

Chapter 5: ABPBI based UF membranes

5.1. Introduction

Numerous separation technologies for solutions polluted by organic solvents could be improved or optimized by the application of solvent resistant polymeric membranes [Hicke (2002)]. The use of UF membranes for treatment of spent solvent cleaning rinses from nickel plating operations was studied by Qin et al. (2004). It was observed that membranes made of CA and PAN could tolerate the organic solvent(s) present in the cleaner and were suitable for treating the spent solvent rinses, whereas PES and PSF membranes were not suitable. Chemically and thermally resistant composite membranes based on poly(acrylonitrile) and poly(amideimide) were prepared by coating hydroxy propyl methyl cellulose (HPMC) and polyether-block-polyamides [Peinemann (2001)]. The formed composite membranes were suitable for the separation of low molecular weight substances from organic solvents. Hicke et al. (2002) reported that membranes from copolymers of acrylonitrile with maleic anhydride were not autoclavable because of hydrolysis. These authors prepared membrane based on poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) followed by post treatment with ammonia. The resultant membrane due to extensive cross-linking showed solvent stability, especially towards DMF. Furthermore, that membrane could be safely sterilized by hot steam at 121 or 140 °C and drying of the membrane on air is possible without any additives.

The PAN/Chitosan composite UF membranes were found to be stable in aqueous acidic (pH 3) and basic (pH 11) medium [Musale (1999)]. Solvent resistant UF membranes based on copolysulfoneimide showed stability towards alcohols, acetone and hexane was reported [Kim, I. (2002d)]. Poly(vinylidene fluoride) (PVDF), polyethersulfone (PES) and poly(sulfone) (PSF) based UF membranes were used for vegetable oil degumming (removal of phospholipids) by Ochoa et al. (2001). Results showed that PVDF based membranes were more stable with hexane than PES and PSF. Chung et al. (1996) manufactured PAN hollow fibers resistant to chloroform for the development of high-performance composite membranes [Qin (2004)]. Singh et al.

(1996) investigated the removal of volatile organic compounds using different UF membranes and obtained above 98% rejection for toluene with a poly(vinylidene fluoride) membrane of a molecular weight cut-off (MWCO) of 18,000 [Qin (2004)]. The poly(imide) based membrane was studied by Iwama et al. (1982). This membrane exhibited excellent stability and high fluxes with most common organic solvents, even when tested at elevated temperatures. Poly(p-phenylene-terephthalamide) based UF membranes were developed by Zschocke et al. (1980), which showed stability in almost all organic solvents including DMSO, NMP and DMAc.

The above literature reports indicate that the presently available membranes have limited stability under harsher environment. Polybenzimidazole (PBI) which is known as the high performance polymer owing to its excellent chemical [Wang, K. 2006c], Chung (1997)] thermal [Wang, K. (2006c), Tsur (1974)] and mechanical stability [Cho (2004)] was investigated as a membrane material for this work. PBI is a generic name of a class of heterocyclic polymers, and the most commonly cited member of this family in the literature is poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (PBI-I). It is widely investigated as the proton exchange membrane (PEM) material [Li (2003, 2004), Fu (2004), Schuster (2003)] and is synthesized by condensation of diaminobenzidine (DAB) and isophthalic acid (IPA) [Vogel (1961)] or their derivatives [Iwakura (1964)]. The applicability of this PBI-I as a membrane material for reverse osmosis (RO) and hemodialysis was demonstrated [Brinegar (1974), Model (1972a, 1972b)]. Its asymmetric [Chung (1998, 1999)] and ultrafiltration (UF) membranes are documented [Cherdrion (1994), Sansone (1987)]. The surface of first generation reverse osmosis PBI membranes was characterized by optical microscopy, scanning electron microscopy, transmission electron microscopy and high resolution scanning electron imaging [Sawyer (1984)]. It was observed that top 20 nm layer had no resolvable pores, whereas the bulk membrane exhibited pores of about 100 nm across. These membranes revealed finger-like macrovoids below the top 500 nm layer. Wang, K. et al. (2006d) reported PBI-I based NF membranes (hollow fibers) with mean effective pore radius of 0.348 nm for cephalixin separation, which was dependent on the pore size and the electrostatic interactions between solute and the membrane. PBI-I based NF membranes with molecular weight cut-off (MWCO) of 525 Da exhibited V-shaped chromate rejection curve with an

increase in pH [Wang, K. (2006e)]. A 98.4% sulfate and 97.2% chromate rejection with less than 4% chloride rejection at pH 13 from chlor-alkali brine [Wang (2007)] and effective removal of divalent heavy metal cations from their sulfate salt and chloride salt solutions [Lv (2008)] was also demonstrated using NF membranes. PBI-I and polyarylate blend membranes showed 60 - 80 gfd flux at 50 psi and 90 - 99% rejection of cytochrome-C (MW = 12,000) [Chung (2004)].

ABPBI, a member of PBI family is prepared by self condensation of 3,4-diaminobenzoic acid [Asensio (2004, 2005), Wolfe (1985)]. It has excellent thermo-chemical and mechanical stability [Cho (2004)] and is demonstrated for PEM application [Gómez-Romero (2005), Kim (2004), Wereta (1978)]. Neither glass transition nor crystalline melting point was observed in the temperature range of -150 to 400 °C for this polymer [Wereta (1978)]. Except PEM, other types of membranes based on ABPBI are not documented, in spite of its excellent thermo-chemical properties. One of the reasons could be that it is soluble only in strong acids such as sulfuric acid, formic acid, trifluoroacetic acid, phosphoric and poly(phosphoric acid) [Asensio (2005)]; while PBI-I based on DAB and IPA is soluble in polar aprotic solvents and the most widely used is *N,N*-dimethyl acetamide [Li (2003)]. Monomer cost and synthesis time for ABPBI are much lower than that for PBI-I.

Present work investigated ABPBI based phase inversion membranes. Effects of various parameters viz., porous support, nonsolvent and polymer concentration on the membrane performance in terms of water flux, MWCO and pore size distribution was studied. The stability of ABPBI membrane towards organic solvents, concentrated acid and base was evaluated. Capability of glycerol treatment to prevent pore collapse was analyzed.

