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Preparation of acrylonitrile-butadiene-styrene membrane : Investigation of solvent/nonsolvent type and additive concentration

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Abstract−In the present study, preparation of acrylonitrile-butadiene-styrene (ABS) membrane was investigated via phase inversion method. ABS membrane is sensitive to preparation conditions. Therefore, the effect of solvent/nonsolvent type and concentration of additive and ABS was evaluated on the morphology, tensile strength and car wash wastewater treatment. Polyethylene glycol was used as an additive. The results show that nonsolvent type significantly affects the morphology and consequently the flux and rejections of the pollution indices. Increasing concentration of additive and ABS in the casting solution leads to formation of denser and thinner membranes that have lower flux and higher rejections of the pollution indices.

Keywords: Copolymers, Mechanical Properties, Membranes, Morphology, Separation Techniques

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) copolymer is widely used due to its good mechanical properties, chemical resistance, relatively low cost and good processing characteristics [1]. Among various applications, there are some researches on the preparation of ABS membrane in two forms of blended [2-7] and mixed matrix [8,9] membrane. These membranes were prepared mostly using solution casting and solvent evaporation method.

Phase inversion method induced by immersion precipitation is a well-known and relatively simple technique for preparation of asymmetric polymer membranes [10]. In this technique, the presence of at least three components of polymer, solvent and nonsolvent is essential. A polymer solution is prepared, cast and then immersed into a nonsolvent coagulation bath. The crucial factors in the preparation of membranes are the phase equilibrium between different components in the coagulation bath and mutual diffusivities between solvent and nonsolvent during the solidification process [10].

Considering the effect of various parameters in immersion precipitation technique, selecting the type of solvent/nonsolvent pair is the first step. Due to the easy accessibility of water, it is a most common nonsolvent. However, Lickly et al. [11] reported the migration of acrylonitrile (AN) from ABS to water especially at high temperatures. Thus, considering other nonsolvents is proper for this purpose.

In the present study, heptane (C7) was used as nonsolvent due to the relatively low migration of AN to it [11]. Hexane (C6) was also used as nonsolvent because of its relative similarity with heptane. On the other hand, two solvents were also applied. Therefore, different solvent/nonsolvent pairs were selected to examine their effects on ABS membrane. Morphology and tensile strength of the membranes were investigated. The performance of the membranes was evaluated by car wash wastewater treatment.

EXPERIMENTAL

1. Materials

Acrylonitrile-butadiene-styrene was supplied from Tabriz Petrochemical Company, under CHEIL license. Also, polyethylene glycol (PEG, M_w=20,000) and 1-methyl-2-pyrrolidone (NMP) were purchased from Merck as an additive and a solvent, respectively. Dimethyl acetamide (DMAc) was supplied from Sigma-Aldrich as a solvent. Car wash wastewater was obtained from a local car wash and was used as the treatment test feed. The values of turbidity, total dissolved solids (TDS) and chemical oxygen demand (COD) of the wastewater were in range of 151-159 NTU, 498-780 mg/*l* and 870-1,230 mg/*l*, respectively.

2. Membrane Preparation

Homogeneous solutions of ABS in two different solvents of NMP

Table 1. Composition of the prepared membranes

Membrane	ABS (wt%)	PEG (wt%)	Solvent (wt%)	Solvent	Nonsolvent
M1	20	0	80	NMP	C7
M2	20	6	74	NMP	C7
M3	20	10	70	NMP	C7
M4	17	6	77	NMP	C7
M5	17	10	73	NMP	C7
M6	20	10	70	DMAc	C7
M7	17	10	73	DMAc	C6
M8	20	10	70	NMP	C6
M9	20	0	80	NMP	Water
M10	20	10	70	NMP	Water

