Effect of Lithium Chloride on the Fabrication of Polyvinylidene Fluoride Nanocomposite Membrane for the Separation of Oil-Water Emulsions

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Abstract. Polyvinylidene fluoride membranes have been broadly applied to scientific research and industrial processes due to its excellent property and applications mainly in water treatment. In this study, the effects of lithium chloride (LiCl) on the porosity, morphology, hydrophilicity and permeability of PVDF-halloysites (PVDF-HNT) nanofiber membranes were investigated. It was observed that the incorporation of LiCl improved the electrospinnability of polymer solution and modifies the morphology of fibers from beaded fiber to a uniform fiber structure. The fabricated membrane was used for the separation of oil-water emulsions via gravitational dead end system, in which the 2% concentration of LiCl as additive, bear out the most amount of volume of water collected. As a result, the fabricated membrane offers a new material for practical applications in oil-water separations.

1. Introduction

Oil spill is a type of environmental pollution. It is discharged by accident or purposely that hovers on the surface of water bodies as a distinct mass and is brought off by currents, tides, or winds. In the Philippines, various incidents of oil spill were reported due to discharge of oil by mistake or on purpose. Oil spill can be partly controlled by combustion, chemical dispersion, and adsorption. A lot of procedures have been developed to eradicate oil spill from polluted water. Oil-water separation is a global challenge due to increasing oily wastewater, and repeated oil spill incidents [1]. One of the solutions for dealing this concern is the reuse of water that involves the adoption of developed technologies, like membrane technology. Membrane technology has been lately launched as an effective method to separate oil-water emulsion due to its capacity to efficiently take away the oil droplets in contrast to the existing conventional method[2,3,4,5,6]. Addition of salt additives (e.g. lithium chloride) to prepare porous membranes has been an effective practice to improve permeability and selectivity. The objective of this study is to fabricate an electrospun membrane for separation of oil-water emulsions. The target is to produce a PVDF nanocomposite membrane that will act as a substrate via electrospinning technique, characterize the fabricated membrane according to surface
morphology, chemical structure, mechanical properties, and hydrophilic/hydrophobic property, determine the effects of incorporating the additives lithium chloride (LiCl) and halloysite nanotubes (HNT) to the polymer solution, and lastly evaluate the membrane separation performance of oil-water emulsions using gravitational set-up.

2. Materials and methods
The materials used in this study are Polyvinylidene fluoride (PVDF, Kynar 2800), commercial halloysite nanoclays (HNT), N-Methyl-2-Pyrrolidone (NMP), lithium chloride (LiCl), distilled water, Triton x-100 (emulsifier) and engine oil. The materials are purchased from Sigma Aldrich and Department of Science and Technology. All reagents used in this study were employed with no further purification. The PVDF-LiCl/HNT solution was prepared with varying concentrations of PVDF and LiCl while the amounts of solvent NMP and HNT were held constant. A total of four blends were prepared for membrane fabrication. The composition of membrane by % weight are shown in Table 1.

| Blend | PVDF | HNT | LiCl | NMP |
|-------|------|-----|------|-----|
| M0    | 20   | 0   | 0    | 80  |
| M1    | 17   | 2   | 1    | 80  |
| M2    | 16   | 2   | 2    | 80  |
| M3    | 15   | 2   | 3    | 80  |

For the fiber production, an electrospinning machine (NANON-010A) was used. The prepared blend solutions of around 8 mL were poured individually into a 10-mL syringe container for electrospinning process. Voltage of 20 kV and feed rate of 0.9 mL per hour are considered in fiber production. Assessment of the produced electrospun membranes is carried out to analyze the surface morphology using Scanning Electron Microscope (SEM), surface chemical composition using Fourier Transform Infrared Spectroscopy (FTIR), mechanical properties using Universal Testing Machine (UTM), membrane pore size using Porometer (Porolux 1000), wettability using Contact Angle (Sessile drop method). The prepared membrane composition for electrospinning process influence the viscosity and ionic conductivity making each four blend solution electrospinnable.

3. Results and discussion

3.1. Membrane Surface Morphology

![SEM images](image)

*Figure 1. SEM images of (a) 0% LiCl, (b) 1% LiCl, (c) 2% LiCl and (d) 3% LiCl*

Scanning Electron Microscope was used to determine the surface morphology of each of the electrospun membranes under magnification of 5000x with an accelerating voltage of 10 kV. Addition of salt in the solution was found to bring a remarkable change to the membrane morphology of the
samples. The remarkable change was due to the addition of salt, lithium chloride, on the membrane, where the morphology of fibers from beaded fiber changes to a more uniform fiber structure. According to studies that addition of small amount of salt will bring about a significant decrease in fiber diameter as shown in Table 2 below which is probably due to higher conductivity from lithium chloride.

Figure 1a exhibits a minimal quantity of beaded fiber with an average fiber diameter of 508.9 ± 22 nm, but when lithium chloride was added the bead-on-string fibers gradually disappeared as shown in figure 1b with average fiber diameter of 352.2 ± 21 nm. The cause of beads formation has been reported when the concentration of solution or the molar weight of the polymer used is too low. Bead formation could be associated to lack of resistance of the polymer solutions to resist electrical force stretching due to low molecular weight or low viscosity of the polymer. In figure 1c, when the amount of lithium chloride was increased to 2%, parallel double-stranded fibers with relatively thinner diameters were achieved. Attributed to the fact that with increasing amount of lithium chloride, higher viscosity of the solution can be achieved; this led to improvement in ionic conductivity of the solutions resulting in reduced possibility of bead formation. However, upon increasing the amount of lithium chloride to 3%, the fiber structures as shown in figure 1d were obtained but with crystallization-associated morphology, it is evident with the presence of lithium chloride in the membrane but with high salt content. This is because high salt content are in meta-stable states that are highly supersaturated with respect to PVDF crystallization.

