



Surface morphology of pvdf membrane and its fouling phenomenon by crude oil emulsion



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ARTICLE INFO

Article history:

Received 8 December 2015

Received in revised form 16 May 2016

Accepted 29 May 2016

Available online 13 June 2016

Keywords:

PVDF membrane

Fouling

Oil emulsion

ABSTRACT

In this study, polyvinylidene fluoride (PVDF) flat sheet membranes were fabricated via phase inversion process for crude oil emulsion separation. The PVDF solutions were formulated by varying polymer concentration from 16 to 19 wt.% with one of the three different solvents: *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP). The membranes morphologies as a result of different polymer concentration and solvents were characterized and their effects on the crude oil emulsion separation were evaluated. Results showed that 18 wt.% PVDF-DMAc membrane was the optimum membrane for oil emulsion in term of flux recovery ratio (FRR) which showed better cleaning ability compared to other membranes. Under cake deposition fouling mode (with proven oil particle size bigger than the pore size), membrane fouling tendency is regardless of porosity or pore size. However, both of these properties do play important roles in the subsequent fouling cleaning process. Membrane with least porosity and smaller pore size has better cleaning properties.

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1. Introduction

Produced water, water that is co-produced during oil and gas manufacturing, represents the largest source of oily wastewaters. It contains various organic and inorganic fractions which include dissolved and dispersed oil compounds, dissolved minerals, production chemical compounds such as corrosion inhibitors and surfactants, production solids and dissolved gases [1].

Daily global production of produced water is 250 million barrels which is three times than that of the produced oil and this factor goes up with the maturity of the oil fields [1]. It can cause pollution on the ground water and poses serious environment threats. Therefore treatment of produced water may be required in order to meet the stringent regulations on the discharge and disposal of produced water in the environment [2–4]. Environmental regulations require that the maximum total oil and grease concentrations in the discharge water to be 10–15 mg/L [5]. However, the major pollutant in produced water generating from oil fields is oil which may range between 100–1000 mg/L or higher depending on the efficiency of de-emulsification and the nature of the crude oil [6].

There are few oil separating methods reported so far concerning the efficiency of the oil refinery wastewater treatment process which included gravity settling, centrifugation, air flotation, fibrous/packed bed coalescence and membrane technology [7–9]. Among these methods, membrane technology has been considered as a promising method to treat the oily wastewater because of its suitable pore size and the capability to remove emulsified oil droplet without any de-emulsification processes [10].

The emergence of PVDF as a popular membrane material can be attributed to its excellent chemical and thermal resistance [11]. Knowledge of a polymer's crystallinity and its resulting membrane morphology is important as a basis of understanding its membrane permeability and selectivity, as well as its various chemical and mechanical properties. Researchers have investigated the influence of an addition of a small concentration of various components on membrane structure. These additives often show specific interactions with one of the other three components. The details of the process including effects of the thermodynamic conditions [12], influence of phase inversion [13], possible mechanisms for membrane formation and the influences of coagulation bath with different mixtures of solvent and non-solvent [14] have been reported by researchers.

Although solvents play an important role in membrane formation, there is not enough information about their effects. In the present study, PVDF flat sheets membranes were fabricated

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by phase inversion process to separate the crude oil emulsion. Three types of solvents, namely DMF, DMAc and NMP were chosen as the solvents by varying the PVDF polymer concentration from 16 to 19 wt.%. These membranes were expected to have varied physicochemical properties that will affect the degree of oil fouling under the environment of high ionic strength that exclude the effect of charge repulsion. These physicochemical properties were related to the membrane fouling tendency. As fouling is a surface phenomenon, surface properties rather than properties are more dominant.

2. Material and methods

2.1. Material

PVDF (TA6010/1001, Solvay Solexis, Shanghai) powder was used as the membrane polymer and was dried in an oven at 70 °C for overnight prior to use. DMF (Merck KGA, Germany) (purity (GC) ≥99.8%), DMAc (Merck, Germany) (Assay (GC, area%) ≥99%) and NMP (Merck, Germany) (purity (GC) ≥99.5%) were used as solvent to dissolve polymer without further purification. Crude oil (Petronas Penapisan Terengganu, Malaysia), sea salt (Sigma Aldrich) and Triton X (Sigma Aldrich) were used in the preparation of crude oil emulsion or synthetic produced water.