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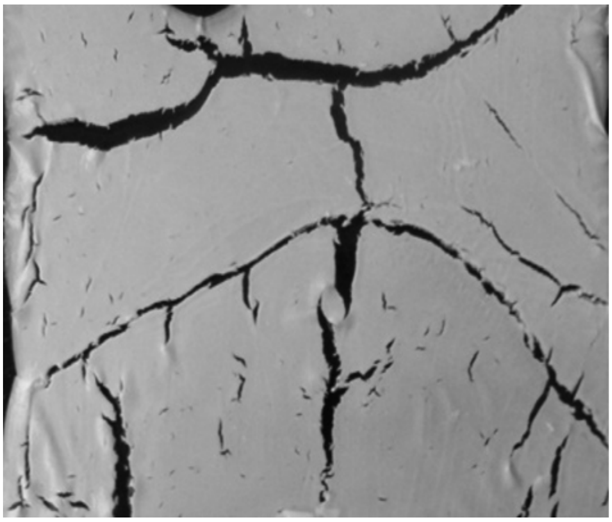

Fig. 1. Undesirable effect of methanol as nonsolvent on ABS membrane structure with respect to surface visual observation photograph.

and DMAc were prepared while PEG was used as an additive. The solution was cast on a glass plate by using a film applicator. The glass plate was immediately moved to the coagulation bath containing the nonsolvent for immersion precipitation. Different compositions of the casting solution and also type of the solvent/nonsolvent pair for each membrane are listed in Table 1.

It is notable that methanol, ethanol and combination of them were also examined as nonsolvent besides three mentioned nonsolvents of C7, C6 and water. But, as the casting solution was immersed in their bath, unusual cracks were appeared at the membrane surface as observed in Fig. 1. Therefore, the membranes could not be used for the characterization.

3. Membrane Characterization

3-1. Fourier Transform Infrared (FTIR) Spectroscopy

Both membranes prepared in water and C7 coagulation baths were characterized by Thermo Nicolet Avatar 370 for spectroscopic investigation. The spectra were prepared with 4 cm^{-1} resolution between 4,000 and 500 cm^{-1}.

3-2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to prepare cross-sectional and surface images of the synthesized membranes. To view the cross section, the membranes were cooled in liquid nitrogen and then fractured. Prior to preparing the images, all membranes were sputter coated with gold for producing good electric conductivity. Electron micrographs were obtained with a KYKY-EM3200 microscope.

3-3. Tensile Strength Test

To prepare membranes for tensile strength test, all the membranes were cut in the same shape. The samples were stretched to the breaking point with Zwick tensile test machine at a speed of 1 mm/min. For each test, three samples were used and the average values for tensile strength were reported.

3-4. Flux and Retention

Performance of the prepared membranes was evaluated by using a membrane setup. Flat sheet membranes with 16 cm^2 effective area were used in a stainless steel membrane module. The permeate flux and also the rejection of pollution indices of car wash wastewater were evaluated at the transmembrane pressure (TMP) of 2 bar and room temperature. The feed and permeate were analyzed for the pollution indices of turbidity, TDS and COD to calculate the rejections.