### Table 2. Fiber diameter of the electrospun membranes

| Membrane | Diameter (nm) |
|-----------|---------------|
| M0        | 508.9 ± 22    |
| M1        | 432.2 ± 22    |
| M2        | 352.2 ± 21    |
| M3        | 308.2 ± 16    |

3.2. Chemical Structure

Fourier Transform Infrared Spectroscopy was used to determine the surface chemical composition. An FTIR result for PVDF nanocomposite membranes with varying concentrations of lithium chloride are illustrated in Figure 2. Decreasing intensities of spectra were observed at 1000 cm⁻¹ to 1500 cm⁻¹. Distinct but very low intensities of halloysite spectra were observed at 1649 cm⁻¹ that corresponds to water interlayer’s OH bending.

![FTIR Spectrum for PVDF:HNT:LiCl in different ratio](image)

**Figure 2.** FTIR Spectrum for PVDF:HNT:LiCl in different ratio (a) Pure PVDF (b) 17:1:1 (c) 16:2:2 (d) 15:2:3
Absorption peaks at 872 cm\(^{-1}\) and 841 cm\(^{-1}\) from PVDF spectra are retained in the blends containing 1%, 2% and 3% LiCl. C-C-C asymmetrical stretching vibration and peak at 1400 cm\(^{-1}\) that corresponds to the C-F stretching vibration of PVDF appeared in lower intensity. From Figure 2 (b)-(d), sharp and strong peak located at 837 cm\(^{-1}\) correspond to the existence of LiCl in membranes while PVDF membrane with no additives illustrate coarse and weak peak at the same wavelength.

### 3.3. Mechanical Property

Since PVDF membranes wear off easily when subjected to abrasive materials, mechanical stability should be taken into account. Young’s modulus and tensile strength were mainly used to evaluate the mechanical property of the produced membrane as shown in Table 3.

| Table 3. Young’s modulus and tensile strength of membrane samples |
|---------------------------------------------------------------|
| Sample | Tensile Strength (MPa) | Young’s modulus (MPa) |
|--------|------------------------|-----------------------|
| M0     | 2.4478                 | 2.3650                |
| M1     | 3.8876                 | 3.4234                |
| M2     | 3.1609                 | 2.1760                |
| M3     | 3.0176                 | 2.0965                |

It is clear that PVDF with halloysitenanoclays have higher tensile strength and Young’s modulus than pure PVDF which suggest that incorporation of halloysitenanoclays gives extra stiffness to the polymer matrix. It is possible that the intrinsic modulus of halloysitenanoclays are present and are relatively easy to disperse in the polymer matrix. But, keeping the amount of halloysite constant while the amount of LiCl increases, the membrane leads to a lower mechanical stability. The possible reason is that LiCl concentration is higher than halloysite concentration. The porous structure created by lithium chloride can be the basis of the significant decrease in Young’s modulus and tensile strength. There must be an optimum amount in HNT/LiCl ratio to develop strength, but excessive amount will decrease the strength.

### 3.4. Contact Angle

The hydrophilicity of the membranes was enhanced significantly by adding different amount of LiCl. As a result, as the amount of LiCl increases, membrane hydrophilicity also increases. As shown in Figure 3, the increase of membrane hydrophilicity was attributed to the nature of lithium chloride being highly polar. Because cation like lithium and anion like chloride can offer good membrane hydrophilicity via ion-dipole interaction, where these lyotropic salts can produce complexes with the carbonyl group in polar aprotic solvent such as N-methyl-2-pyrrolidone (NMP).

![Figure 3. WCA of membranes with varying concentration of LiCl](image-url)
3.5. Oil-Water Separation Performance

The four electrospun membranes underwent oil-water separation test for 24 hours. It is obvious that incorporation of LiCl showed a significant improvement on the volume of water collected. For pure PVDF membrane, no water was collected after 24 hours this was due to the hydrophobic nature of the membrane. In the membrane with 1% LiCl, 4.3 mL of water was collected after 24 hours with no trace of oil. Membrane with 2% LiCl showed improvement in the volume of water collected by about 6.1 mL with no trace of oil after 24 hours. However, membrane with 3% LiCl after 24 hours exposure to oil-water separation test the membrane was tattered. The possible reason might be due to high content of LiCl and low tensile strength where it absorbs plenty of water which caused the breakage of the membrane. Given the results on Table 4, membrane with 2% LiCl gave the best result for membrane oil-water separation performance.

| Membrane | Volume of water collected (mL) |
|-----------|-------------------------------|
| M0        | 0                             |
| M1        | 4.3                           |
| M2        | 6.1                           |
| M3        | 0                             |

4. Conclusion

A novel PVDF oil-water separation nanocomposite membrane was effectively fabricated through the addition of lithium chloride via electrospinning technique. From the results gathered in this study, it can be concluded that lithium chloride as additive plays a significant part in improving the membrane performance of nanomaterials which changes the fiber morphology from beaded fiber to a more uniform fiber structure. Successful incorporation of lithium chloride on the membrane surface, confirmed by FTIR which showed significant peaks, can effectively solve poor dispersion in the membrane. These improvements are attributed to a decrease in roughness, which can prevent oil droplets from adsorbing or entering in the membrane surface and pores but increases water permeation rate into the membrane. Li+ and Cl- interacts strongly via ion-dipole interactions which targets the PVDF making it more porous, fibrous and hydrophilic. Therefore, the modification converts the membrane from highly hydrophobic to hydrophilic under oil when wet with water. This nano-enabled membrane study will definitely help the treatment of oily wastewater as an effective modification technique and key element for sustainable development in the field of membrane technology.

5. References

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