5.2. Experimental

3,4-Diaminobenzoic acid (DABA, 97%) and poly(ethyleneglycol) (PEG) of different molecular weights were obtained from Aldrich chemicals (USA). Poly(phosphoric acid) (PPA, ca 84% as phosphorus pentoxide) was procured from Alfa Aesar (USA). NaOH, H₂SO₄ (98%), methane sulfonic acid (MSA), HCl, glycerol, *N,N*-dimethyl formamide (DMF), *N,N*-dimethyl acetamide (DMAc), toluene, tetrahydrofuran

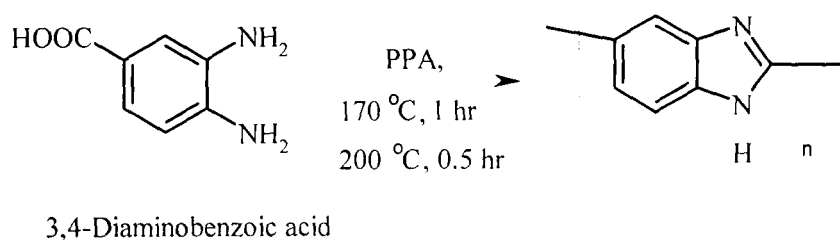
(THF), chloroform (CHCl_3), hexane, isopropyl alcohol (IPA) and isobutyl alcohol (IBA) were procured from SD fine chemicals (India). All these chemicals were of AR/GR grade and were used without further purification. The nonwoven support fabrics, viz., Viledon H3160 and FO2470 were procured from Freudenberg (Germany), while Hollytex 3324 and 3265 were procured from Ahlstrom (USA). Properties of these supports available from suppliers are given in Table 5.1.

Table 5.1 Physical properties of porous supports.

Porous support	Weight (g.m^{-2})	Thickness (mm)	Air permeability	Tensile strength	Elongation (%)
FO2470	60	0.12	200 ($\text{dm}^3 \cdot \text{s}^{-1} \cdot \text{m}^{-2}$)	200 -100 N/5 cm	28 - 33
H3160	60	0.07	30 ($\text{dm}^3 \cdot \text{s}^{-1} \cdot \text{m}^{-2}$)	210 N/50 mm	22
3324	99.9	0.13	9 cfm	CD 28 lbs.in ⁻¹ MD 60 lbs.in ⁻¹	CD 80
3265	81.2	0.13	20 cfm	CD 21 lbs.yd ⁻² MD 65 lbs.in ⁻¹	CD 70

5.2.1. Synthesis and characterization of ABPBI

ABPBI was synthesized by condensation of DABA in PPA [Asensio (2005)] as shown in Scheme 5.1 below.



Scheme 5.1 Synthesis route of ABPBI.

A three necked 1 liter round-bottom flask equipped with an overhead stirrer, N₂ inlet and CaCl₂ guard tube was charged with PPA (500 g) and heated upto 170 °C. 25 g of DABA (0.1644 mol) was added while stirring and heating continued for an hour. The temperature was raised to 200 °C and allowed to stir for 30 minutes. The reaction mixture was precipitated into stirred water; obtained polymer was crushed and thoroughly washed till neutral to pH. It was then kept under 10% aq. NaOH solution for 24 hours, washed with water till neutral to pH, soaked in acetone for 15 hours and dried in vacuum oven at 80 °C for a week. It was preserved in the desiccator until use.

Inherent viscosity of ABPBI was determined by using Ubbelohde viscometer with 0.2 g.dL⁻¹ solution in conc. H₂SO₄ at 35 °C. Wide-angle X-ray diffraction (WAXD) spectra of polymer was recorded using PANalytical X'pert Pro MPD X-ray diffractometer with Cu-K_α radiation in 2θ range of 5-40°. Thermogravimetric analysis (TGA) of polymer was performed by using Perkin Elmer TGA-7 under nitrogen atmosphere at the heating rate of 10 °C.min⁻¹.

5.2.2. Membrane preparation

The dope solutions of ABPBI were prepared while varying polymer concentration (4% and 6% w/w) using MSA as the solvent at 70 °C and stirring under dry atmosphere for 48 hours. Higher concentration led to a gel formation and was not pursued further. The formed solution was allowed to cool to the ambient temperature and then degassed to remove trapped gases. The dope solution viscosity was measured using Brookfield digital viscometer (Model DV-1) at 0.5 RPM at the ambient temperature. Membranes were prepared using Sheen Automatic Film Applicator-1132 on different non-woven support fabrics as shown in Figure 5.1. The knife movement was set to 15 cm.sec⁻¹ transverse speed with a gap of 250 μm. The membranes were casted on porous fabric supports (FO2470, H3160, 3324 and 3265) at 20 °C gelation temperature and exposed in air for 8 seconds prior to dipping in nonsolvent bath. Water or 0.5N NaOH was used as the nonsolvent. The total thickness (along with support) of the supported membrane was ~ 200 μm. These membranes were washed with running water till neutral to pH and then stored at 4 °C until use. The identification of membranes is given in Table 5.2.



Figure 5.1 Sheen automatic film applicator.

5.2.3. Membrane characterization

5.2.3.1. Flux analysis

The flux analysis of ABPBI membrane was done in dead end cell with active area 14.5 cm^2 as described in Section 3.2.4.1.

5.2.3.2. Rejection analysis

The rejection analysis of ABPBI membranes was done using various molecular weight PEGs (0.1% w/v concentration in feed) in dead end cell with active area of 14.5 cm^2 . The analysis of PEG was done as described in Section 4.2.2.2.

5.2.3.3. Pore size analysis

The ABPBI membrane pore size and its distribution were determined by liquid-liquid displacement method as described in Section 3.2.5.2.

The mean pore diameter of ABPBI membranes was determined by solute rejection method as described in Section 4.2.3.

5.2.3.4. Scanning Electron Microscopy (SEM)

The membrane cross sections were analyzed by using SEM and low vacuum SEM mode. The details of SEM instrument and sample preparation are given in Section 3.2.8. The cross section of ABPBI membrane in low vacuum SEM mode was analyzed by Quanta 200 3D SEM using large field detector (LFD). The sample chamber pressure was 200 Pascal. The membrane sample was treated with 10, 20 and 50% glycerol (in each glycerol concentration for 24 hours), sequentially and used for imaging.

5.2.3.5. Stability of ABPBI membrane in organic solvents, acid and base solution

Membrane stability was analyzed in DMF, DMAc, IPA, toluene, THF, CHCl_3 , hexane, H_2SO_4 (25N) and NaOH (2.5N) at the ambient temperature. Membranes were also autoclaved at 15 psi pressure and 121 °C for 20 min. Membranes with known water flux were dipped in the respective solvent for 24 hours at the ambient temperature and flux of organic solvents was measured. For water immiscible solvents, the membranes were initially dipped in IPA for 24 hours and then in respective solvent for 24 hours, and again in IPA for the same time, before measuring the water flux for the comparison with the initial flux. The change in thickness before and after solvent treatment was also measured. Results were repeated at least for three coupons and then averaged.

