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Progress in Interfacial Polymerization Technique on Composite Membrane Preparation

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Abstract. The concept of interfacial polymerization (IP) has been known for more than 45 years since it was first reported by Mogan in 1965. Since then, there have been intensive and continuous efforts from academic and industry to further improve performances of composite membranes prepared using IP technique. Novel/modified procedures on IP process have been recommended with the aim of improving interfacially-synthesized polyamide layer through forming a defect-free selective skin onto membrane and establishing a strong adhesion between top selective layer and bottom microporous substrate membrane. Previous results indicated that enhanced properties of composite membrane could be produced using modified IP process. More attention however should be paid on composite hollow fiber preparation in order to make the membrane full use in industrial applications.

Keywords: nanofiltration, reverse osmosis, interfacial polymerization, polyamide, water treatment.

1. Introduction

Today, thin film composite (TFC) membranes prepared by coating a very thin layer of aromatic polyamide (PA) onto microporous membrane are well accepted for water and wastewater treatment processes. Preparation of TFC membrane in general is based on interfacial polymerization (IP) reaction between two monomers – a polyfunctional amine dissolved in water solution and a polyfunctional acid chloride dissolved in hydrocarbon solvent. By employing this approach, an ultrathin polymeric layer (300–400 nm) can be established and adhered to microporous supporting membrane, leading to a good combination of water permeability and selectivity. In the past decades, many attempts have been reported to enhance properties of composite membrane through variation of many parameters involved in membrane preparation process [1–4]. Of these, researches focused on the effects of reactive monomer type, concentration of reactant, reaction time and additive added during IP process are of particular interest among membrane community.

Though TFC membranes prepared using conventional IP have been very attractive within academic community as a kind of didactic application, continuous efforts are still devoted to modify the procedure of interfacial polymerization process. It is realized that the modified IP procedure can become imperative for improving the interfacial properties of TFC flat membranes and/or forming a defect-free selective skin onto a hollow fiber substrate. This paper aims to give an overview of the development of TFC membrane using modified/novel IP approach and provide good insights to composite membrane research and development.

2. Brief Historical Development of Thin-Film Composite Membrane

In the early development of composite membrane, Mogan was the very first researcher to propose the use of interfacial polycondensation approach to form a thin polymeric layer onto a substrate [5]. The approach however did not succeed in industrial fabrication until Cadotte and his co-workers discovered that

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through the optimization of formation conditions, a series of composite membranes with surprisingly high flux could be made by interfacial crosslinking of piperazine with trimesoyl chloride/isophthaloyl chloride mixture [6–7].

In general, polymerization reaction takes place at the interface of the two liquids which are insoluble to each other. Fig.1 depicts the schematic diagrams of the TFC membrane preparation using typical IP technique. In order to establish a very thin PA active layer on top of a supporting membrane, the substrate typically will be first immersed into an aqueous solution consisting of amine monomer (mostly between 0.1–1% w/v) prior to immersion in second organic solution of acyl chloride monomer (mostly between 0.05–0.2% w/v). The membrane is then subject to heat treatment (70–90^{o}C) to densitify the polymerization properties of PA layer and/or enhance adhesion of PA thin layer to surface of support membrane. Due to the significant advantages of IP technique in optimizing independently the properties of skin layer and microporous substrate layer, a wide variety of TFC membranes has been successfully developed by many companies, allowing the applications of membranes for various industrial separation processes.

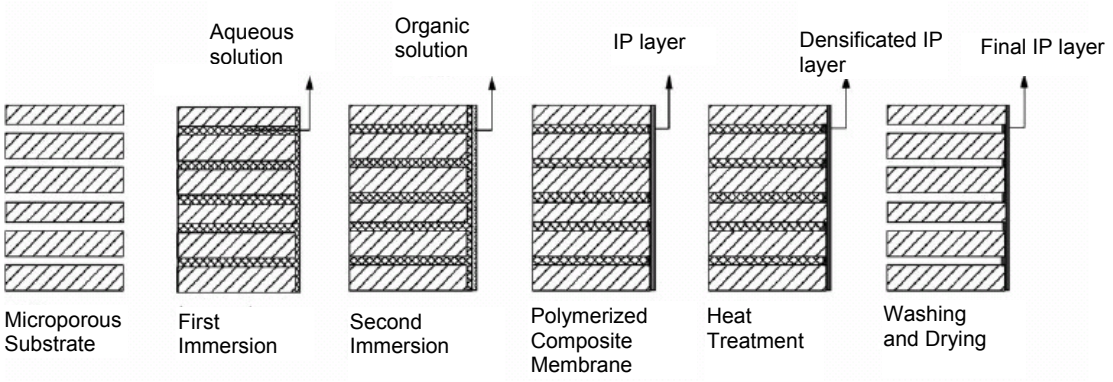

Fig.1: Schematic diagrams of the preparation process of TFC membrane by conventional IP technique

