

Fabrication of Nanofiltration Membrane from Polysulfone Ultrafiltration Membrane Via Photo Polymerization

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Abstract:

UV-induced grafting technique was used as a flexible method for surface modification of Polysulfone (PSf) ultrafiltration (UF) membranes in order to prepare hydrophilic nanofiltration (NF) membranes. Flat sheet Polysulfone (PSf) ultrafiltration membranes were prepared via phase inversion method. N-methylene-2-pyrrolidone (NMP) and polyethylene glycol (PEG) of three different molecular weights (MW) (200, 400 and 600 Da) were used as solvent and the polymeric additive in casting solution respectively. Effect of PEG MW and grafting conditions including monomer concentration and irradiation time on membrane performance as pure water flux (PWF), salts rejection and PEG retention at 300 kPa operation pressure was studied. Several surface analytical techniques including FTIR-ATR, SEM and AFM were used to characterize the changes resulting from modification. The results showed PWF drastically decreases and salt rejection increases where monomer concentration and irradiation time are increased which corresponds to a decrease in pore size from 3.42 to 2.62 nm. According to AFM photographs the RMS roughness of this membrane is 2.3 nm which is in NF range.

Keywords: Polysulfone, Phase Inversion, Nanofiltration membrane, Polyethylene glycol, UV graft, Acrylic Acid.

1- INTRODUCTION

Water pollution is one of the most significant environmental problems in the world. Nanofiltration is a promising technique for wastewater reclamation, industrial water production, water softening, and in the separation of compounds having different molecular weights. Nanofiltration (NF) membrane can be prepared from origin ultrafiltration (UF) membrane during a modification step. PSf UF membrane was prepared via phase inversion. In this method, the final structure of UF membrane is influenced by many factors including polymer, solvent, nonsolvent, additive and their

concentrations in the casting solution [1,2]. Modification of UF membrane can be performed through either membrane material modification [3-5] or membrane surface modification [6,8]. In the present work, both of these modifications were applied. PEG was used in casting solution for membrane material modification (forming pores). The effect of PEG with different molecular weight on membrane morphology and its performance was investigated by many researchers. Kim et al. [9] investigated the effect of PEG 200 on asymmetric polyetherimide membrane performance and revealed that the presence of PEG 200 in the casting solution improved the solute rejection rate. Idris and Yet [10] studied the influence of the different

molecular weight PEG and the amount of PEG on cellulose acetate asymmetric dialysis membrane performance. They observed that the low amount of PEG, less than 5 wt% in the dope solutions strongly enhance the urea clearance while too high amount of PEG, more than 12 wt% reduced the membrane performance. They also found that low molecular weight of PEG produces better dialysis membranes in urea separation term. Idris et al. [11] in their other report also investigated the effect of PEG (200, 400 and 600) on performance and morphology of polyethersulfone UF membranes. They concluded that membranes with PEG of higher molecular weights have higher pure water permeation and larger pores. The MWCO of the membranes increased from 26 to 45 kDa when the molecular weight of PEG is increased from 200 to 600. Chakrabarty et al. [3] from their study on the effect of MW of PEG additives (400, 6000 and 20000 gr/mol) in the casting solution concluded that this factor has a significant influence on membrane morphology, separation and permeation performance. Then, in the next step, UV photografting process was applied in the presence of acrylic acid (AA) for membrane surface modification (decreasing in pore size, giving negative charge to membrane surface and finally causing formation of NF membrane). This method has been applied by some researchers in order to modify membrane surface [8,12,13]. The goal of this research is to conduct a detailed investigation on effect of PEG MW and graft condition on membrane morphology and performance.

2. MATERIALS AND METHODS

2.1. Materials

Polysulfone (PSf, MW: 75000 Da) was supplied by Acros Organics and used as a membrane material. N-methylene-2-pyrrolidone (NMP) from Merck as a solvent for PSf was used without further purification. Poly(ethylene glycol) (PEG) with average molecular weights (200, 400, 600, 2000, 6000, 10000 and 20000 Da.) were purchased from Merck. Acrylic acid (AA) was purchased from Merck and used as received. Other chemicals were supplied from Merck.