5.2.3.6. Effect of glycerol treatment

Two concentrations of glycerol, 10 and 50% (v/v) were used for assessing their capability to refrain from pore collapse. Membranes were dipped into 10% glycerol solution for 24 hours. The 50% glycerol treatment was done by sequential dipping in 10% (8 hours), 20% (16 hours) and finally in 50% glycerol solution (24 hours). After the glycerol treatment, these membranes were allowed to dry in the oven at 60 °C for 24 hours. These dried membranes were dipped in water overnight before measuring the flux. The effect of repeated 50% glycerol treatment (removal and recharge) on water flux of the membrane was also analyzed.

5.3. Results and discussion

5.3.1. ABPBI synthesis and characterization

The self polycondensation of DABA (Scheme 5.1) in PPA, which acts as a solvent as well as dehydrating agent [Harris (1993)] offered ABPBI. The reaction time of an hour at 170 °C and 30 minutes at 200 °C was enough to offer polymer with inherent viscosity of 1.72 - 2.17 dL.g⁻¹. The WAXD analysis of the polymer in powder form indicated its amorphous nature (Figure 5.2) having average interchain spacing (*d*-spacing) of 3.01 Å. It is reported that films of ABPBI prepared from methanesulfonic acid, chlorosulfonic acid or formic acid/*m*-cresol induces crystallinity [Wereta (1978)], owing to the nature of solvents and heating conditions [Sannigrahi (2006), Wainright (2003)]. Amorphous nature of phosphoric acid doped as well as undoped ABPBI dense membranes with *d* spacing of 3.4 Å is reported [Asensio (2004)]. Thermogravimetric analysis of ABPBI showed initial loss up to ~ 355 °C, which could be attributed to the loss of absorbed water. The polymer was stable up to 610 °C, while char yield at 900 °C was 45% as shown in Figure 5.3.

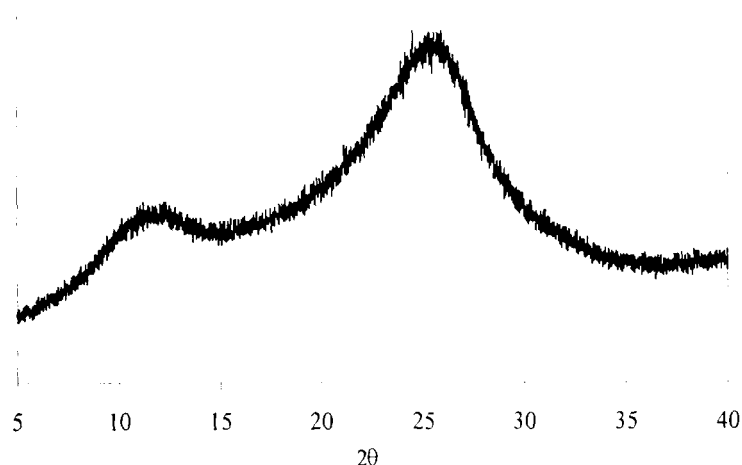


Figure 5.2 WAXD spectrum of ABPBI.

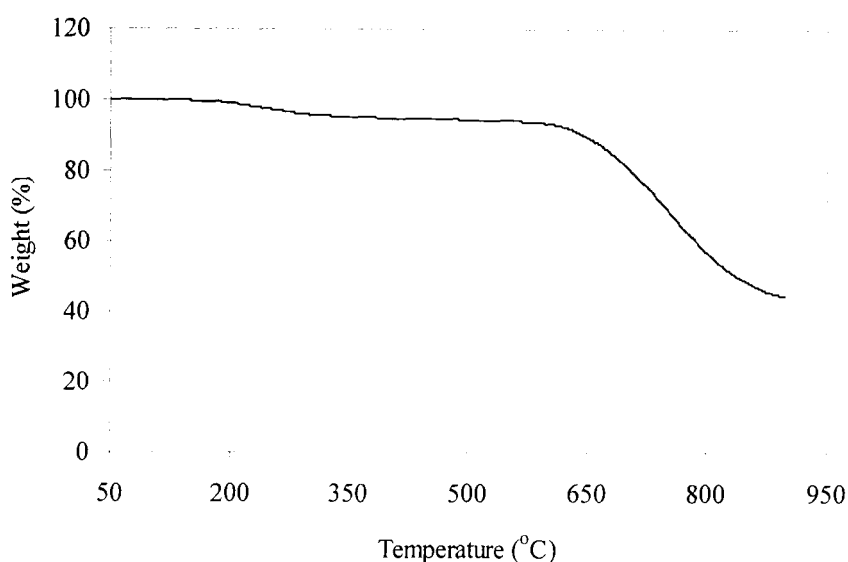


Figure 5.3 TGA spectrum of ABPBI.

5.3.2. Membrane preparation

ABPBI based UF membranes were prepared by varying porous supports, nonsolvent and polymer concentration in the dope solution. Supported membranes using two different dope solution concentrations (4% and 6%) were prepared using MSA as the solvent. The dope solution viscosity of 6% and 4% polymer concentration was 3040 cP and 17255 cP at 5 RPM, respectively. The phase inversion membranes using these solutions were prepared with either water or 0.5N NaOH as the nonsolvent at the ambient temperature. The effect of these variants on membrane performance is discussed in following sections.

5.3.2.1. Effect of porous support material

The effect of support material was studied as their properties are known to affect the membrane performance [Section (3.3.4), Munari (1990)]. Membranes with 6% dope solution concentration were prepared by using polypropylene support FO2470 and polyester supports H3160, 3324 and 3265. Formed membranes were designated as M-1, M-2, M-3 and M-4, respectively. Water flux at 2 bar transmembrane pressure for M-1 was $16.3 \text{ l.m}^{-2}.\text{h}^{-1}$, while for M-2, M-3 and M-4 it was 3, 3.2 and $5.3 \text{ l.m}^{-2}.\text{h}^{-1}$, respectively (Table 5.2). The lower flux in case of membranes prepared using polyester