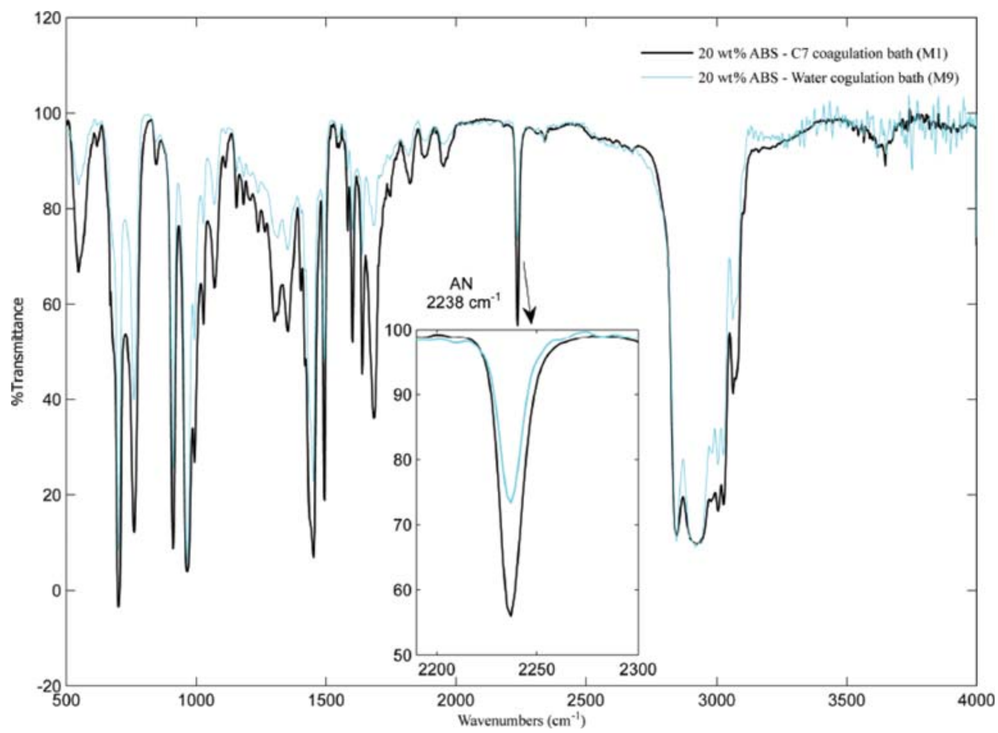

Fig. 2. FTIR spectra of ABS membranes prepared in water and C7 coagulation baths.

RESULTS AND DISCUSSION

1. FTIR Analysis

The FTIR spectra of M1 and M9 are shown in Fig. 2 to investigate the existence of AN migration from ABS to water. With respect to this figure, the peak at 2,238 cm^{-1} is ascribed to nitrile group of AN. Furthermore, the peaks at 1,602 and 1,494 cm^{-1} are related to the ring modes of styrene, and the peaks at 967 and 911 cm^{-1} refer to the butadiene component [12]. The FTIR spectra were zoomed in on the characteristic peak of AN to investigate the migration effect. The intensity alteration with change in coagulation bath is observable, that is, the AN migration from ABS to water occurs.

2. Morphological Studies of the Membranes

The cross sectional SEM images of membranes prepared using NMP solvent are shown in Fig. 3. When the casting solution is immersed into the nonsolvent bath, the precipitation starts due to low miscibility between the polymer and nonsolvent [13]. NMP is an aprotic amide solvent [14]. Aprotic amide solvents generally have a very high mutual affinity with water [15]. Thus, due to this very high mutual affinity, the membranes prepared with using solvent/nonsolvent pair of NMP/water, i.e., M9 and M10, have a finger-like structure with respect to Fig. 3 [16]. On the other hand, NMP has a sparing solubility in C7 [17]; consequently, the NMP/C7 pair creates denser structure, i.e., M1 and M3 structures, in comparison with NMP/ water pair [16].

In water coagulation bath, the addition of PEG can lead to a dual influence on morphology of the membrane. Presence of hydrophilic PEG as a material with nonsolvent properties can increase thermodynamic instability, which causes instantaneous demixing and thus improves final membrane porosity. From another point of view, PEG, especially when used at high molecular weight, increases the viscosity of the casting solution. Higher viscosity creates denser struc-