2.2. Original Membrane Preparation

Original PSf membranes were prepared through phase inversion process using a homogenous polymeric solution containing PSf (17%), PEG (8% wt) and N-methyl-2-pyrrolidone (NMP) (75% wt). After achieving a homogenous and transparent solution, dope solution was cast using an adjustable casting knife on a glass plate. Then the glass plate bearing PSf solution film was immersed into water coagulation. After about 1 minute of phase inversion progress (solvent exchange between polymer and non-solvent), membrane is formed (see Figure 1). During phase inversion process, dissolving PEG in water causes formation of porous PSf membrane. This achieved membrane belongs to UF category of membranes.

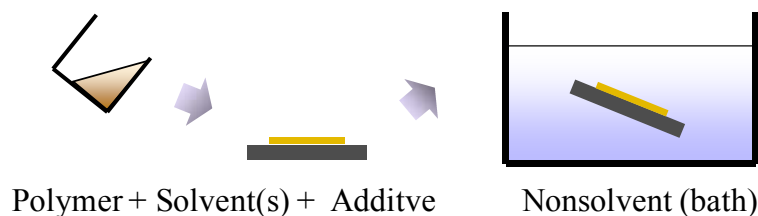


Figure 1: A schematic drawing of phase inversion method.

2.3. Membrane Modification

After fabrication of PSfUF membrane via phase separation method, membrane modification by UV-assisted grafting polymerization in the presence of AA, was performed. UV-induced grafting process, increases membrane wet ability and shifts membrane pore size distribution to a smaller size and makes NF membrane. A schematic drawing of UV irradiation chamber is shown in Figure 2.

3. RESULTS AND DISCUSSIONS

3.1. FT-IR Spectroscopy

The efficiency of UV-graft reaction was checked by FT-IR measurement. The spectra of membrane samples were compared before and after UV-irradiation treatment. In b, c and d spectra of Figure 3, there are two bands, one at 3300 cm^{-1} assigned for OH and another large

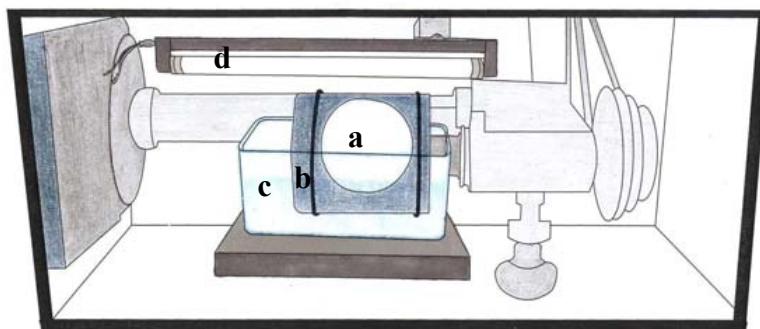


Figure 2: UV-Irradiation chamber including: (a) membrane sample, (b) rotating cylinder, (c) monomer solution, (d) UV-lamp.

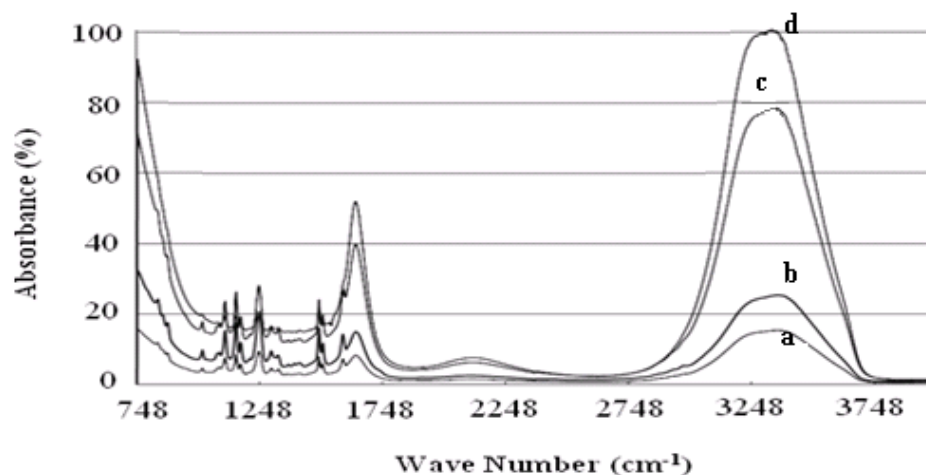


Figure 3: FT-IR spectroscopy of membranes: (a) origin membrane; (b) photografted membrane ($[AA]=6\%$) for 10min; (c) for 20min and (d) for 30min.