support than with polypropylene support was an outcome of the lower number of pores and lower surface porosity of these type membranes (Table 5.2). The pore size distribution analysis (Figure 5.4) showed that the membrane M-1 prepared with FO 2470 (polypropylene) support offered more number of pores near to smaller pore size. The total number of pores in this case were 3.92×10^7 and surface porosity was 0.0055% (Table 5.2). Mosqueda-Jimenez et al. (2004) reported $\sim 0.05\%$ surface porosity for the PES based UF membrane with $\sim 19 \text{ l.m.}^{-2}\text{h.}^{-1}$ flux at 3.45 bar. In comparison to this porosity, the porosity of M-1 (0.0055%) is much lower, though the membrane offered similar water flux. In order to investigate the reasons behind observed lower porosity, SEM analysis was performed. The delamination of membrane from its support occurred when the membranes were exposed to the vacuum conditions during SEM analysis, offering no clue on porosity (Figure 5.5a). Thus SEM was performed under low vacuum mode of E-SEM. This effort also could not indicated any porosity (Figure 5.5b). Thus, unsupported membrane was analyzed, which shows sponge-like structure (Figure 5.5c). It is reported by Wang et al. that the delayed demixing during membrane formation can lead to the sponge-like structure [Wang (2007)]. In present case, a basic PBI was dissolved in highly acidic solvent. The resultant acid-base complex may not be easily broken by water used as a nonsolvent, since it is not stronger base than PBI. This could result in delayed demixing during membrane formation resulting in sponge-like pore structure. With this kind of nature of the pores (sponge type), high surface porosity should have been obtained. On the contrary, PSD analysis showed very low porosity. This indicates that pores in the sponge type open structure could not be interconnected, resulting in overall low surface porosity. The calculations of the pore size in liquid-liquid displacement method were done on the assumption that the pores are parallel and are not interconnected [Gijssbertsen (2004)]. It is also reported that the sublayer resistance is always larger than the unconnected pore resistance in an isotropic membrane with interconnected pores and thus the estimated pore size distribution is always shifted towards smaller pore sizes than they really are. This also could be one of the reasons for lower observed surface porosity.

Secondly, for PSD analysis of UF membranes with finger-like porosity, the membrane thickness (skin layer thickness) is assumed to be equal to the thickness of

dense layer of the membrane usually $\sim 0.1 \mu\text{m}$ [Capennelli (1983)]. This may not be essentially true for present membrane possessing sponge-like structure. If the PSD analysis is done with actual membrane thickness (excluding support thickness), obtained results on surface porosity are far apart from the one obtained by assuming $\sim 1 \mu\text{m}$ as the membrane thickness. This data is given in the Table 5.2. This higher surface porosity can be correlated to the observed water flux.

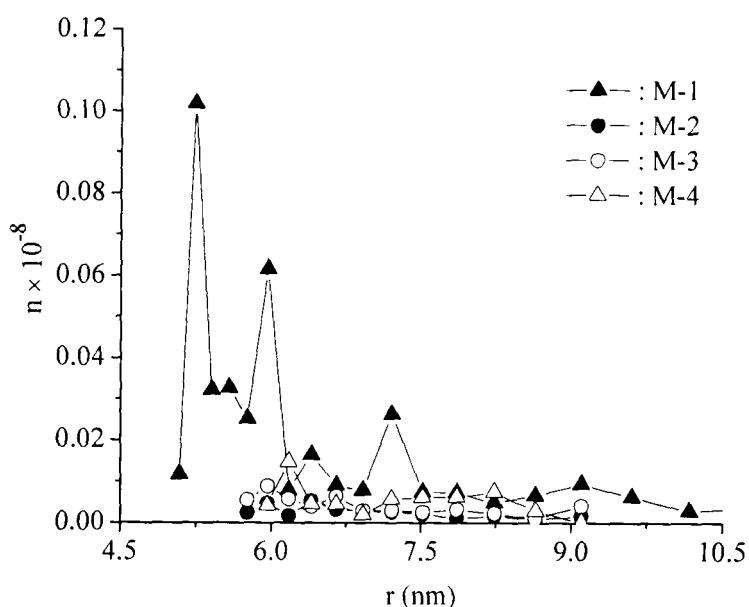
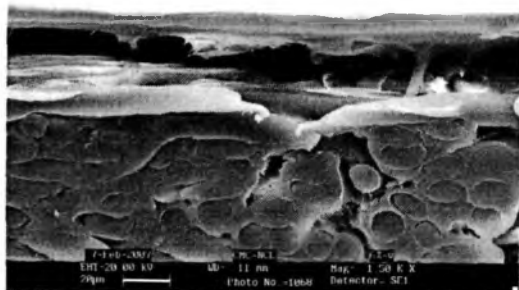


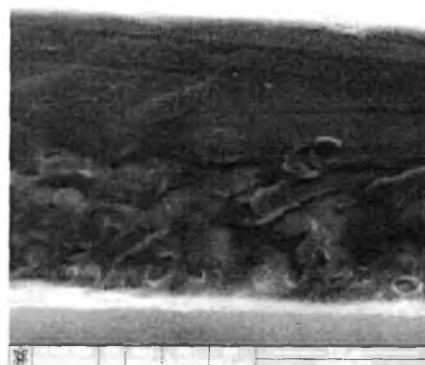
Figure 5.4 Pore size distribution of membranes prepared using different supports and 6% ABPBI in dope solution.

The surface porosity can also be determined by solute rejection method [Singh (1998), Aimar (1990)]. In present case, the fluxes after the PEG rejection even after washing with 0.1N NaOH could not be regained. Thus, surface porosity was not determined by this method.

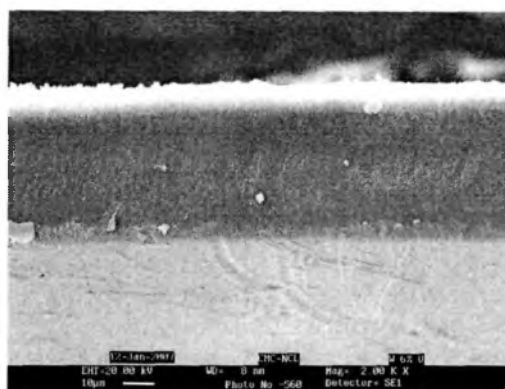
Air permeability of the polypropylene support is higher than the polyester supports used (Table 5.1). This could be one of the reasons for higher flux obtained in case of earlier support. Among the membranes prepared using polyester supports, 3265 porous support (M-4) exhibited maximum total number of pores and surface porosity due to the more open porous structure of 3265 support.



(a)



(b)



(c)

Figure 5.5 SEM cross section images of (a), (b) supported and (c) unsupported ABPBI membrane.

Table 5.2 Water flux, rejection and pore size analysis by solute rejection method of membranes prepared using different porous supports.