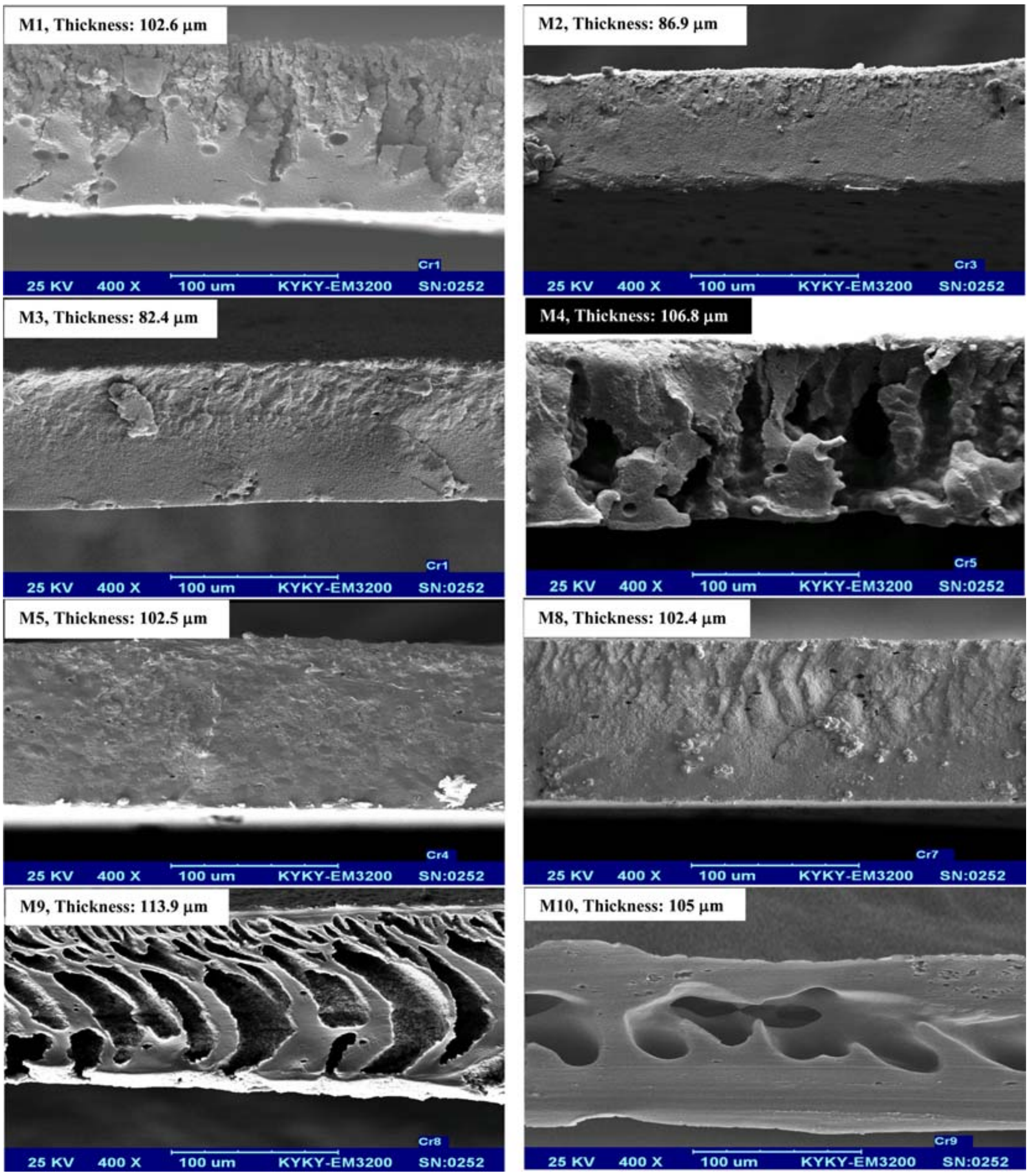

Fig. 3. Cross sectional SEM images of some of prepared membranes.