band at 1720 cm^{-1} due to C=O stretching of carboxylic group that indicate the success of photo polymerization. ATR/FT-IR spectra of modified membrane shows that by increase in irradiation time, absorbance peak intensity decreases that can be contributed to increase in AA deposition on the surface. Whilst in spectra of original membrane (a), there is no band at 3300 and 1720 cm^{-1} .

3.2. SEM Analysis

By means of SEM images, morphology changes in surface of prepared membranes, before and after photo-polymerization, are shown in Figure 4. Actually polymerization of monomers on the surface and depth of membrane pores leads to a decrease in the pore size as previously mentioned.

3.3. AFM Analysis

From AFM images of membrane surface, various morphological parameters can be obtained including membrane grain size and roughness. Two dimensional AFM images are shown in Figure 5. From these photographs, it can be observed that there is not a well defined

pore structure in membrane surface similar to that of track etching membrane [14] but their surface is more or less rough and of grains with different size. It is perceivable from this figure that by increasing in irradiation time, grain size decreases. There are several definition for roughness such as “the peak to valley distance” (the distance between the highest data point to the lowest data point of the surface), “the mean roughness” (the mean value of the surface relative to the center plane as formulated in equation 3) and “the root mean square roughness (RMS)” that is given by the standard deviation of the data. From 3-dimensional photographs of one original and modified membranes can be seen that by increasing the irradiation time, “the peak to valley distance” decreases and RMS roughness decreases from 6.4 to 2.3 nm . On the basis of information existent in references, asymmetric reverse osmosis and nanofiltration membranes feature small roughness parameters, ranging from 0.84 to 5.14 nm [15], so this roughness range confirms that membranes are in NF membrane category. The size of grain elements and surface roughness become lower and more uniform with increase in irradiation time, which is an evidence of decrease in membrane

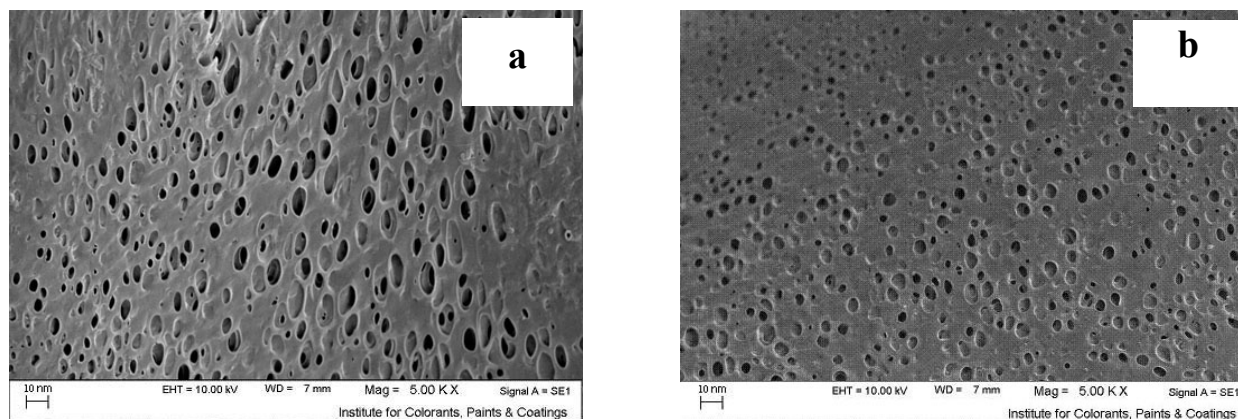


Figure 4: SEM images of membranes: (a) origin membrane; (b) photografted membrane ($[AA]=6\%$, $t_{irr}=30\text{ min}$).