Polymer concentration in dope solution (%)	Membrane code	Support used	Nonsolvent used	Water flux, J_w , at 2 bar ($\text{l}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	PEG _{6k} rejection (%)	Properties studied					
						By liquid-liquid displacement method			By solute rejection method		
						Total no. of pores per unit surface	Mean pore diameter (nm)	Surface porosity (%)	Mean pore diameter, μ_p (nm)	Geometric standard deviation, σ_p	
6	M-1	FO2470	Water	16.3 ± 2.8	93.3	3.92×10^7 (3.37×10^{10}) ^b	12.7	0.0055 (4.58)	3.21	1.51	
	M-2	H3160	Water	3.0 ± 0.6	37.9	2.80×10^6 (2.41×10^9) ^b	13.45	0.0004 (0.38)	5.66	1.68	
	M-3	3324	Water	3.2 ± 0.1	38	5.39×10^6 (4.65×10^9) ^b	12.80	0.0003 (0.27)	5.33	1.78	
	M-4	3265	Water	5.3 ± 0.8	52	5.50×10^6 (4.73×10^9) ^b	14.85	0.0012 (1.05)	4.22	1.95	
	M-5	FO2470	NaOH	$9.3^a \pm 0.7$	83.8	-	-	-	-	-	
	M-6	FO2470	Water	30.2 ± 6.6	90.8	7.47×10^7 (6.23×10^{10}) ^b	13.2	0.011 (9.87)	3.38	1.37	

^a: At 1 bar pressure, ^b: Values determined using 86.2 μm pore length.

Figure 5.6 shows that MWCO of membranes prepared with polyester supports (M-2, M-3 and M-4) was higher (~ 35 kDa) than that of membrane prepared with polypropylene support (~ 6 kDa). This could be explained on the basis of porosity of these membranes. The mean pore diameter determined by using liquid-liquid displacement method and solute rejection method showed that M-1 offered lower mean pore diameter as compared to the membranes M-2, M-3 and M-4 (Table 5.2). Higher number of pores in case of M-1 than that for M-2, M-3 or M-4 could be responsible for the higher water flux of this membrane. The values of mean pore diameter and σ_p were determined by solute rejection method by plotting the graph between PEG diameter versus PEG rejection (Figure 5.7). This analysis is also in good agreement with the lower pore size for the membrane M-1 than that of other types as obtained by liquid-liquid displacement method. In comparison to the mean pore diameters of membranes obtained by solute rejection method, the liquid liquid displacement method showed higher values. This is also observed by Kim et al. (1994) and stated that the controlling pore dimension for separation is the surface skin dimension. On the basis of these analyses, polypropylene appears to be the better choice than polyester as the support fabric.

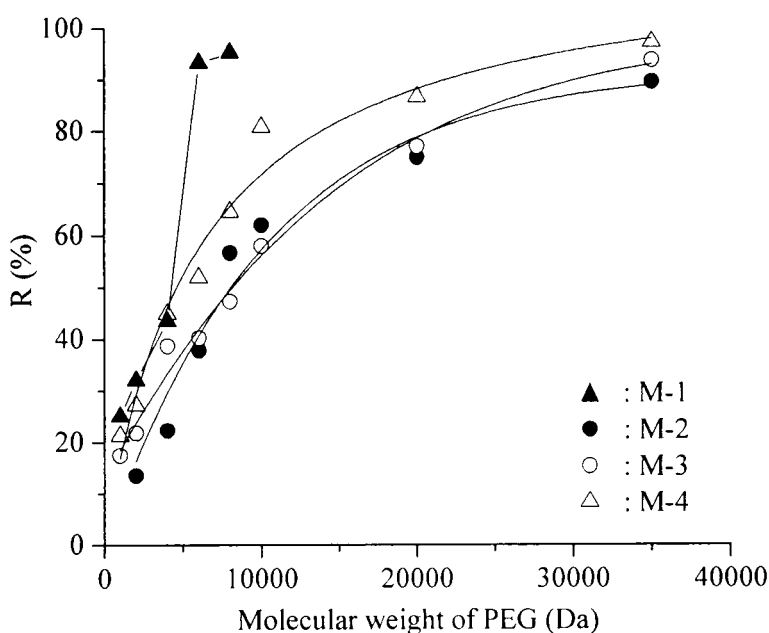


Figure 5.6 Rejection (R) of membranes prepared using different supports and 6% ABPBI in dope solution.

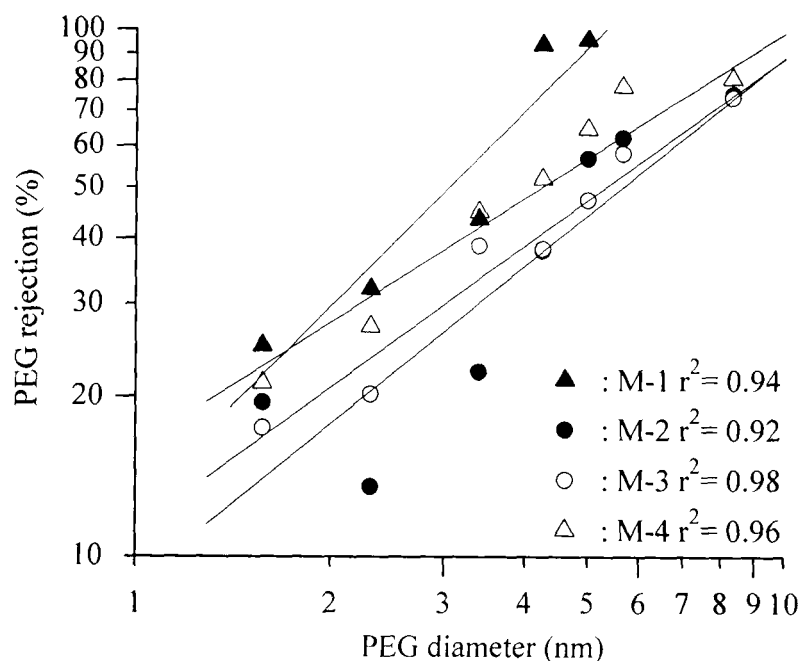


Figure 5.7 PEG rejection versus PEG diameter for membranes prepared using 6% dope solution concentration on different supports.

