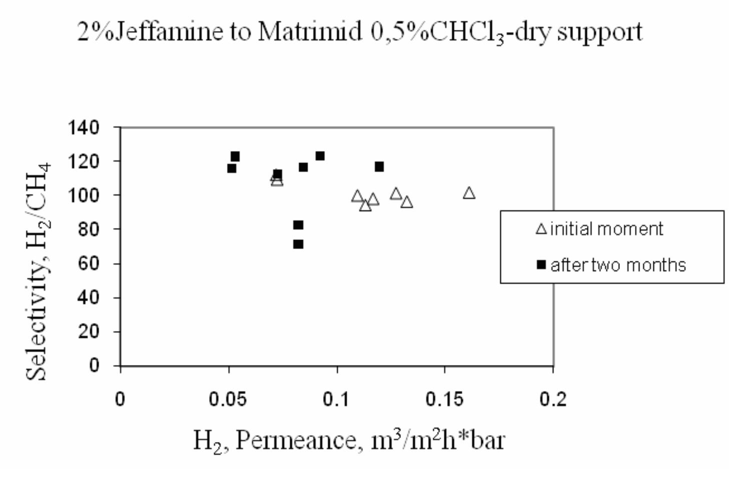
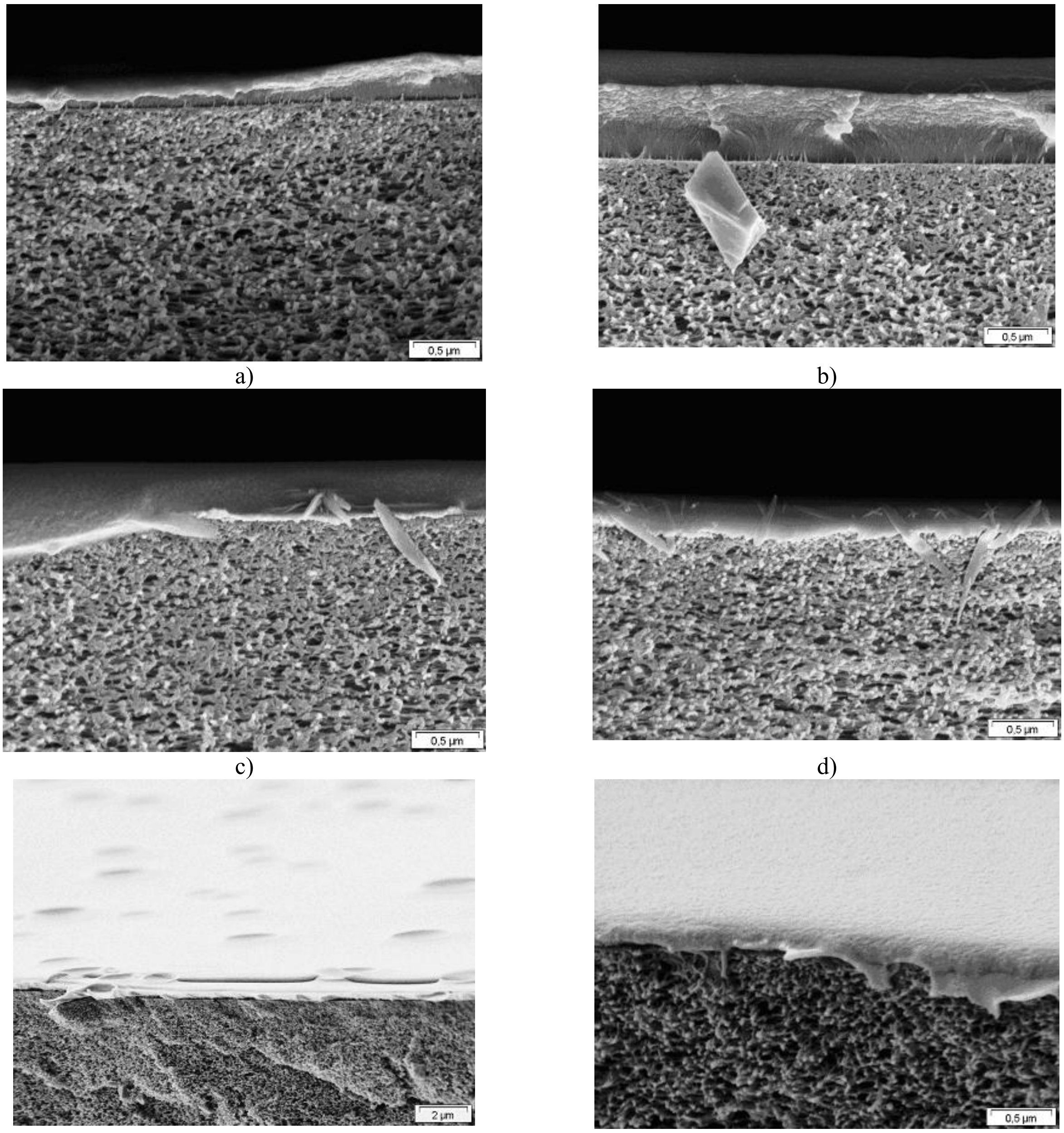


Fig. 8. Gas transport properties for membranes prepared on dry support measured after two months



a) b) c) d) e) f)

Fig. 9. SEM micrographs of cross-sections of: a) 2% Jeffamine to Matrimid 0.5% in $CHCl_3$(PAN support, dry); b) 2% Jeffamine to Matrimid 0.5% in CH_2Cl_2(PAN support, dry); c) 2% Jeffamine to Matrimid 0.5% in $CHCl_3$(PAN support, wet); d) Jeffamine to Matrimid 0.5% in CH_2Cl_2(PAN support, wet); e) 0.5% Matrimid in $CHCl_3$(PAN support, dry); f) 2% Jeffamine to Matrimid 0.5% in$CHCl_3$+0.35% cyclohexane (PAN support, wet)

4 Conclusions

H_2/CH_4 selectivity of membranes could be increased by cross-linking. The gas permeation properties of these composite membranes depend on the type and concentration of the cross-linking agent, on the type and concentration of solvent and non-solvent used and also on the type of support used. Cross-linking modification is an effective method to develop next generation gas separation membranes for rigorous environments. Cross-linked membranes may exhibit higher selectivity, because the material is stabilized against plasticization and becomes more resistant to chemicals.

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