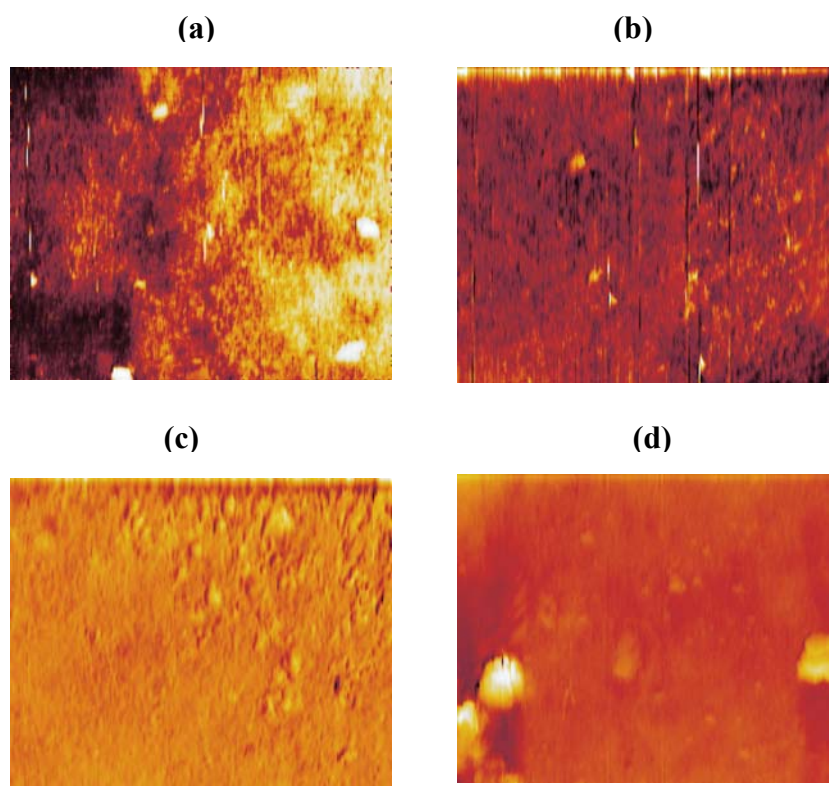


Figure 5: Two dimensional AFM images: (a) origin membrane; (b) photografted membrane ([AA] =6%) for 10 min; (c) for 20 min and (d) for 30 min in.