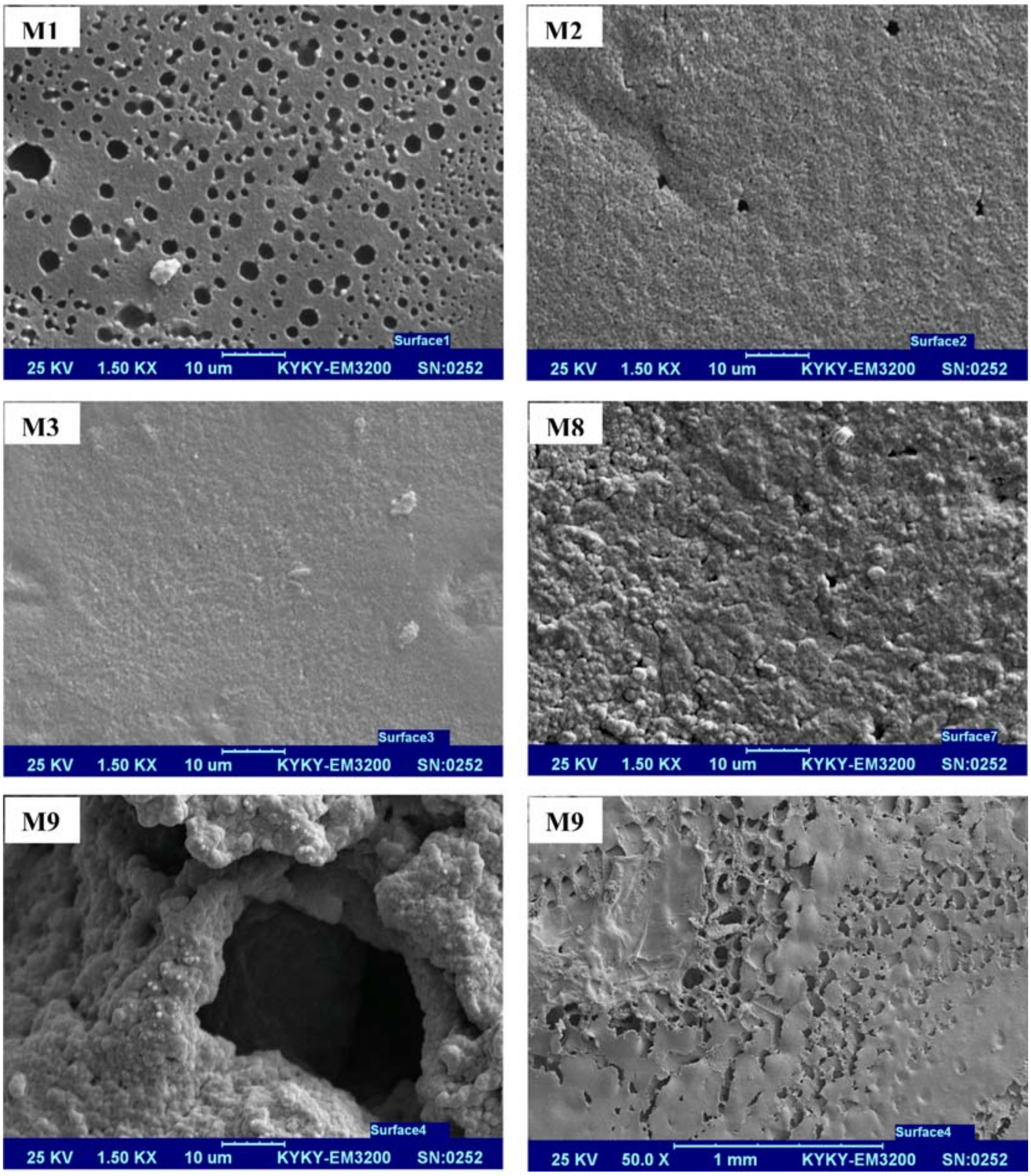

Fig. 4. Surface SEM images of some of prepared membranes.

ture via decreasing exchange rate of solvent/nonsolvent pair [18, 19]. In this study, PEG had high molecular weight and was applied at the concentration levels of 6 wt% and 10 wt%. Therefore, the effect of viscosity increase was dominant. Higher viscosity decreased the diffusion rate of C7 in the cast film in order to be exchanged with NMP. Lower exchange rate of the solvent/nonsolvent pair reduced the growth rate of initial nuclei and formed a denser structure. Thus, for both cases of ABS/NMP/C7 and ABS/NMP/water, increasing the PEG concentration from 0 wt% to 10 wt% resulted in decreasing the membrane porosity and thickness.

Cross sectional images of M4 and M5 in comparison with those of M2 and M3 show the effect of ABS concentration on the final membrane structure. Indeed, higher ABS concentration increases viscosity of the casting solution, which directly slows the demixing process in the coagulation bath. Delayed demixing reduces the growth rate of nuclei in the structure during phase inversion. This causes a denser structure to form. Accordingly, a higher ABS concentration in M2 and M3 resulted in denser and thinner membranes. This result is in agreement with other researchers' findings [20].

Comparison among the surface SEM images of M1, M2 and M3 with regarding Fig. 4 confirms the reduction of porosity with addition of PEG. Comparison of the surface SEM images of M9 with M1 proves the negative effect of the AN migration to water coagulation bath on the membrane structure during the precipitation process. This phenomenon is completely observable in the surface SEM image of M9 with lower zoom of 50X in Fig. 4.

