



Investigation on membrane morphological and chemical properties changes at different reaction times and its effect on dye removal

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ABSTRACT

The thin film composite (TFC) membranes were prepared and examined under different reaction times between piperazine and trimesoyl chloride. The physical and chemical properties of the membranes produced were investigated and related to their performance in terms of flux and rejection of methylene blue. Morphological studies were performed with Atomic Force Microscope (AFM) to determine the membrane's surface roughness, whereas chemical properties (bonding ratio of hydroxyl and carbonyl) of the membranes were evaluated based on Fourier Transform Infrared (FTIR). It was found that the interfacial polymerization (IP) process was almost instantaneous in which the dense film layer was developed within 10 s of reaction time. Longer reaction time (10–30 s) reduced the flux through film growth, whereas 50–70 s further reduced the flux due to polymer crosslinking. The AFM images showed that the membrane roughness increased steadily with the reaction time and formed supernodes on membrane surface. The formation of supernodes at elongated reaction time imposed higher diffusional resistance to the membrane with minimum improvement of rejection due to the poor packing density of nodules aggregate. On the other hand, at very short reaction time (5 s), the membrane produced had the highest flux. However, the membrane produced at 5 s exhibited poor rejection of methylene blue and poor reproducibility due to the uncontrolled instantaneous IP. Besides, the prepared polypiperazinamide membrane showed good fouling resistance towards cationic dye.

Keywords: Interfacial polymerization; Nodular structure; Membrane; AFM; Bonding ratio; Thin Film Composite Membrane; Polyamide; Nanofiltration; Dye; FTIR

1. Introduction

Thin film composite (TFC) polyamide membrane is a widely used membrane in nanofiltration mainly due to its superior hydrophilicity and it could be operated under wider range of pH [1]. Besides, TFC membrane has an

advantage of structure tailoring for both the support and skin layer [2]. Recent research focused on the molecular design of the thin film by employing different monomer such as hexamethylene 1,6-diisocyanate and hexamethylene 1,6-diisocyanate [3], ethylenediamine [4], 5-isocyanato-isophthaloyl chloride [5] and poly(dimethylsiloxane) [6] with the aim to produce membranes with higher flux and superior rejection capability.

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There are continuous efforts to produce membrane with both high flux and rejection by producing super thin and dense separating layer [7]. However, as the membrane becomes denser, a concomitant flux reduction will be experienced, a condition which is not favoured for nanofiltration. Membrane performance could be enhanced if the morphology of the separating layer or the microstructure can be fully understood. Recently, some work had been carried out to study the microstructure of the separating layer. Freger [8], for example, suggested that the central fraction of the skin layer had the highest density and played the major role as selective barrier. The high flux RO explained the phenomenon of increased flux was attributed to the thinner dense central layer instead of the increased surface roughness. The relationship between membrane physicochemical properties and performance was studied by Yu et al. [9]. They found that surface charge was the controlling factor for dye removal at low dye and salt concentrations, while surface roughness was more influential at higher dye concentration. Kong et al. [10] added co-solvent to the nonpolar organic solvent to obtain the skin layer with different chemical and physical properties. While most literature shows that higher roughness gives higher flux, the bulk of the literature mentioned above are limited to macroscopic study.

Chemical and microscopic study on the skin/separating layer is needed, so that a more effective molecular design can be carried out to obtain optimum separating layer. Khulbe et al. [11] thoroughly reviewed the works on characterization of synthetic polymeric membranes using Atomic Force Microscope (AFM). The nodular structure on the flat sheet membrane and hollow fibre membrane had been reported based on AFM. The works carried out by Mansourpanah et al. [12] and the group provided some detailed studies on the effect of surfactant on the membrane performance. It was found that membrane with low surfactant content exhibited nodular surface structure. Saha and Joshi [13] found that the PIP-TMC membrane showed dispersed granular surface with visible open-pore structures; these structures varied with different monomers combination. Liu et al. [5] tried out the new TFC from isocyanato-isophthaloyl chloride and *m*-phenylenediamine. The membranes exhibited small-scale surface roughness of a typical nodular (ridge and valleys) structure, which led to a better resistance of membrane fouling.

Therefore, it becomes our focus in this work to study the physical and chemical properties of interfacial polymerized membrane under different reaction times based on its functional group and microstructure. The changes of these properties were related to its membrane performance in terms of flux and rejection. Since interfacial polymerization (IP) taking place

at the close interface is critical to obtain nodular structure, this work was carried out under surfactant free condition.