5.3.2.2. Effect of nonsolvent

The dope solution for membrane casting was prepared with MSA as the solvent. Since ABPBI is a basic polymer owing to the presence of two nitrogen atoms carrying lone pair of electrons per repeat unit, the acid molecules are anticipated to be associated with the polymer matrix. It is well known that ABPBI sorbs H_3PO_4 [Asensio (2002)]. During the phase separation process, if NaOH is used as the nonsolvent, instead of water, it is possible that the sorbed acid can also be taken away by using NaOH since it is a stronger base than the $-\text{NH}$ functionality of ABPBI. Membranes M-1 and M-5 offered $8.6 \text{ l.m.}^{-2}\text{h.}^{-1}$, $9.3 \text{ l.m.}^{-2}\text{h.}^{-1}$ water flux at 1 bar transmembrane pressure, respectively (Table 5.2). The MWCO of these membranes was 6 kDa as shown in Figure 5.8. Since the porosity is same as that of membrane prepared with water as nonsolvent, the factor controlling pore formation is not the type of nonsolvent. In view of low concentration of

the dope solution, microfiltration type of membranes could have been expected. On the contrary, the porosity obtained is in the range of low MWCO UF type. The polymer concentration, nonsolvent used seems to have negligible effect on porosity.

5.3.2.3. Effect of polymer concentration

Membranes were prepared by using 6% (M-1) and 4% (M-6) dope solution concentration by using water as a nonsolvent. M-1 and M-6 exhibited 8.6 and 17 l.m⁻².h⁻¹ dead end flux at 1 bar transmembrane pressure, respectively. It is known that the membrane prepared with higher polymer concentration shows lower flux [Nouzaki (2002), Paul (1992)]. M-6 offered almost double flux than M-1, but they exhibited similar MWCO (6 kDa) as shown in Figure 5.8. This behavior can be explained on the basis of pore size distribution analysis of the membrane (Figure 5.9). The difference in flux performance can be correlated with pore density and surface porosity of the membrane.

The membrane M-1 offered lower pore density and surface porosity than M-6 as given in Table 5.2. Thus, the membrane M-1 exhibited lower water flux than the membrane M-6. The mean pore diameter of M-1 determined by liquid-liquid displacement method as well as solute by rejection method is comparable to that of M-6 (Table 5.2) and thus exhibited similar MWCO. The mean pore diameter and σ_p was calculated by plotting graph between PEG diameter versus PEG rejection (Figure 5.10). It was observed that the value of σ_p in case of membrane M-1 and M-6 are close to each other. Michael et al. (1980) stated that, due to close values of σ_p , virtually all the membranes were quite similar in their microstructure. Membrane M-6 showed higher flux as compared to membrane M-1 with similar rejection performance, thus for further analysis M-6 was used.

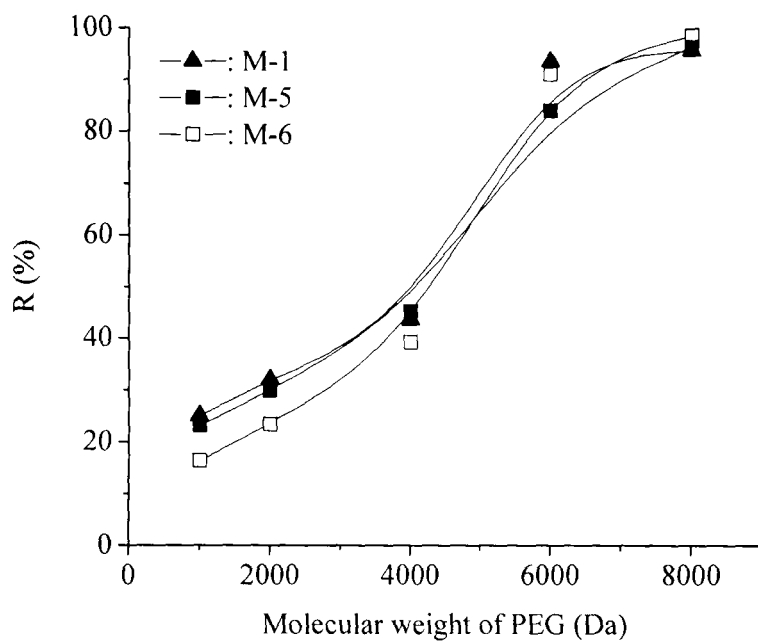


Figure 5.8 Rejection (R) of ABPBI membranes prepared by varying polymer concentration in dope solution and nonsolvent.

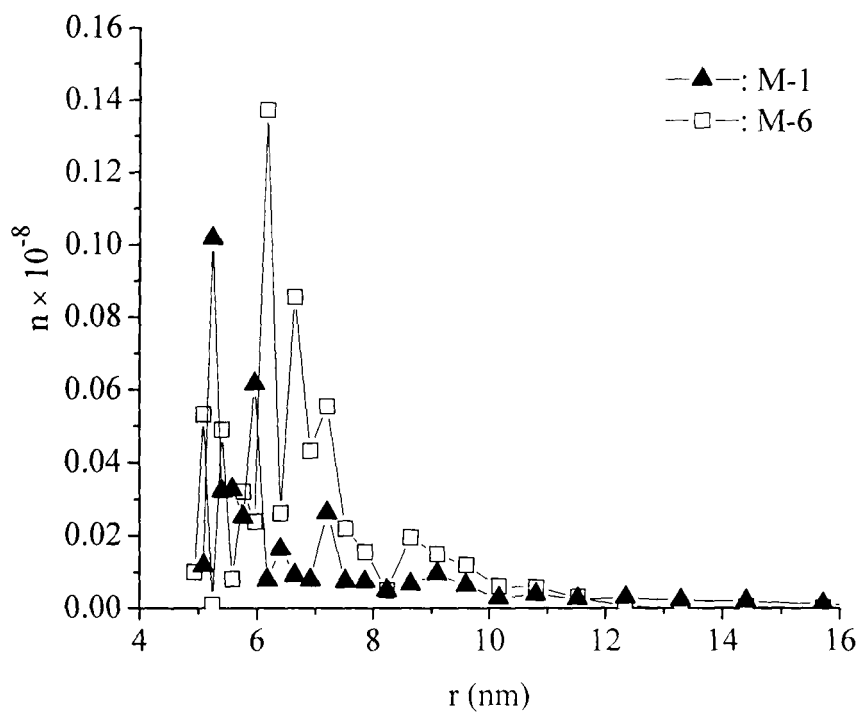


Figure 5.9 Pore size distribution of ABPBI based membranes.