3. Trend and Progress of Thin-Film Composite Membrane

A wide variety of research and general information on TFC membrane preparation and characterization is available in literature. The recent progress in the development of TFC membranes has been comprehensively reviewed by several authors, covering the state-of-the art technology in improving membrane performances with respect to permeability/selectivity, chlorine tolerance, solvent stability, fouling resistance, etc [8–10]. The research activities on the improvements of TFC membranes can be generally divided into three main areas, i.e. (1) top active layer improvements by using newly developed monomer and/or innovative nano-scale particles such as titanium oxide and carbon nanotubes, (2) development of thermally and chemically stable supporting membranes, and (3) modification on the conventional IP technique. This paper does not intend to provide exhaustive review on all these research progress, but will instead focus on the state-of-the art approach on IP process applied for flat membranes and cylindrical hollow fiber composite membranes preparation.

4. Novel/Modified Interfacial Polymerization on Composite Membrane Preparation

Conventionally, IP process is conducted by immersing substrate membrane in aqueous solution followed by organic solution which is immiscible with the first aqueous solution. The sequence however can be reversed for those hydrophobic substrates. It is because hydrophobic substrate can be well-contacted with organic solution of acylc chlorine monomer, leading to higher degree of cross-linked polyamide layer. Conventional IP technique has been widely applied to prepare composite flat membranes. It is hardly to find any document about hollow fiber composite membranes prepared from typical IP process. Unlike membrane

of plate and frame or spiral-wound configurations, composite hollow fiber is experiencing a very slow growth, primarily due to the differences in geometry and handling of solution flow. In recent years, concerted efforts have been devoted to modify the procedure of interfacial polymerization process with the aim of improving the interfacial properties of TFC flat membranes and/or forming a defect-free PA skin on a hollow fiber substrate.

In 2010, concern was raised on the excessive unreacted polyfunctional acid chlorine monomers on the surface of active skin layer following the growing PA film which acts as barrier, restricting the diffusion of amine monomers on the organic phase side. To tackle this problem, Zou et al. [11] used amino monomer to react again with the unreacted acyl chloride groups by placing the membrane in aqueous solution for second time. The membranes prepared using this modified approach yielded a larger amount of amino groups ($–NH_2$) on skin surface and demonstrated better antifouling properties than that of membranes prepared by typical IP approach. According to the authors, multifunctional TFC membranes are possible to be fabricated via this approach by using different polyfunctional amine monomers in the third phase.

It is generally agreed that forming a perfect PA film onto hollow fiber outer surface is much more challenging than forming a thin film onto its lumen surface as coating on outer surface of hollow fibers could make the neighboring fibers stick to each other, leading to non-reproducibility of TFC hollow fiber membranes. Due to this reason, research work on preparation of interfacially-synthesized PA layer onto the lumen surface of hollow fiber is rather easy to carry out and has therefore gained some attention from several research groups in recent years [12–15]. One of the earliest mentions of the TFC hollow fiber membrane was disclosed by Baker et al. [16] in 1986. In this U.S. patent, it is claimed that very high percentage of NaCl rejection could be achieved by forming an interfacially-polymerized ultrathin layer (cross-linking between PEI and IPC or TDI) on lumen side of hollow fiber support. In this case, the inventors modified slightly standard IP procedures employed on flat membrane so as it is suitable for adaptation to the hollow fiber support.

In 2007, Yang et al. [12] adopted an easier method to remove the excess PIP solution and droplets by flushing nitrogen gas slowly through the lumen side of the fibers. Results showed that this modified IP procedure is able to produce composite hollow fiber membrane with better stability for long term running, most likely due to the good compatibility between PA active layer and substrate membrane. Two years prior to the work done by Yang et al., Verissimo et al. [13] found that an intermediate organic solvent between the aqueous amine solution and the organic acid chloride solution could be applied to establish an ultrathin polymeric layer on the inner surface of hollow fiber. Employing an intermediate solvent during IP process is reported not only able to reduce the pin-holes on PA layer but also create a stronger adhesion between PA layer and hollow fiber support. Korikov et al. [14] on the other hand pointed out that only the appropriate combination of all controlling factors (i.e. hydrophilization of fiber, concentration of monomer and reaction time, degree of removal of excess monomer from lumen side and heat treatment of PA layer formed) during IP process could lead to intact coating in the lumen side of hydrophobic polypropylene hollow fibers. They recommended to use acetone as pre-wetting solution followed by continuous circulation of hot chromic acid solution to hydrophilize pores of PP fibers prior to conventional IP coating process in order to ensure a prefect interfacially film formed [14].