2. Materials and methods

2.1. Membrane preparation

The TFC membranes were prepared by interfacial polymerized aqueous diamine containing 2% (w/w) piperazine (Merck, USA) with 0.1% (w/v) trimesoyl chloride (Merck, USA) in Hexane (Merck, USA) solution. Ultrafiltration polysulfone which is the porous support layer was dipped into the diamine solution for 10 min, drained by the rubber roller, and followed by the dipping in the Hexane solution at predetermined time. The reactions were carried out at different times of 5, 10, 30, 50 and 70 s, and followed by drying at room temperature (25°C) for at least 24 h.

2.2. Membrane permeation test

The membrane permeation tests were carried out using the Amicon 8200 stirred cell. The effective area of the membrane mounted under the cell was 28.27 cm² (excluding the area cover by the O-ring). Throughout the experiment, the stirring speed of the stirrer was fixed at 350 rpm using the controllable magnetic stirrer (Heidoph MR3000D, Germany). The membrane permeation test on 10 ppm methylene blue (Merck) was carried out at 350 kPa and the concentration of methylene blue was determined using visible spectrophotometer (Thermo Spectronic, USA, Model GENESYS 20).

2.3. Atomic force microscope

The average surface roughnesses of the membranes were measured using an AFM (Park Scientific, Korea, XE-100) in non-contact mode. Small strips of membrane were placed on specific sample holders and an area of 10 μm $\times$ 10 μm s was scanned. Boussu et al. [14] found that the scan size might affect the average surface roughness. Therefore, for comparison purpose, the same scan size was used for all samples.

2.4. FTIR

The area under the infrared peak at a given wavelength is proportional to the amount of chemical bonds excited at that wavelength [15]; therefore, Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) is a suitable method to determine the extent of reaction of interfacial polymerised film layer. ATR-FTIR (OMNIC FTIR iS10 Nicolet Thermo Scientific, USA)

was used to obtain the IR spectra of the prepared membranes. The hydroxyl ($-OH$) and amide ($-CONH$) groups of the membrane were determined at 3407 and 1647 cm^{-1} , respectively. The areas under the peak were measured based on the data of 15 different points.

3. Results and discussion

3.1. Reaction time and membrane roughness

Reaction time for IP could play an important role in determining the morphology of the thin film as they might determine the extent of polymerization between piperazine and trimesoyl chloride. In this work, the surface morphology of the skin layers which reacted for 5, 10 and 30, 50 and 70 s were examined under AFM. As shown in Fig. 1, the nodular size and surface roughness were significantly increased with the reaction time. The RMS values of membranes were 13.46, 27.08, 37.73, 39.62 and 58.32 nm for reaction time of 5, 10 and 30, 50 and 70 s, respectively. It could be observed that at lower reaction time, the membrane produced had smoother surface characteristic with smaller and uniform nodule structure. On the other hand, at longer reaction time, the surface roughness increased as a result of aggregated nodules. This indicated that the IP process was almost instantaneous, as reported in the literature [16]. At longer reaction time, the adjacent nodules tend to crosslink to form the supernodules. Supernodular aggregates were normally covered by a thin layer of polymer so that individual nodular aggregates were not identifiable [11]. The formation of supernodule is likely to cause flux reduction due to its thicker layer and poor rejection due to its lower packing density or open structure.

3.2. Reaction time and bonding formation

The formation of amide group could provide a significant indication on the degree of monomer crosslinking, hydrolysis of acyl chloride and film growth phenomena. As trimesoyl chloride continuously reacted with piperazine, $-C=O$ group was expected to increase. Higher intensity of the $-C=O$ group reflected the higher extent of reaction between the monomer. On the other hand, the presence of hydroxyl ($-OH$) group signified the hydrolysis of trimesoyl chloride. At the beginning of the reaction, the diffusion of water in the membrane matrix facilitated the hydrolysis of the trimesoyl chloride. The hydrolysis was prominent at the initial stage mainly due to the loose structure of the skin layer.

At longer reaction time, it was expected that both the $-C=O$ and $-OH$ groups would increase. However, by determining the ratio between these two functional

groups, the unsteady film forming conditions could be speculated. Fig. 2 shows that the area under the peak of $-C=O$ (1647 cm^{-1}) and peak of $-OH$ (3407 cm^{-1}) increased with reaction time, indicating that the film growth, crosslinking and hydrolysis of the membrane layer increased proportionally to the reaction time.