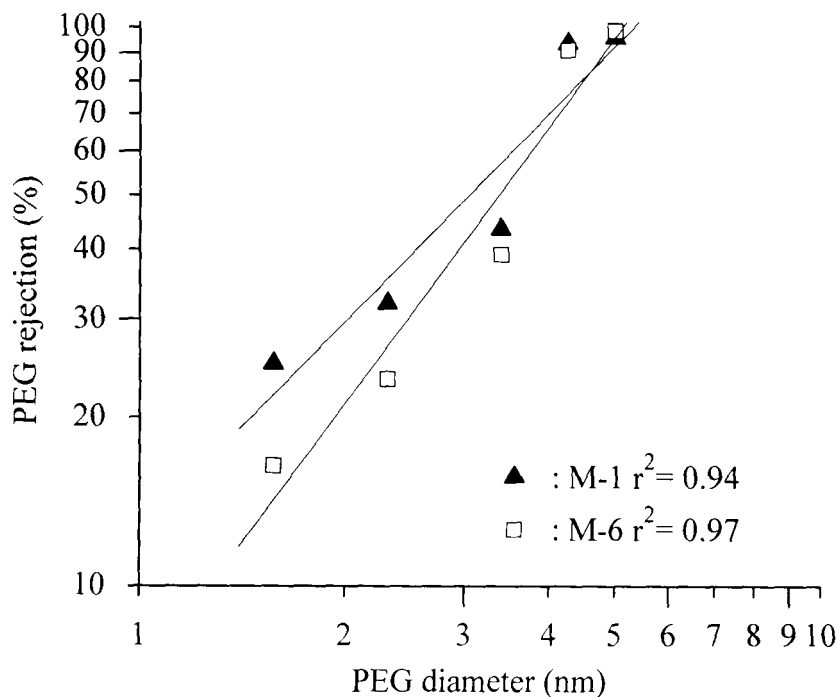


Figure 5.10 PEG rejection versus PEG diameter for M-1 and M-6.

5.3.3. Membrane stability in organic solvents

The membrane prepared using polypropylene support (M-6) was used to evaluate the stability of ABPBI based membranes in various organic solvents, autoclaving conditions as well as concentrated acid (H_2SO_4) and base (NaOH). The polypropylene support was chosen as it is more stable in basic environment than the polyester support [Daisley (2006)]. The solvent flux through the membrane was measured after dipping into the respective solvent for 24 hours. In case of water immiscible solvents like chloroform, toluene and hexane, membranes were dipped initially in IPA (24 hours) and then in the respective solvents (24 hours). The properties of solvent and their flux through the membrane are given in Table 5.3. Higher solvent fluxes were obtained in case of non polar solvents than that of polar solvents. No correlation was seen between the solvent flux and dielectric constant of the solvent. Machado et al. (1999) observed that there is relatively small effect of dielectric constant on the solvent flux due to the difference in dielectric constant of solvent and polymeric membrane material. It is known that the solvent with higher viscosity exhibited lower flux through polyimide based ultrafiltration

membranes [Iwama (1982)]. M-6 showed highest flux for THF having viscosity of 0.55 cP, which is lowest among other solvents. Though the viscosity of THF is comparable with that of chloroform and toluene, membrane showed lower solvent fluxes for the later solvents. This shows that polarity of the solvent could also be important. No clear correlation could be observed between solvent flux and solubility parameters or surface tension. In hexane, the membrane was delaminated from the support, which could be due to its nonpolar nature.

The effect of solvent treatment on the membrane morphology was analyzed by measuring water flux after the solvent treatment and compared with initial flux. The membrane showed 59.4% and 59.2% reduction in water flux after chloroform and toluene treatment, respectively. In aqueous environment (polar solvents), strong hydrogen bonding due to nitrogen associated with hydrogen atom [Wang, K. (2006c)] is favourable. This is not possible in case of non polar solvents. Thus, there could be shrinkage of pores in presence of these non polar solvents. Such change in pore size due to shrinkage was analyzed by PEG rejection. PEG_{4k} was selected for the rejection analysis as the untreated membrane showed 39% rejection. The membranes treated with chloroform and toluene offered 85% and 55% rejection, respectively. The increase in rejection performance confirmed the reduction in pore size after the solvent treatment. Effect of chloroform and toluene treatment was also analyzed in case of the membrane M-1. But membrane showed delamination from the support after treated with chloroform and just 16% change in water flux after the toluene treatment. The membrane M-6 showed large decrease in water flux after the toluene treatment as compared to M-1. It may be due to high porosity of M-6, which led to more shrinkage as compared to M-1 having low porosity. The membrane prepared using polypropylene support was delaminated; while polyester support based membranes were stable after the hexane treatment. This could be because of good adherence of polymer film with hydrophilic polyester support as compared to the hydrophobic polypropylene support.

The membranes M-2 and M-4 offered up to 62% and 69% reduction in water flux, respectively, after the hexane treatment as shown in Table 5.4. Among the polyester based membranes, 3324 was a better support as M-3 showed 41% decrease in water flux, which is lowest variation as compared to the same for M-2 and M-4. This decrease in

flux is due to the non polar nature of hexane. Membranes treated with polar solvents (DMF, DMAc, IPA and THF) showed marginal change in water flux and showed excellent stability towards these solvents.

M-6 showed good stability after autoclaving with marginal change in water flux (Table 5.3). This showed additional advantage of ABPBI membrane towards thermal stability in presence of steam. Especially for membrane application in medicine, pharmaceutical and food industry there is a strong demand for safely sterilizable membranes [Hicke (2002)].

Table 5.3 Stability of membrane M-6 towards organic solvents.

Solvent used	η_{solvent}^b (cP)	δ^b (cal.cm ⁻³) ^{1/2}	ϵ^b at 20°C	σ^b Dyne.cm ⁻¹ at 20°C	J_{solvent} (l.m ⁻² .h ⁻¹ .bar ⁻¹)	% Reduction in membrane thickness	% Change in J_w
DMF	0.82	12.1	36.7	35	14.7	8	13.46
DMAc	0.92	11.0	37.8	34	6.6	15	10.11
IPA	2	11.5	18.3	21.7	7.0	4	8.68
Chloroform	0.57	9.3	4.8	27.16	13.6	33	-59.42 (85%) ^a
THF	0.55	9.1	7.6	2.8	33.3	9	-12.84
Toluene	0.59	8.9	2.38	28.5	12.7	27	-59.23 (55%) ^a
Hexane	0.31	6.9	1.9	18.4	^c	20	-
Autoclaving	-	-	-	-	-	13	-14.51

^a: PEG_{4k} rejection

^b: From reference [Smallwood, 1996]

^c: Membrane delaminated from support.

Table 5.4 Hexane stability of membranes prepared using different porous supports.

