

Preparation of Low fouling Polyethersulfone Membranes by Simultaneously Phase Separation and Redox Polymerization

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Abstract. This paper presents preparation of low fouling PES membranes by non solvent induced phase separation (NIPS) coupled with redox polymerization. The membrane characterization included water permeability, morphology structure (by SEM) and surface chemistry (by FTIR). Water permeability measurements showed that the membranes have water permeability within the range 10-50 L/h.m².bar. Addition of PEG dan PEGMA into polymer solution increased water permeability, whereas blending redox initiator and crosslinker, MBAA in polymer solution decreased water permeability. Surface morphology of membranes by SEM showed that unmodified PES membrane had smaller pore size than PEG or PEGMA modified PES membranes. Furthermore, PES-PEG or PES-PEGMA membranes modified by blending with redox initiator and MBAA as crosslinker showed smaller pore size than unmodified membrane. FTIR analysis showed that all membranes have typical spectra of PES polymer; however no additional peak was observed for the membranes prepared with addition of PEG/PEGMA, initiator redox and also crosslinker. The addition of PEG/PEGMA, redox initiator and crosslinker resulted in membranes with high rejection and an acceptable flux as well as more stable due to relatively high fouling resistance.

Keywords: fouling, NIPS, redox polymerization, low fouling UF membranes

1. Introduction

UF membrane technology has been applied in various industries such as water and wastewater treatment, beverage and food processing, medicine and pharmaceutical industry [1-4]. But along with the increasing application of ultrafiltration, fouling which causing significant loss of performance with respect to flux and often selectivity is still the biggest problem. Furthermore, fouling can also shorten the membrane life.

Even though several methods to control fouling of the membrane have been developed [5,6], but in many cases fouling is determined by the membrane itself [7,8]. Therefore, preparation of low fouling membranes is urgently needed. The hydrophobic character of PES polymer has driven modification of PES membrane. Three different approaches have been developed to increase the hydrophilicity of PES membranes, namely (i) modification of polymer membranes (pre-modification) [9] (ii) mixing the polymer membranes with additives [10-11] and (iii) modification of the surface after membrane



preparation (post-modification) [12]. However, each approach has drawbacks such as takes a long time, stability of additives in the polymer matrix is low, and also some treatments can cause changes in membrane structure. Integration of NIPS and chemical modification is the best solution because it is a simple and effective way to make low fouling membranes with high stability. Development of NIPS modified by redox polymerization is expected to be able to synthesize low fouling UF membrane in a single process with high stability of hydrophilic character.

In general, the objective of this research is to synthesize low fouling UF membranes by using NIPS integrated with redox polymerization. In particular, this research investigates the effects of additives, initiator redox and crosslinking agent on the characteristics and stability of the resulting membranes. In addition, fouling behaviour is also investigated.

2. Experimental Method

2.1. Materials

PES polymer Ultrason E 6020P was purchased from BASF. N-methyl-2-pyrrolidone (NMP) was purchased from Merck. Polyethylene glycol (PEG) and N,N'-methylenebisacrylamide (MBAA) were purchased from Sigma-Aldrich. Poly(ethyleneglycol) methacrylate (PEGMA 400) was purchased from Polysciences. TEMED (N,N,N',N'-tetramethylethylenediamine), ammonium peroxydisulfate (APDS), potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate dihydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) were purchased from Fluka Chemicals. Bovine serum albumin (BSA) was purchased from ICN Biomedicals.

2.2. Membrane preparation

PES polymer was dissolved in NMP. PEG and PEGMA were then added to the polymer solution. In addition, oxidizing agent (TEMED) and MBAA were also added into polymer solution. The homogeneous polymer solution was left without stirring until no bubbles are observed. The polymer solution was cast with a thickness of 200 μm using a steel casting knife on a glass substrate. Thereafter, the proto-membrane was solidified by immersing in a coagulation bath containing water and reducing agent (APS) for one hour. The resulting membranes were washed and soaked in the water for 24 h before drying.

2.3. Membrane characterization

Membrane characterization included water permeability, morphology structure (by SEM) and surface chemistry (by FTIR). Measurement of water permeability followed our previous publication [18]. The top surface morphology of the membrane was observed by using a Quanta 400 FEG (FEI) environmental scanning electron microscope (ESEM). Before observation, sputtering to coat the outer surface of the sample with gold/palladium should be conducted. The membrane surface chemistry was analyzed by using the Varian 3100 Fourier transform infrared spectroscopy (FTIR) Excalibur series.

3. Results and Discussion

3.1. Water permeability

Measurement of water permeability was performed for unmodified and modified membranes. The effects of PEG, PEGMA, redox initiators and crosslinking agent were investigated. The results are depicted in Figure 1.

