

CHAPTER I

INTRODUCTION

1.1 General Background

Composite membranes became increasingly popular due to their ability to combine the advantages of multiple materials, which could be thin film layers or mixed matrix forms. The composite membrane could be fabricated using various techniques, for example, dip coating, spin coating, and Langmuir-Blodgett (LB) techniques. The distinct materials were added to the membrane substrate to enhance its performance, such as anti-fouling, improved strength, and high selectivity (Arundhathi et al., 2024). The various materials were used as fillers for composite membrane fabrication. For example, graphene oxide (GO) was incorporated into ceramic membranes for gas separation, water treatment to enhance mechanical properties, and anti-fouling (Zubair et al., 2024). Chitosan/polysulfone (PSf) composite membrane was applied in the fields of water purification and wound healing due to its biocompatibility and antimicrobial properties (Wang et al., 2020). Besides, the addition of stimuli-responsive material to polymeric membranes has been referred to as a smart or intelligent composite membrane. These can reversibly change in their permeability, selectivity, and separation efficiency in response to various triggers like temperature, pH, light, or chemical stimuli (Yu et al., 2023). The responsive ability of smart composite membranes was used in various applications such as water purification, controlled release devices, and biosensing (Liu et al., 2024; Liu et al., 2017; Vazquez et al., 2024). With their remarkable responsive ability, smart composite membranes hold great promise for addressing complex challenges and advancing the fields of filtration, separation, and controlled transport in diverse industries.

Over the past decade, stimuli-responsive materials have revolutionized polymeric membrane technology giving rise to the concept of “smart” or “intelligent” membranes. These membranes exhibit a remarkable capacity to respond dynamically to environmental stimuli such as temperature, pH, and magnetic fields. This responsiveness enables their integration into advanced applications, including water purification, controlled release systems, and biosensing technologies (Herrmann et al., 2021; Vikulina et al., 2020; Xu et al., 2022).

Among the stimuli-responsive materials, poly (*N*-isopropyl acrylamide) (PNIPAm). PNIPAm has emerged as one of the most extensively studied and widely applied in recent years. PNIPAm is a thermoresponsive polymer characterized by its unique ability to undergo a coil-to-globule phase transition at its lower critical solution temperature (LCST), approximately 32 °C (Xiao et al., 2022). Below the LCST, the PNIPAm chains expand as hydrogen bonds form between the hydrophilic amide (–CONH–) groups of the polymer and surrounding water molecules. However, at temperatures above the LCST, the increased molecular kinetic energy disrupts hydrogen bonding, leading to a predominant hydrophobic interaction involving the polymer's isopropyl group (–CH(CH₃)₂). This transition causes the PNIPAm chains to collapse and expel water, resulting in dehydration (Jain et al., 2015; Lanza et al., 2017). This unique property of PNIPAm has made it an attractive material for applications such as drug delivery, tissue engineering, and biosensors (Rana & De la Hoz Siegler, 2021; Thirupathi et al., 2022; Zhou et al., 2016). When incorporated with a membrane, PNIPAm can transform a passive membrane into a smart membrane that can regulate transport properties, making them ideal for advanced applications in drug delivery, tissue engineering, and biosensors.

PNIPAm-based composite membranes have been synthesized on various substrates (Drikvand et al., 2022; Salehi et al., 2022; Wang et al., 2012). Among the substrates, polyethylene terephthalate (PET) has been extensively utilized in various forms, such as films, fabrics, and membranes (Alem et al., 2008; Drikvand et al., 2022; Mauricio et al., 2009). The exceptional advantages PET-based support membranes

include high chemical resistance, superior mechanical properties, and excellent permeability (Apel, 2001; Silvestre et al., 2022). In addition, their inherent hydrophobic nature further enhances their performance, preventing unwanted moisture absorption (Zaman et al., 2013).