Membrane code	% Reduction in membrane thickness	% Change in J_w
M-1	16.0	Delaminated
M-2	57.5	-61.6
M-3	22.6	-41.1
M-4	28.8	-69.3

5.3.4. Membrane stability in concentrated acid and base

The ABPBI membrane (M-6) stability towards concentrated acid (25N H₂SO₄) and base (2.5N NaOH) was analyzed. In 30N H₂SO₄ solution membrane was stable only for 10 seconds with 14.6% decrease in flux. After prolonged exposure, polymer ultimately started dissolving. Thus, lower concentration of H₂SO₄ was evaluated. On visual observation, it was found that in 25N H₂SO₄ solution membranes (M-1, M-6) were stable, for long time (24 hours). Thus, this concentration was used for the further study. Membranes M-1 and M-6 exhibited marginal decrease in water flux after treatments with 25N H₂SO₄ and 2.5N NaOH as shown in Table 5.5. All these membranes after the concentrated acid and base treatment showed marginal reduction in thickness (11 to 26%). ABPBI based UF membranes offered excellent stability in concentrated acid and base. On the other hand, solvent resistant membranes based on poly-(*p*-phenyleneterephthalamide) showed limited stability, i.e. towards 2N H₂SO₄ and NaOH at pH 12 [Zschocke (1980)].

Table 5.5 Change in water flux after treatment of concentrated acid and base.

Membrane code	25N H ₂ SO ₄ treatment		2.5N NaOH treatment	
	% Reduction in membrane thickness	% Change in J_w	% Reduction in membrane thickness	% Change in J_w
M-1	22.9	-23.7	12.7	-7.3
M-6	26.0	-36.1	11.5	-1.5

5.3.5. Effect of drying and glycerol treatment

In view of studying the effect of drying on the membrane porosity, M-6 was dried at 60 °C in oven for 24 hours. The membrane showed 98% and 34% decrease in flux and thickness, respectively (Table 5.6) due to shrinkage. This membrane after immersing in water for prolonged time (24 hours) did not regain thickness or flux. Such irreversible shrinkage after drying in case of poly-(*p*- phenylenetere-phthalamide) based membrane was observed by Zschocke et al. (1980). Pore morphology of the dried membrane was analyzed by SEM. The delamination of polymer film from the support was observed after drying as shown in Figure 5.5a. SEM cross section images of dried membrane clearly shows collapsed pore structure, which led to the decrease in flux and membrane thickness.

Table 5.6 Effect of drying on water flux.

Treatment protocol	Drying at 60 °C	Dipped in 10% Glycerol + 60 °C	Dipped in 50% Glycerol ^a + 60 °C
% Change in J_w	-97.96	-92.51	-17.6
% Change in thickness	-34.18	-22.03	-3.50

^a: Initially dipped in 10% (8 hour) + 20% (16 hour) + 50% (24 hour)

To avoid pore collapse, membranes were dipped in 10% glycerol and then dried at 60 °C. The decrease in water flux was upto 93% and indicates that 10% glycerol treatment is not sufficient to avoid pore collapse. Thus, membranes were treated with 10%, 20% and 50% glycerol solution sequentially, and dried at 60 °C. The membrane showed only 17.6% decrease in water flux with marginal decrease in thickness as given in Table 5.6. Thus, the pore collapsing of ABPBI membrane can be avoided by 50% glycerol treatment as shown in Figure 5.5b. This imaging was done by using 50% glycerol treated membrane without any prior treatment in low vacuum SEM mode.

To study the effect of glycerol treatment, the glycerol in the pores was replaced by water and the flux was measured. Such replacement of glycerol by water in the pores was repeated four times. The reduction in flux was observed for the first treatment and then it became almost constant as shown in Figure 5.11.

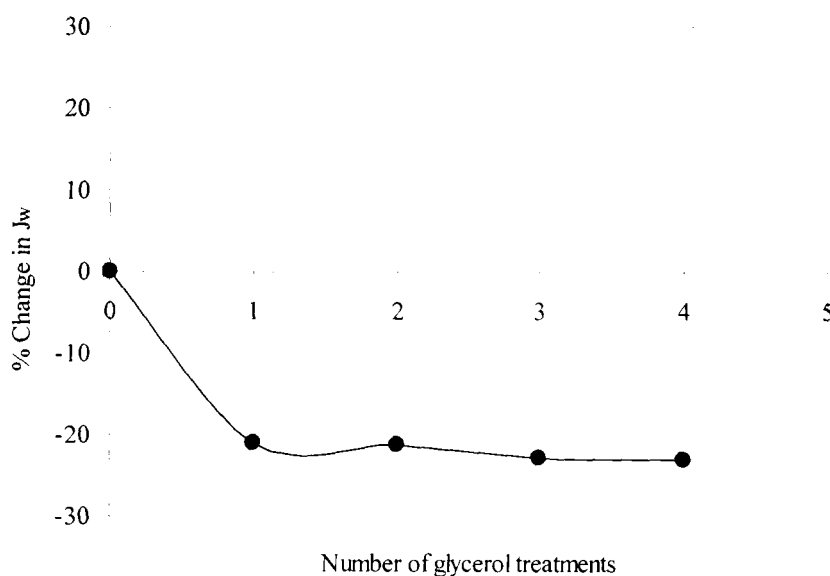


Figure 5.11 Change in J_w after repeated glycerol treatment for membrane M-6.

5.4. Conclusions

The ABPBI was synthesized by self condensation of 3,4-diaminobenzoic acid with inherent viscosity of $1.72 - 2.17 \text{ dL.g}^{-1}$. ABPBI based membranes were prepared by phase inversion method by varying porous support material, polymer concentration and non solvent. The membrane prepared using polypropylene support offered higher flux than polyester based membranes. The polypropylene based membrane (M-1 and M-6) showed 6 kDa MWCO while it was 35 kDa for polyester based membranes (M-2, M-3 and M-4). The pore size and the surface porosity of the membrane are the governing factors. On the basis of flux, MWCO and pore size distribution the polypropylene appeared to be the better porous support. The non solvent (water/0.5N NaOH) had negligible effect as the membrane M-1 and M-5 showed similar performance. The M-6 showed higher flux due to its higher surface porosity than M-1 while both the membrane showed 6 kDa MWCO as their pore diameters are comparable. The membrane M-6 showed excellent stability towards organic solvents, autoclave condition, concentrated acid ($25 \text{ N H}_2\text{SO}_4$) and base (2.5 N NaOH). The dried membrane showed pore collapse as clearly seen in SEM which can be avoided by 10%, 20% and 50% glycerol treatment. This was confirmed by flux analysis.