The membrane with low reaction rate (diffusional control) but underwent hydrolysis had higher bonding ratio ($OH/C=O$), whereas membrane with both extensive TMC incorporation and hydrolysis exhibited a constant bonding ratio. On the other hand, crosslinking process suppressed the hydrolysis process, and therefore could lower down the bonding ratio. Fig. 3 shows that within short reaction time (5–10 s), no extensive incorporation of TMC was observed and the membranes were subjected to hydrolysis by the aqueous phase. Within 10–50 s, spontaneous film growth continued with the incorporation of new monomer (TMC) that carries $-C=O$ functional groups. However, the films produced were still loose as noticeable hydrolysis phenomenon was observed through the higher bonding ratio. Beyond 50 s of reaction time, crosslinking within the polymer film was progressively high as could be observed from the decreasing bonding ratio which indicated that the dense membrane layer was formed.

3.3. Flux and rejection of methylene blue

Fig. 4 shows that membrane flux decreased with the increased of reaction time from 10 to 50 s and further reduced from 50 to 70 s. The trend of flux reduction is in accordance with the bonding ratio and membrane morphology. As discussed in Section 3.2, the initial flux reduction was due to the diffusional resistance of growing film and the later flux reduction was due to the steric hindrance of crosslinking. The same phenomenon was observed by Zhen et al who found that extensive crosslinking might produce a denser membrane with lower permeability [17]. It could be clearly seen from Fig. 4 that the trend of flux reduction is also agree well with the data obtained from AFM. At lower reaction time (5 s), the surface has smaller and uniform nodules which produced thinner film layer as well as loose structure. On the other hand, the supernodules formed at longer reaction time increased the membrane tortuosity therefore reduced its flux. Supernodule provides minimum benefit in terms of rejection due to its open structure [13]. Although the flux of membrane with 5 s reaction time was doubled than the other membranes, however, the film layer was not well cross linked and consequently gave a poor dye rejection performance ($<80\%$). It is worth to note that the membrane prepared within 5 s reaction time has poorer reproducibility compared to the other membranes, indicating that the reaction is