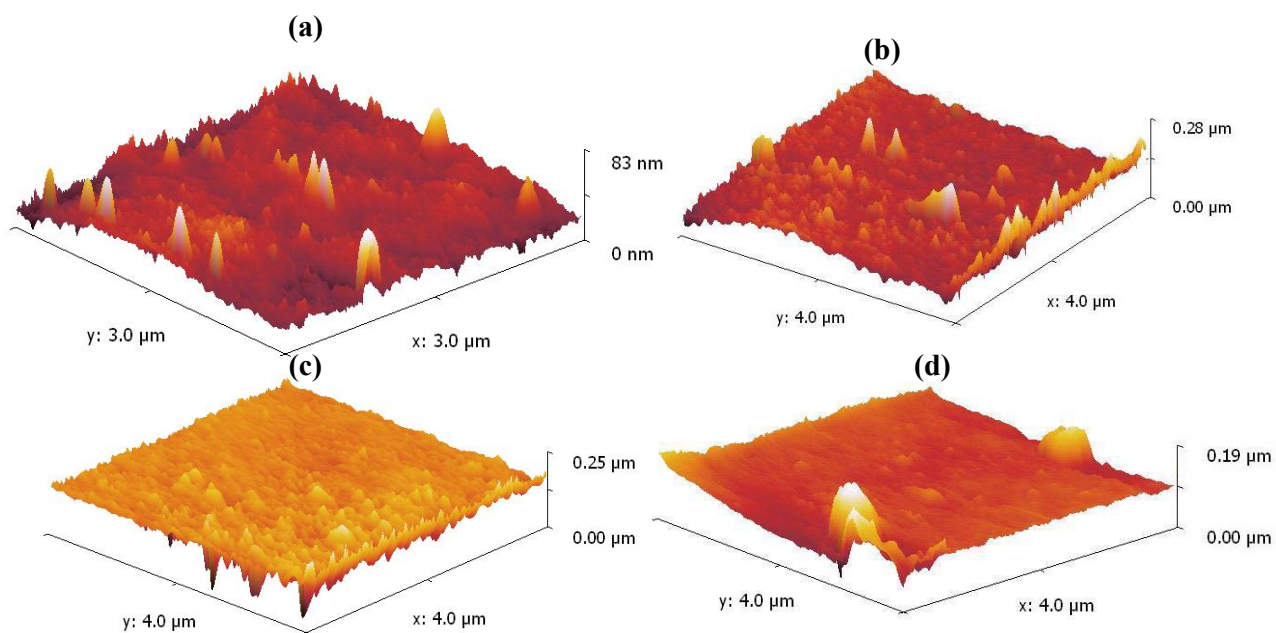


Figure 6: Three dimensional AFM images: (a) origin membrane; (b) photografted membrane ([AA] =6%) for 10 min; (c) for 20 min and (d) for 30 min in.

pore size since changes in roughness parameter is proportional to the changes in pore size [15-16]. This decrease in the surface roughness is an evidence of pore size decrease [15].

3.4. Filtration experiments

3.4.1. Flux Performance

Effect of additive MW and graft condition on PWF was investigated. Figure 7 shows effect of MW of PEG on PWF. As seen from figure, membrane which were formed from PSf/NMP solution without any additive (initial point in figure 7), exhibits no PWF at 300 kPa but applying PEG as pore former in casting solution, induces formation a porous structure in which PWF increases with increase in MW of pore former because of bigger tracks left out behind PEG dissolving in water during phase inversion process.

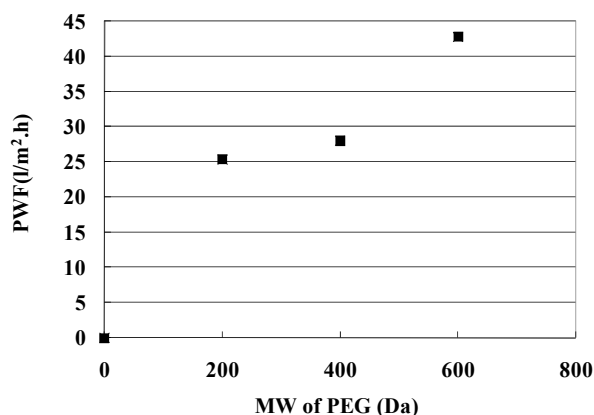


Figure 7: PWF of different membranes vs. Molecular weight of PEG additive.

Figures 8 and 9 show the effect of AA concentration and irradiation time on PWF respectively. Polymerization of AA on membrane surface causes formation of PAA around pores, reduction in pore size and consequently decline in PWF.

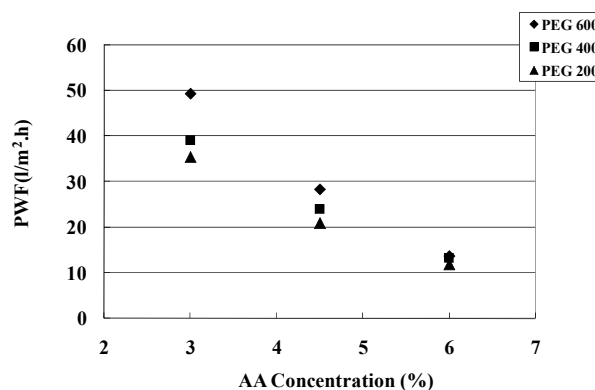


Figure 8: Effect of AA concentration on PWF in grafted membranes (t_{irr} = 30 min).