2.2. Membrane preparation

The membrane casting solutions were prepared by dissolving PVDF in one of the following solvents: DMAc, DMF and NMP. Four different polymer concentration namely 16 wt.%, 17 wt.%, 18 wt.% and 19 wt.% with solvent adjusted to 84 wt.%, 83 wt.%, 82 wt.% and 81 wt.% accordingly. These membranes were labeled as C for DMAc, F for DMF and P for NMP. For example, C-18 means 18 wt.% PVDF in DMAc solution. The solution was stirred at 250 rpm at 65 °C for 4 h to ensure complete dissolution of the polymers then left for overnight stirring at 40 °C to form homogeneous solution. The prepared casting solution was casted on a flat glass plate wrapped with tightly woven polyester fabric which acts as the membrane support to provide mechanical strength. The casting process was carried out at constant speed of 0.06 cm/s. The membrane casting thickness was fixed at 200 μm [15,16].

2.3. Membrane characterization

2.3.1. Field emission scanning electron microscope (FESEM)

Surface and cross sectional morphology of the membranes were determined using a field emission scanning electron microscope (FESEM) (SUPRA 35 VP, Carl Zeiss Inc.). Prior to the analysis, the membrane was immersed into liquid nitrogen for few minutes followed by freeze-fracturing to obtain perfect cut structure. After this process, the membrane sample was ready to be examined under FESEM at potential of 5.0 kV.

2.3.2. Porosity

Prior to the analysis, dry membrane sample was weighted. Then it was immersed into 2-butanol and degassed for 30 s to prevent air trapped in the membrane pores. After 2 h of immersing in 2-butanol, the membrane surface was dried by using filter paper and weighed immediately to avoid evaporation of 2-butanol from the membrane pores. The membrane porosity was calculated based on Eq. (1):

$$\varepsilon_p = \frac{\frac{w_1 - w_2}{\rho_b}}{\frac{w_1 - w_2}{\rho_b} + \frac{w_2}{\rho_p}} \quad (1)$$

Table 1
Hansen solubility parameters (δ) of solvents, water and PVDF.

	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})
NMP	18	12.3	7.2
DMF	17.4	13.7	11.3
DMAc	16.8	11.5	10.2
H ₂ O	15.6	16	42.3
PVDF	17.2	12.5	9.2

where ε is the porosity of the membrane, w_1 is the weight of the wet membrane (g), w_2 is the weight of the dry membrane (g), ρ_p is the specific gravity of the PVDF polymer and ρ_b is the specific gravity of 2-butanol.

2.3.3. Pore size distribution

The internal pore size of the membrane was determined via Capillary Flow Porometer, Porolux 1000 (Benelux Scientific, Germany). Membrane sample with a diameter of 20 mm was immersed in perfluoroethers (wetting liquid) and characterized using the 'dry-up-wet-up' method which the pore size distribution was estimated using PMI software.

2.3.4. Contact angle

The membranes surface wettability was characterized using water contact angle instrument (Model 300 Advanced Goniometer, Rame-Hart Instrument Co., U.S.A.) based on sessile drop technique. The membrane sample was pasted onto a glass slide using double-sided tape to ensure that membranes surface were flat. A droplet of deionized water was dropped onto the membrane surface using the motor-driven microsyringe. The acquired image was analyzed using DROPimage software to obtain contact angle.

2.3.5. Fourier transform infrared spectroscopy (FTIR)

FTIR was used to investigate the possible functional groups and chemical bonding appeared on the fouled membranes. The FTIR (Nicolet iS10, Thermo Scientific) was equipped with an OMNI-sample attenuated total reflection (ATR) smart accessory and was coupled to a diamond crystal operated at incidence angle of 45°. Each spectrum, which was recorded as the average of 32 scans were taken with a resolution of 4 cm⁻¹ was collected at operating wave number ranging from 4000 to 625 cm⁻¹.

2.4. Solubility parameter

To explain the formation mechanism of asymmetric membrane structures and its correlation with membrane performance, both thermodynamic (phase behavior) and kinetic (mass transfer) aspects of the formation process have to be considered. The Hildebrand solubility parameter approach [17], and especially its later extension by Hansen [18], is generally seen as a practically useful and acceptable, even though not perfect, description of the mutual affinity between polymers, solvents and non-solvents. The solubility parameter (δ_t) of liquids and polymers can be defined as Eq. (2).

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (2)$$

where δ_d , δ_p and δ_h denote the contributions of dispersive interactions (d), polar bonding (p) and hydrogen bonding (h) respectively. The solubility parameters of the used solvents (S) and non-solvents (NS), shown in Table 1 were obtained from literature [19,20]. The solubility parameter difference $\Delta\delta_{S-NS}$ between the solvent system of the casting solution and the non-solvent system of the

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