Compared to composite hollow fiber membranes with PA thin layer formed inside the lumen, forming a cross-linked PA layer on outer surface of a microporous hollow fiber support has never been reported in journals. Relevant information could only be found in patents [17–18]. Forming a uniform polymeric ultrathin layer on outer surface of a microporous hollow fiber support membrane is very difficult and challenging, particularly in a continuous manner. It is because hollow fiber outer surface inevitably gets in touch with driving rollers during spinning process, leading to peeling or damage of PA thin layer which responsible for solute separation. In order to form a non-defect PA layer, Kumano et al. [18] in a patent filed on August 17, 1995 proposed to pass the composite hollow fiber (after IP process) through third solution which contained an organic fluorine compound as shown in Fig.2. Heat treatment was then introduced to composite membranes soon after the membrane passed through third solution bath. It is true that membranes with excellent permeability and selectivity could be produced using this invented method, but the sophistication of process control makes it less attractive to membrane industries.

From the standpoint of commercial large-scale production, the current technology of composite hollow fiber membrane preparation is still far from maturity to compete with commercially available composite membranes of flat film and spiral wound format, owing to low reproducibility of the resultant composite hollow fiber coupled with sophisticated fabrication process. However, from the angle of membrane development, this area is one of the subjects deserving a focused research attention in order to make full use of hollow fiber membrane prepared via IP approach.

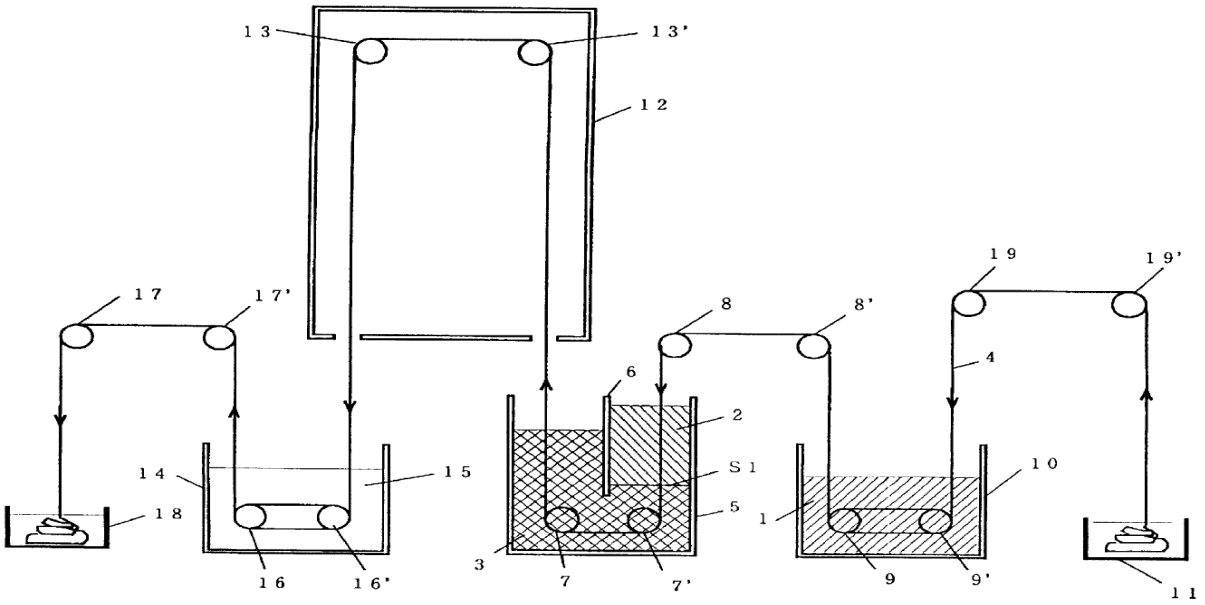

Fig. 2. Schematic diagram showing the production of a composite hollow fiber membrane using contact model, (1) first solution (containing multifunctional compound A, (2) second solution (containing multifunctional compound B), (3) third solution (containing organic fluorine compound), (4) membrane, (5) second bath, (6) partition, (7,7'/8,8'/9,9'/13,13'/16,16'/17,17'/19,19') driving rollers, (10) first bath, (11) supply bath, (12) drying chamber, (14) washing bath, (15) washing solution, (18) receiving bath, and (S1) liquid-liquid interface.

5. Conclusions

Thin film composite membranes have experienced tremendous improvement since the concept of interfacial polymerization was first introduced by Mogan in 1965. Currently, TFC membranes are not only used dominantly in commercial water and wastewater treatment processes but also showed huge potential to be used in other applications involving gas separation, pervaporation, etc. Efforts should continue to improve IP process in order to further enhance permeability and selectivity of composite membranes as well as to develop a strong adhesion between layers and establish a non-defect selective thin layer onto both flat and hollow fiber membranes.

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