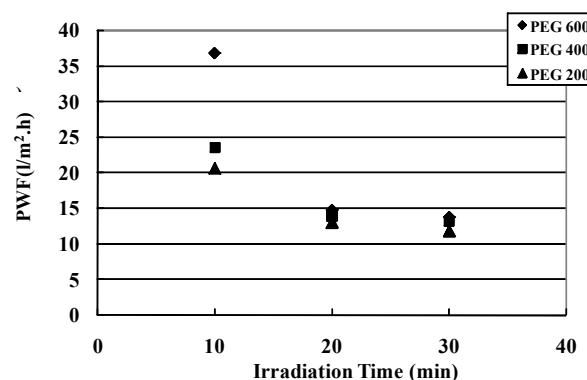


Figure 9: Effect of irradiation time on PWF of grafted membranes ([AA]=6%).

3.4.2. Rejection Performance

In rejection tests, feed solutions of two different metallic salts (Na_2SO_4 and NaCl) were filtrated and rejection of various salt solutions versus monomer concentration and irradiation time was illustrated in Figures 10 and 11 respectively. During graft process, intension of graft parameter leads to increase in negative charge density around pores, increase in repulsive force and finally increase in rejection to anions in solution.

It is worth noticing that the rejection related to every salt is different from others. Generally rejection decreases in the following order:



Since our negatively charged NF membrane reject electrolyte solutes with higher charge density ($\text{SO}_4^{2-} > \text{Cl}^-$). This order is according to Donnan effect [17].

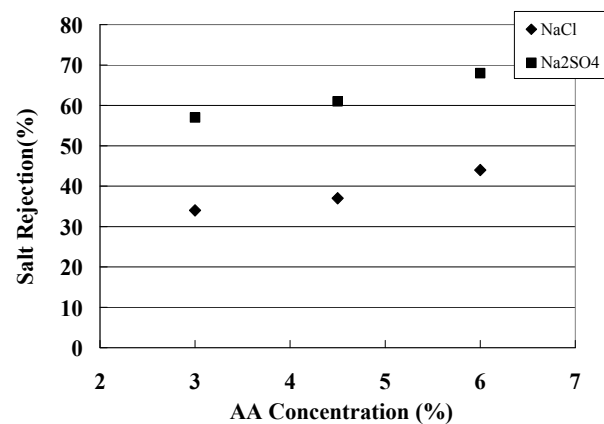


Figure 10: Rejection of electrolytes (Na_2SO_4 and NaCl) vs. AA concentration. (membrane with PEG200 additive, $t_{irr}=30$ min).

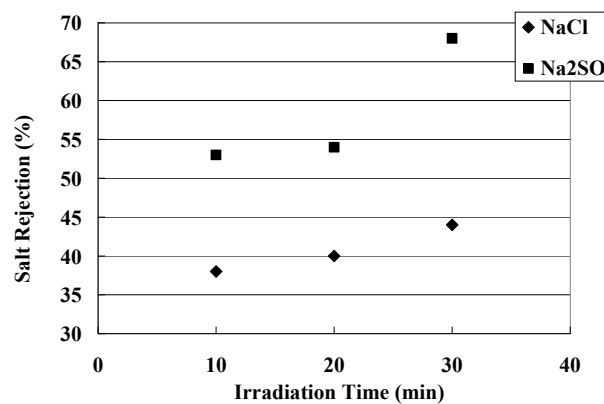


Figure 11: Rejection of electrolytes (Na_2SO_4 and CaCl_2) vs. irradiation time. (membrane with PEG200 additive, $[\text{AA}]_r=6\%$).

3.4.3. MWCO Measurement

Molecular weight cut off (MWCO) of a particular membrane corresponds to MW of neutral solutes having solute rejection beyond

90%. Here for measuring molecular weight cut-off (MWCO), four PEG solutions with MW of 2000, 6000, 10000 and 20000 Da in 50 ppm concentration were prepared. The analytical method for determining PEG concentration is given by Misra et al. [18]. Rejection behaviour of origin membranes composed of different MW of PEG (200, 400 and 600) was investigated and membrane pore size was estimated [19]. The results are shown in Figure 12. As seen from this figure, by increase the MW of PEG which was used in membrane preparation from 200 to 600 Da, MWCO and pore size increase from 6000 to 8000 Da and from 3.42 to 4 nm respectively.