Fig. 5 shows the surface and cross-sectional SEM images of M6 and M7. DMAc is another aprotic amide solvent in addition to NMP [14]. Regarding recent figures, a comparison of the images of M3 with M6, M8 and M10 shows the membrane morphology depends particularly on type of the nonsolvent and using different solvents for same nonsolvent does not change it [21].

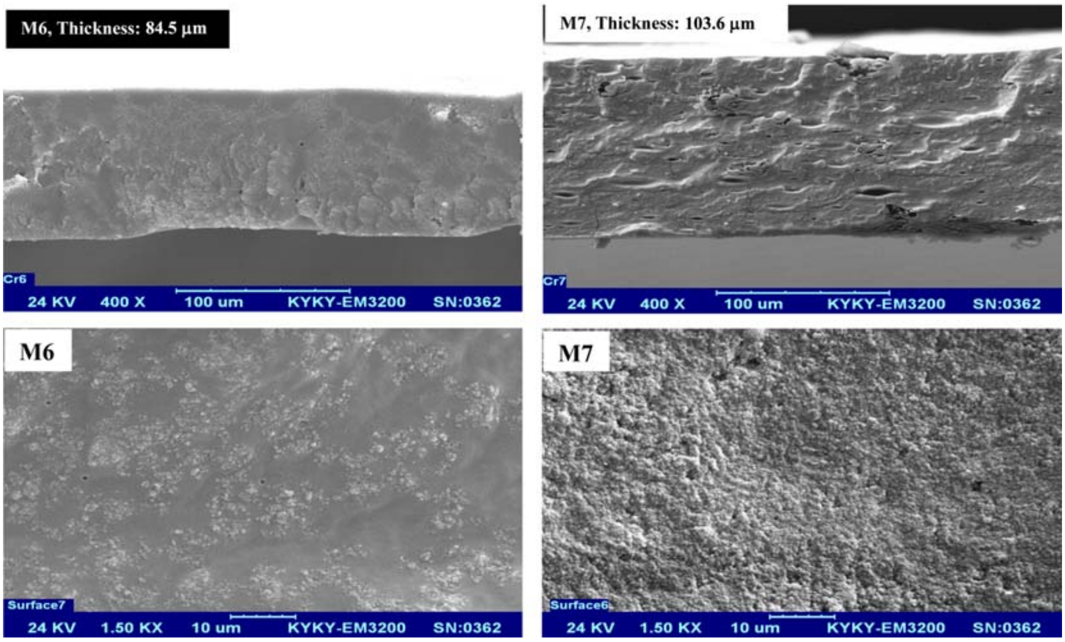

Fig. 5. Surface and cross sectional SEM images of M6 and M7.

3. Mechanical Property of Membrane

Strength of the membranes is influenced by the membrane porosity. Exactly, existence of the pores with larger size in the sublayer causes less membrane mechanical strength [22]. Therefore, the porosity reduction leads to improved tensile strength of the membranes. Tensile strength of the prepared membranes is shown in Table 2. The obtained results for tensile strength are consistent with the trend of variation of porosity in the membranes. The results demonstrated that denser structure of the membranes prepared in C7 and C6 coagulation bath required higher forces for the rupture. Whereas, finger-like pores resulted in weaker structure for the membranes prepared in water coagulation bath. On the other hand, increasing both ABS and PEG concentrations improved tensile strength of the membrane via reduction of the membrane porosity.

4. Membrane Performance

To study the performance of the prepared membranes, permeation tests were carried out to find the permeate flux and rejection of the pollution indices. The influence of type of solvent and nonsolvent and also concentration of ABS and additive on the stable flux are presented in Table 2. Rejections of the pollution indices are shown in Fig. 6. With comparison of performance of M10 with M8 and M3 and also M9 with M1, it can be concluded that more porous membranes prepared at water coagulation bath have higher stable flux and lower rejection percentages. Consequently, these findings