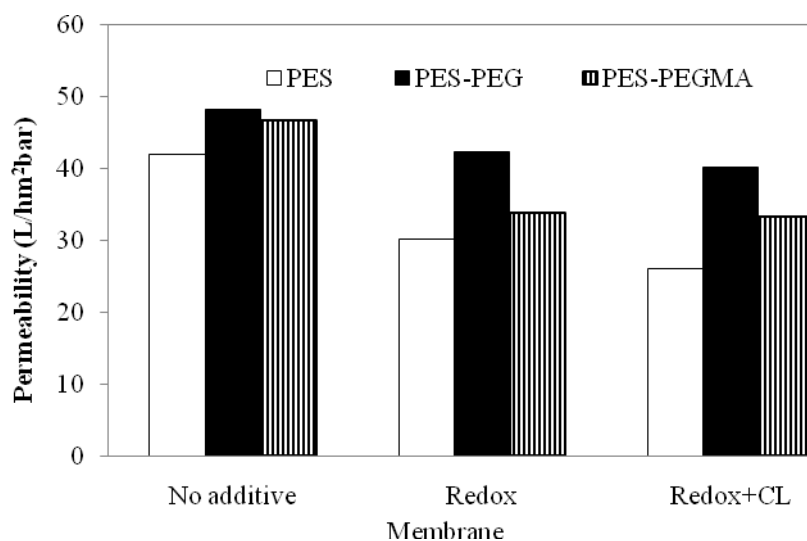


Figure 1. Permeability of unmodified membrane and modified membranes

The water permeability data presented in Figure 1 suggest that the resulted membranes are in the range of UF membranes, which have water permeability of 10–50 L/h.m².bar [1]. Addition of PEG and PEGMA increased water permeability. PEG is a hydrophilic polymer, which will increase the hydrophilic character of PES membrane. In addition, the presence of PEG into polymer solution may favor the formation of larger pores and porosity, resulting in an increase of water flux. This is in agreement with the results obtained by previous authors [13–16]. Similar phenomenon was obtained using PEGMA as the additive and in agreement with the result obtained by Susanto et al. [12].

Blending redox initiator in polymer solution decreased water permeability of modified membrane. The presence of initiator may stimulate the chemical reaction which may reduce pore size. Similar phenomenon is also seen for MBAA addition in the polymer solution. The addition of crosslinker may form a network structure. This result is in agreement with the experiment conducted by Peeva et al. [17]. Crosslinking with MBAA yielded denser hydrogel layers on the porous base membrane and consequently decrease water permeability.

3.2. Surface morphology

Figures 2, 3 and 4 show surface morphology of unmodified PES and PEG/PEGMA modified PES membranes. It is observed that all membranes had pore sizes within the nanometer range. Comparing the unmodified PES and modified PES membranes by PEG or PEGMA addition, it is seen that all membranes had significant difference in pore size. Similar with previous authors, unmodified PES membrane had smaller pore size than PEG or PEGMA modified PES membranes [14,18]. These results support previous explanation about water permeability of membranes. PES-PEG or PES-PEGMA membranes modified by blending with redox initiator and MBAA as crosslinker showed smaller pore size than unmodified membrane. Redox initiator generated radicals on the membrane surface to create new functional groups on the membrane surfaces [19].

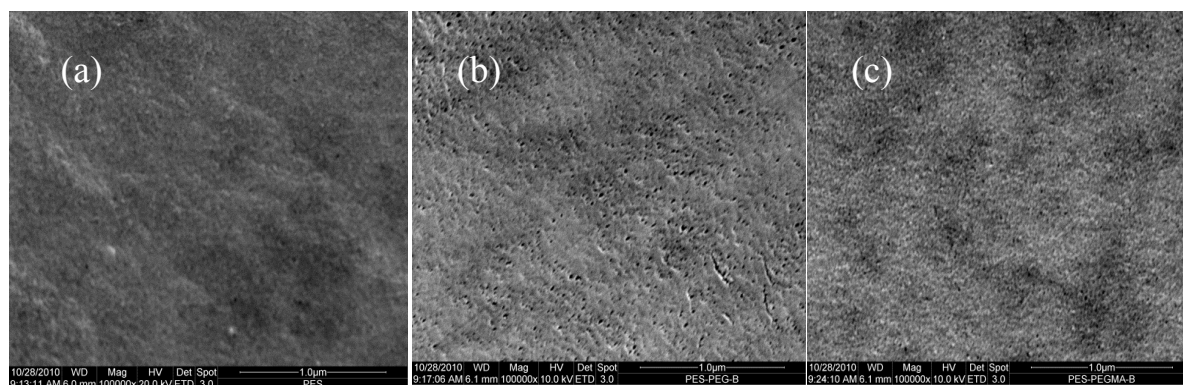


Figure 2. Surface morphology of membrane: (a) PES only, (b) PES-PEG, (c) PES-PEGMA