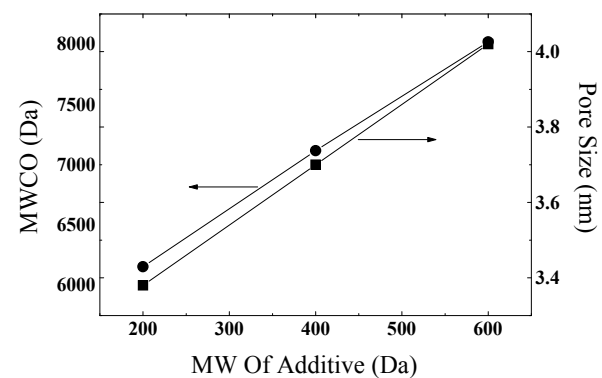


Figure 12: PEG Rejection and pore size of different unmodified membranes vs MW of PEG.

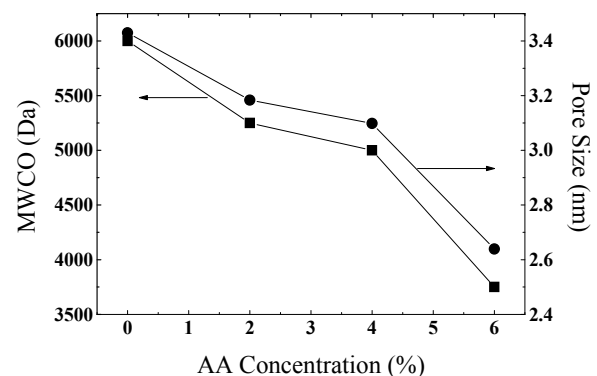


Figure 13: PEG Rejection vs. MW of PEG by modified membranes (PEG as additive is PEG-200, $t_{irr}=30$ min).

Effect of photo polymerization condition (monomer concentration and irradiation time) on PEG rejection was measured as well (see Figures. 13 and 14). Increase in irradiation time and AA concentration is followed by increase in PEG rejection and decline in MWCO. The most intensive graft condition ($[AA]=6\%$ and $t_{irr}=30$ min) results in a membrane with MWCO of 6000Da and pore size of 2.62 nm.

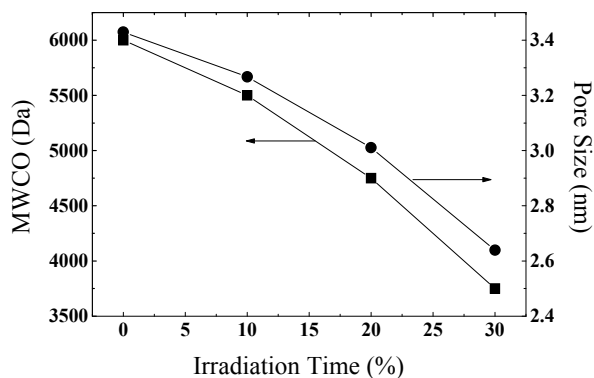


Figure 14: PEG Rejection vs. MW of PEG by modified membranes (PEG as additive is PEG-200, $[AA] = 6\%$ wt).

4. CONCLUSIONS

In this study hydrophilic nanofiltration membranes have been successfully fabricated using UV-induced grafting polymerization in presence of acrylic acid as a vinyl monomer. PEG was applied as pore former agent in casting solution as far as a membrane with no PEG, had no pore and no PWF. Results showed that PWF increases with an increase in MW of PEG because of increase in membrane pore size. In graft polymerization process, increase in graft intensity (monomer concentration and irradiation time) leads to decrease in pore size from 3.42 to 2.62 nm which is accompanied by PWF decrease, salt rejection increase and MWCO decrease. Prepared NF membranes have the high rejection to different salts which

demonstrates that these membranes carry negative charge on their surface. As a result from the experiments, the UV-graft polymerization not only can introduce carboxylic basic group onto the membrane surface, but also can decrease pore size of membrane. Occurrence and intensity of AA polymerization onto the membrane surface were confirmed by FT-IR spectroscopy. SEM images showed that grafting of acrylic acid on membrane surface decreases the size of pores. Polymerizing AA onto pore surface and pore walls leads to decrease in RMS surface roughness from 6.4 to 2.3 nm.

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