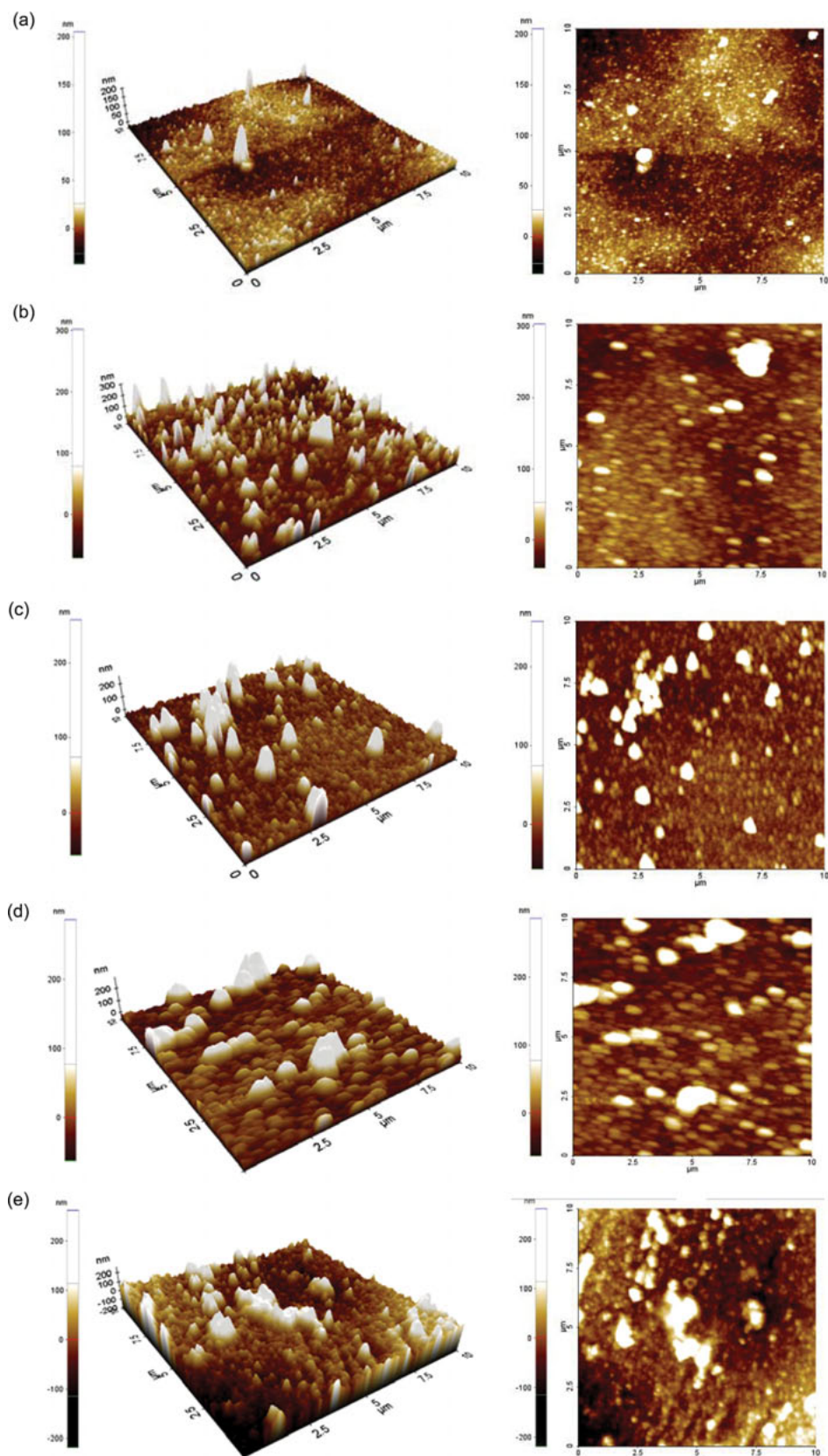


Fig. 1. AFM images of membrane surface prepared under different reaction times (a) 5 s, (b) 10 s, (c) 30 s, (d) 50 s and (e) 70 s.

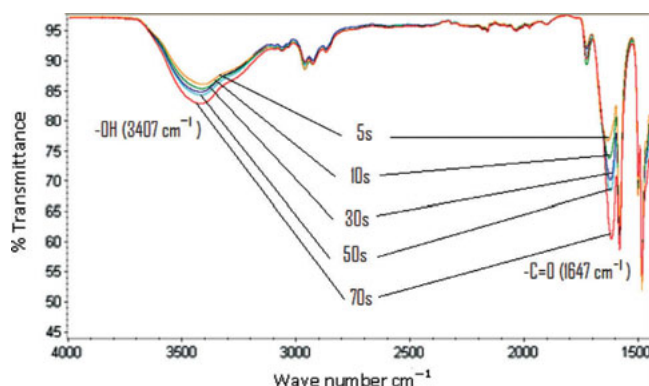


Fig. 2. FTIR spectrum showing the -C=O and -OH functional groups at different reaction times.

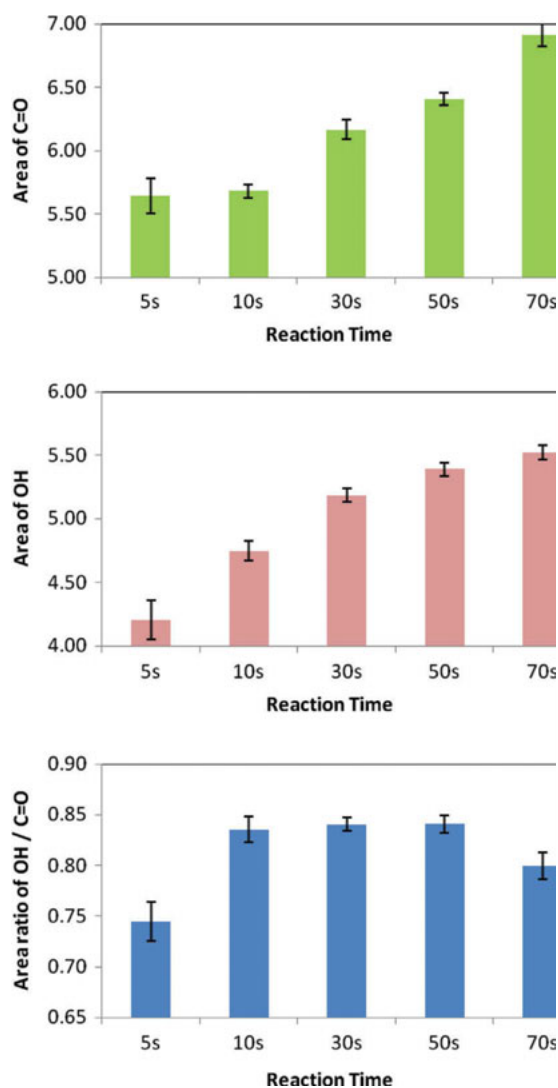


Fig. 3. Bondings and bonding ratios of membrane prepared under different reaction times.