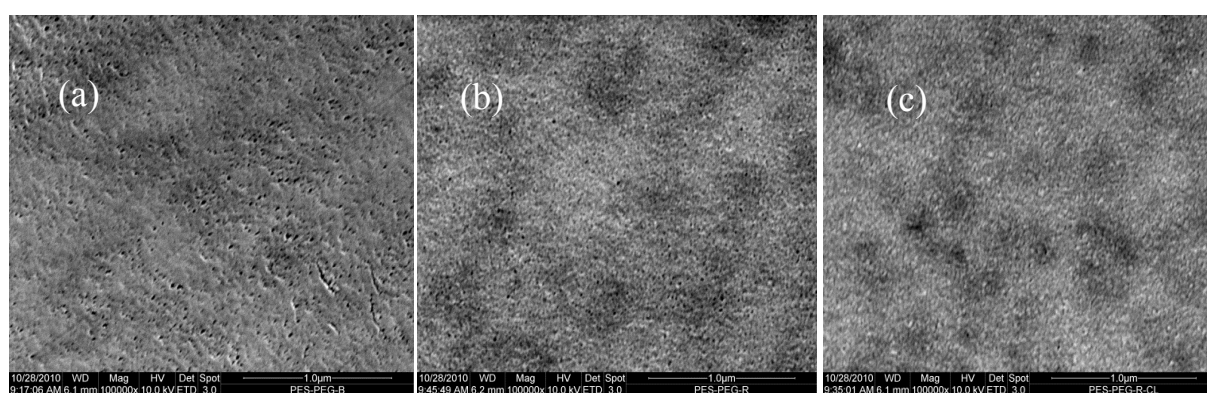


Figure 3. Surface morphology of membrane: (a) PES-PEG, (b) PES-PEG-R, (c) PES-PEG-R-CL

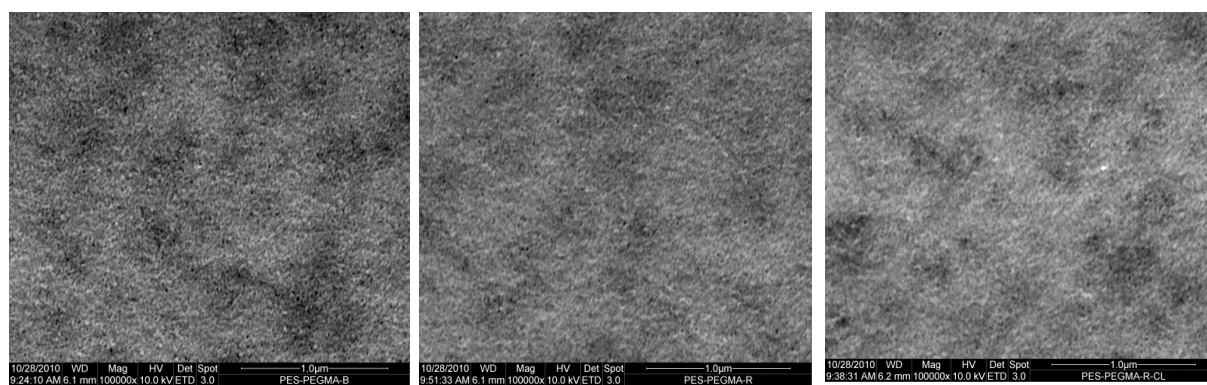


Figure 4. Surface morphology of membrane: (a) PES-PEGMA, (b) PES-PEGMA-R, (c) PES-PEGMA-R-CL

3.3. Surface chemistry

Surface chemistry of membrane was characterized by FTIR. All membranes showed typical spectra of PES, i.e., aromatic bands at 1578 and 1485cm^{-1} from the benzene ring and C–C bond stretch and aromatic ether band around 1240cm^{-1} (IR spectra are not shown). However no additional peak was observed for the membranes prepared with addition of PEG, PEGMA and MBAA. The reason for this result would be overlapping bands of the strongest bands for PEG and PEGMA with bands for PES. Indeed, a significant increase in absorbance at $\sim 1105\text{cm}^{-1}$, due to additional intensity of C–O bond stretch from PEG was observed. This confirms the presence of additives in the membrane polymer matrix. Addition of PEGMA to the PES membrane showed a new band associated with the

C=O vibration in the ester molecule, which is located at 1714 cm^{-1} . Such overlapping band is also found in previous publications by Susanto and Ulbricht [18] and Belfer et al. [20].

4. Conclusion

Modification of PES UF membranes by redox polymerization using hydrophilic monomers (PEG/PEGMA), initiator redox and also MBAA as crosslinker has been successfully developed. Water permeability measurement suggested that all membranes should be UF membrane. Addition of PEG and PEGMA increased water permeability. By contrast blending redox initiator and crosslinker into polymer solution decreased water permeability. Surface morphology of membranes indicated that the pore sizes are within the nanometer range. Unmodified PES membrane had smaller pore size than PEG or PEGMA modified PES membrane. Furthermore, PES-PEG or PES-PEGMA membranes modified by redox initiator and MBAA showed smaller pore size than unmodified membrane. FTIR analysis showed that no additional peak was observed for the modified membranes. The fouling resistance of unmodified and modified membranes are under evaluation.

5. References

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