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Nanofiltration thin-film composite polyester polyethersulfone-based membranes prepared by interfacial polymerization

M.N. Abu Seman[a], M. Khayet[b], N. Hilal[a,*]

[a] Centre for Clean Water Technologies, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK
[b] Department of Applied Physics I, Faculty of Physics, University Complutense of Madrid, Av. Complutense s/n, 28040, Madrid, Spain

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ABSTRACT

Nanofiltration polyester thin-film composite membranes have been prepared by interfacial polymerization using commercial polyethersulfone membrane support. Different monomer bisphenol A (BPA) concentrations in the aqueous solution and various interfacial polymerization times in the organic solution containing trimesoyl chloride (TMC) were studied. The success of the conducted interfacial polymerization procedure was corroborated by FTIR-ATR. Irreversible fouling of both the unmodified polyethersulfone and the modified polyester thin-film composite polyethersulfone membranes have been studied using humic acid model solutions at different pH values. It was observed that polyester thin-film composite membranes exhibited practically no tendency to be irreversibly fouled by humic acid molecules at neutral environment. However, the permeate flux was decreased and the irreversible fouling factor was enhanced with decreasing the pH to a value of 3.

1. Introduction

Surface chemistry and morphology of membranes play an important role in the transmembrane transport of components as well as on the efficiency of the membrane process [1]. Besides bulk modification of membrane material, surface modification of previously formed membranes is a promising approach to confer new properties to the existing membranes providing surfaces with tailor-made separation properties, energies and chemical functionalities different from those of the bulk membrane material. Generally, the objective for modification is not only to increase the flux and/or selectivity but also to improve the chemical resistance (i.e. solvent resistance, swelling, or fouling resistance), control of pore size, elimination of defects, etc. [2].

Among the different successful membrane surface modification techniques, interfacial polymerization is of particular interest. This method is a breakthrough in the history of membrane technology since it was developed by Cadotte at the North Star Research Institute for reverse osmosis applications [2]. Thin-film composite membrane prepared by interfacial polymerization was developed in order to overcome the limitation and problems encountered by asymmetric membrane formed by the phase inversion method [3]. The advantage of interfacial polymerization is that the reaction is self-inhibiting through passage of a limited supply of reactants through the already formed layer resulting in an extremely thin film of thickness within 50 nm range [4]. The skin or thin layer produced by this technique will determine the overall solute retention, permeate flux and, in general, will control the efficiency of the membrane process. It must be pointed out that this technique also can be applied to obtain modified membranes with pores larger than those of reverse osmosis (RO) applications and useful for UF and possibly for nanofiltration (NF) processes [5]. One of the advantages of interfacial polymerization technique is that the thin layer can be optimized for particular function by varying the monomer concentration in each solution (both aqueous and organic solutions), monomer ratios or reaction time of the interfacial polymerization [6–8]. In general, there are various factors affecting the structural morphology and composition of the formed thin layer such as the concentration of monomers in the corresponding liquid solutions, the partition coefficients of the monomers, the reactivity ratios where blends of monomers are employed, the solubility of nascent polymer in the solvent phase, the overall kinetics and diffusion rates of the monomers, the presence of by products (such as hydrogen chloride in the case of amine with acyl chloride), the hydrolysis or other potentially competitive by-reactions, the crosslinking reaction, the support material and the post-reactions or treatments of the resulting thin layer [9]. However, some problems may be faced during interfacial polymerization decreasing the efficiency of the process such as the highly non-uniform pattern of polymer density and charge across the

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* Corresponding author at: Centre for Clean Water Technologies, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK. Tel.: +44 0115 951 4168; fax: +44 0115 951 4115.
E-mail address: Nidal.Hilal@nottingham.ac.uk (N. Hilal).

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active layer, the interfacial polymerization reaction may take place partly in aqueous phase and the microvoids in the formed active thin layer [10].

Compared to thin-film polyamide membranes prepared by interfacial polymerization, only few researcher studies have been carried out using this technique to prepare other polymeric thin-film polyester and polyesteramide membranes. Polyester RO membrane has been synthesized by Kwak et al. [11] and compared to polyamide membrane. It was claimed that the RO polyester membrane had water permeate flux eleven times higher than that of polyamide membrane and therefore could be used in low RO pressure application maintaining a reasonable rejection. By varying monomer concentration and reaction time, Mohammad et al. [8] produced polyester NF membranes exhibiting rejection factors of NaCl (0.001 M aqueous solution) with values up to 60% and permeate flux of about 1.8×10^{-2} kg/m^{2}s under operating pressure of 4.5×10^5 Pa. Polyesteramide NF membranes have been prepared by Razdan and Kulkarni [6] and Jayarani and Kulkarni [12] by combining phenol and amine monomers in aqueous solutions during interfacial polymerization. The incorporation of ester linkage increased the oxidation resistance of the membrane and this significantly increased the membrane tolerance on chlorine attack. This indicate that this composite membrane is practically used in desalination process to remove high concentration of salt and in treating waste water from pulp and paper industry which contain very high chlorine content.