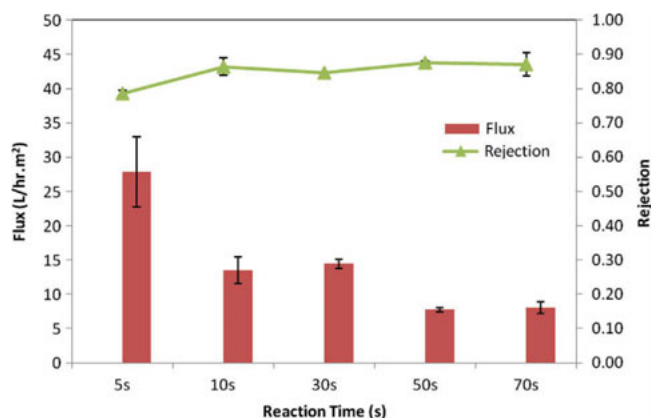


Fig. 4. Flux and rejection of methylene blue with membrane prepared under different reaction time.

random and instantaneous. Conversely, at longer reaction time (>50 s), the further reduction in flux due to crosslinking provide little improvement on dye rejection with the expense of flux reduction. This suggested that membrane synthesis should be controlled within 10 s to prevent excessive film growth.

As reported in our previous paper [18], for polypiperazinamide membrane, the rejection order of divalent cations and anions following the order of $\text{MgSO}_4 > \text{Na}_2\text{SO}_4 > \text{MgCl}_2 > \text{NaCl}$ indicated that polypiperazinamide membrane is more negatively charged. However, in this work we found that the membrane exposed to the cationic environment due to methylene blue has as no noticeable fouling phenomenon. Fig. 5 shows that all the prepared membranes show no sign of fouling or flux reduction even operated for more than 2 h except membrane prepared at 5 and 10 s. As mentioned earlier, membrane prepared at 5 and 10 s were not stable due to the loose structure and it is susceptible to compression. In contrary, membranes prepared at longer

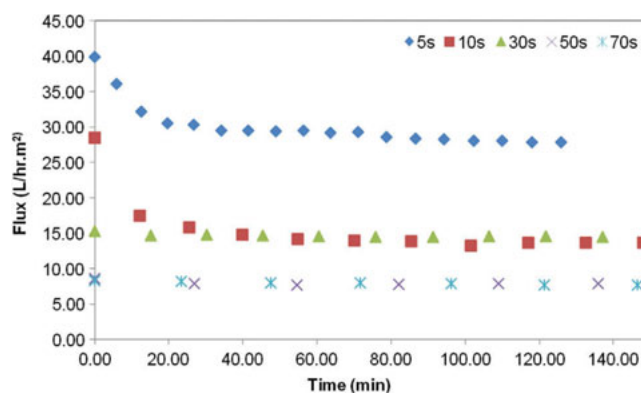


Fig. 5. Flux changes of the membrane prepared at different reaction time.

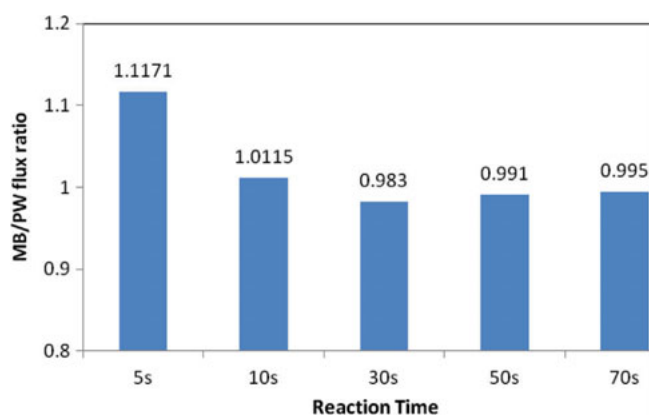


Fig. 6. Methylene blue and water flux ratio at different reaction time.

polymerization time have better pressure resistance due to the extensive crosslinking between TMC and piperazine. The instability of membranes prepared at 5 and 10 s reaction time can be further confirm based on the flux ratio of methylene blue and pure water as shown in Fig. 6 in which for membranes with 5 and 10 s reaction time, the flux of methylene blue is higher than the pure water flux resulted in the flux ratio higher than 1.

4. Conclusions

The flux and rejection performance of dye based on interfacial polymerised nanofiltration membrane could be understood through the chemical and physical properties of the membrane. The bonding ratio (hydroxyl/carbonyl) of the membrane prepared under different reaction time could provide an indicator on the membrane physical properties such as degree of film growth, hydrolysis and crosslinking. Membrane prepared under longer reaction time resulted in higher surface roughness which was caused by the formation of super-nodular structure. The formation of supernodule is an unwanted phenomenon as it caused further flux reduction and minimum rejection improvement due to its open structure. It was suggested that for dye removal, the reaction time should within 10 to 30 s for its stability, optimum flux and rejection. Besides, the prepared polypiperazinamide membrane has low tendency of fouling by cationic dye.

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