Table 2. Properties of the prepared membranes

Membrane	Tensile strength (MPa)	Stable flux (l/m$^2\cdot$h)
M1	8.05±0.03	75.5±2.2
M2	8.71±0.04	34±0.8
M3	9.83±0.05	30.2±1
M4	8±0.03	56.6±0.4
M5	8.23±0.06	45.3±0.7
M6	9.46±0.03	32.9±0.9
M7	8.07±0.04	58.1±0.5
M8	8.21±0.03	52.8±1.6
M9	7.13±0.21	188.7±5.2
M10	7.93±0.04	151±4

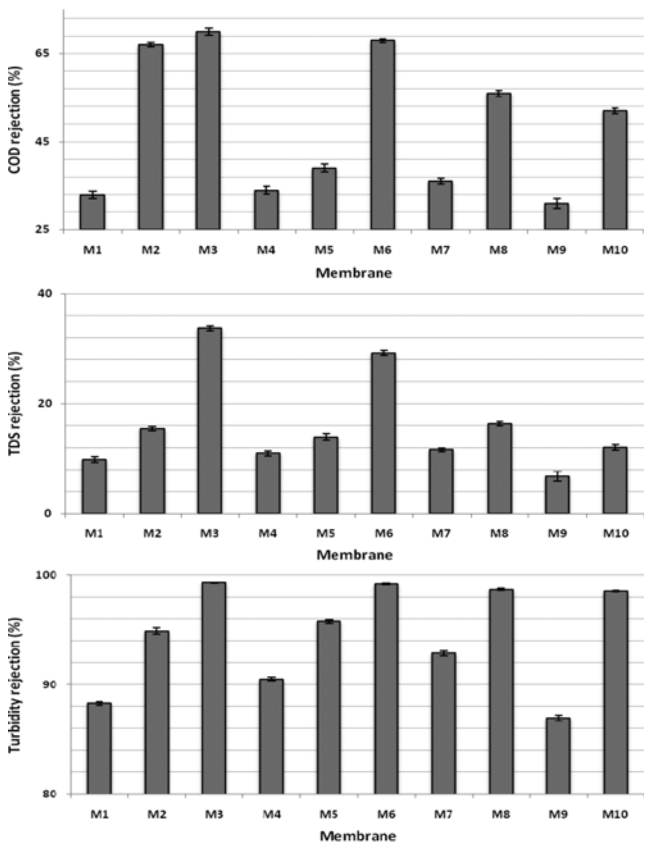

Fig. 6. Rejection of the pollution indices of car wash wastewater.

confirm the results of cross sectional SEM images. On the other hand, relatively alike performance of M3 and M6 proves almost similar effect of NMP and DMAc as solvent on the membrane structure. According to Table 2 and Fig. 6, the most similar membrane to M3 due to performance is M6. Comparison of the performance of M4 with M2 and M5 with M3 demonstrates that increasing the ABS concentration increases the rejection percentages and decreases the stable flux. For example, COD rejection increases from 34% for M4 to 67% for M2. Addition of high molecular weight PEG has similar effects on the performance of the prepared membranes in both water and C7 coagulation baths. Thus, increasing PEG concentration at constant ABS concentration decreases the stable flux and increases the rejection percentages. Comparison of the performance of M1 with M3 proves clearly the key role of PEG as an additive. Accordingly, COD, TDS and turbidity rejection increases from 33 to 70%, 9.9 to 33.66% and 88.28 to 99.31%, respectively. However, stable flux decreases from 75.5 to 30.2 $l/m^2 \cdot h$. Generally, these logical trends are consistent with both cross-sectional and surface structures of the membranes.

CONCLUSION

The effects of solvent/nonsolvent type and concentration of additive and ABS on the characteristics of ABS membranes such as the permeate flux, rejection of the pollution indices and morphology were studied. The results show:

a. According to FTIR spectra and surface SEM images, the AN migration occurs in water coagulation bath.

b. The shape of the pores and porosity were affected by the solvent/nonsolvent pair. So, high mutual affinity NMP with water created the finger-like pores in the sublayer. On the other hand, low mutual affinity of NMP with C7 led to formation of denser structure.

c. Denser and thinner membranes were prepared by increasing concentration of PEG and ABS in the casting solution.

d. Higher tensile strength of the membranes issued from lower porosity in the structure.

e. Denser membranes had lower flux and higher rejection of the pollution indices of car wash wastewater.

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