Polyamide membrane has been explored since over the last 30 years and continued until now with application of variation of amine monomers and acyl chlorides [13,14]. This may be one of the reasons why polyester polymer membrane is not popular and therefore it is still considered new in the field of composite thin-film membrane development.

The main objective of the present paper is to prepare polyester thin-film composite membranes with improved NF antifouling properties by means of interfacial polymerization using bisphenol A (BPA) and trimesoyl chloride (TMC) as monomers. A high negatively charged thin layer that improve antifouling characteristics by increasing repulsion force towards humic acid molecules, can be produced by interfacial polymerization technique [8]. Different BPA monomer concentrations and interfacial polymerization time have been considered. Humic acid has been employed as a model organic foulant and different humic acid aqueous solutions of different pH values have been tested. The effects of pH of aqueous solutions on the irreversible fouling of both the modified and unmodified membranes have been studied.

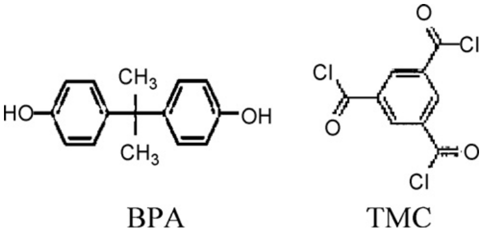

Fig. 1. Chemical structure of the monomers used: bisphenol A (BPA) and trimesoyl chloride (TMC).

2. Experimental

2.1. Materials

The monomers bisphenol A (BPA) and trimesoyl chloride (TMC) were purchased from Sigma–Aldrich Co. Their chemical structures are shown in Fig. 1.

The solvent hexane (reagent grade) was purchased from Fisher Scientific, UK. Humic acid (Sigma–Aldrich Co.) of molecular weight of 4.1 kDa was chosen as a model organic foulant [15]. To adjust the pH of the feed humic acid solutions to the required values, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were supplied by Sigma–Aldrich Co. and Acros Organics, respectively.

The asymmetric commercial membrane NFPES10 purchased from Hoechst Company (Germany) with pore size within 0.2–0.5 nm [16] and 75 μm thickness (based on SEM image without backing material) was used as base support for interfacial polymerization.

2.2. Preparation of thin-film composite polyester membrane by interfacial polymerization technique

The membrane NFPES10 was first cleaned with distilled water and subsequently left in ultrasonic distilled water bath for 1 min. These two steps were repeated 3 times in order to remove any preservative agent (i.e. glycerine) added by manufacturer during production. The cleaned membrane was immersed in a BPA aqueous solution for 15 min. Since the monomer BPA has very low solubility in water, it was dissolved in an aqueous solution of NaOH at pH of about 11. The BPA monomer concentration in the aqueous solution was varied between 0.1% (w/v) and 2% (w/v). The pre-soaked membrane taken out from the aqueous solution was positioned vertically for 2 min to drain the excess monomer on the membrane surface. Then, this membrane was dipped in the

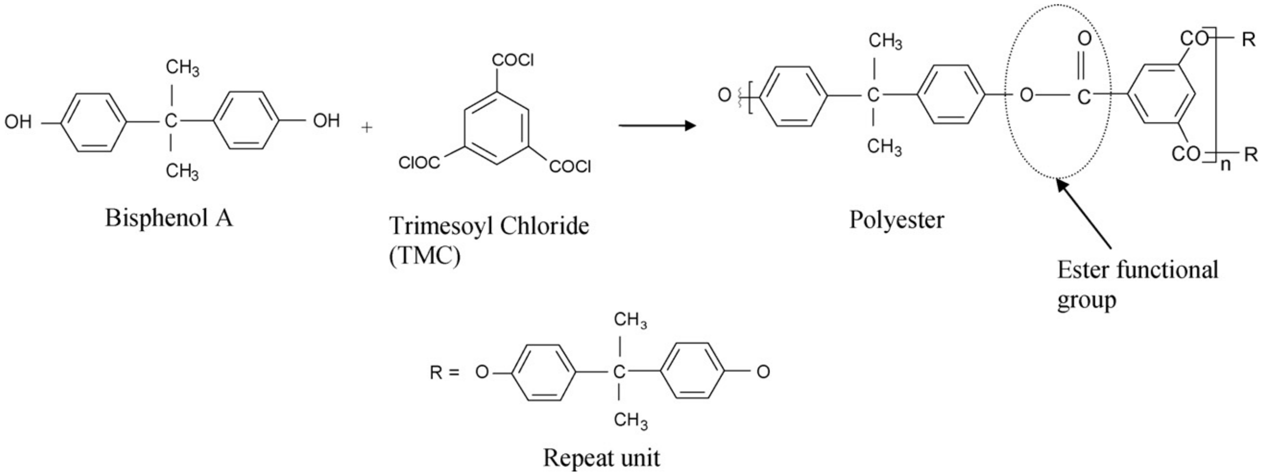

Fig. 2. Reaction carried out between the monomers BPA and TMC for formation of polyester.