The PNIPAm-PET composite membranes have been developed to leverage these unique properties, finding applications in smart gating systems, bio-separation, and cell culture (Nagase, 2021; Praveen et al., 2017; Tripathi et al., 2014). Despite their potential, the fabrication of PNIPAm-based composite membranes presents significant challenges. Conventional methods such as dip coating and spray coating often result in inconsistent coating thickness and limited material compatibility. Several methods have been developed to fabricate smart membrane effectively. To address these issues, innovative approaches have been developed to improve fabrication efficiency and performance. Among these, microwave-assisted polymerization offers a promising solution by drastically reducing reaction time and conserving energy. Unlike conventional heating, which relies on gradual thermal conduction, microwave energy directly heats the polymerization solution, accelerating the process and achieving high grafting yields (Katesripongsa & Trongsatitkul, 2019; Kobayashi & Müllen, 2015). This method has proven especially effective for synthesizing PNIPAm-grafted membranes. For instance, our previous work showed that microwave-assisted polymerization reduced the grafting time of PNIPAm onto a plasma-activated surface of Nylon membrane to just 30 minutes—compared to several hours with traditional oil-bath heating—while achieving high grafting yields of approximately 83% (T. Kajornprai et al., 2023). This acceleration significantly enhances productivity and aligns with sustainable and energy-efficient manufacturing goals (Kempe et al., 2011). However, the plasma-activate technique used to initiate the polymerization process was expensive and limits scalability. An alternative method was needed to improve the fabrication with improved scalability and cost-effectiveness.

Solvent-assisted polymerization has emerged as a promising alternative, leveraging solvents with solubility parameters (δ) similar to the substrate to enhance monomer diffusion and substrate swelling. The solvent swelling promotes the disruption of intermolecular cohesive forces between polymer chains and increases chain mobility. Consequently, monomers can diffuse more effectively into the swollen substrate leading to improved incorporation into the membrane structure. (Hsieh et al., 1984; Rahman et al., 2014; Zohuri, 2012). Hsieh *et al.* (1984) revealed the effectiveness of dimethyl sulfoxide (DMSO) as a swelling agent in promoting the diffusion and incorporation of acrylic acid into PET films. Among six organic solvents: dimethyl sulfoxide (DMSO), γ -butyrolactone, dimethyl formamide (DMF), pyridine, tetrachloroethane, and chlorobenzene, DMSO exhibited the highest monomer inclusion at 100 °C. The monomer inclusion efficiency followed the order of pyridine, tetrachloroethane, DMF, chlorobenzene, γ -butyrolactone, and DMSO, with DMSO proving most effective in enhancing the diffusion process.

In addition to microwave-assisted methods, vacuum-suction filtration has been shown to improve the structural properties of composite membranes. Marvin *et al.* (2022) demonstrated that the vacuum-suction filtration assisted in the pervaporation dehydration of aqueous isopropanol solution of the thin film composite polyamide membranes. The vacuum-assisted technique promoted a higher degree of crosslinking, increased surface roughness, and a denser membrane structure as compared to membranes fabricated without vacuum assistance. These advancements highlight the potential of combining advanced synthesis methods to optimize composite membrane performance across various applications.

This study focuses on developing a scalable, simply fabrication process for PNIPAm-PET composite membranes by combining solvent- and microwave-assisted polymerization techniques. DMSO was used as a swelling agent to enhance diffusion and facilitate the incorporation of the NIPAm monomer into the PET membranes, followed by microwave-assisted polymerization to ensure rapid and efficient PNIPAm

deposition. The effects of microwave output power (300–1000 W), irradiation time (5–15 min), NIPAm concentration, vacuum-assisted technique, and crosslinker addition on weight gain were systematically studied. The composite membranes were subjected to chemical and morphological analysis to assess their structure and thermoresponsive properties. The water vapor and gas permeability (CO_2 and O_2) of the membranes were measured at temperatures below and above the PNIPAm's LCST (25 and 40 °C) to evaluate their ability to regulate the permeance of water vapor and gas by opening and closing the PNIPAm gating mechanism. Finally, a high permselectivity composite membrane was selected to demonstrate its potential as a smart packaging application for extending the shelf life of fresh produce. A temperature simulation study was conducted to mimic real-life scenarios that packaged fresh produce may encounter during transportation and storage or shelf display. Gas concentrations were measured, and the quality of the fresh asparagus was evaluated to assess the membrane's ability to regulate conditions and prolong shelf life under simulated transport temperatures.

1.2 Research objectives

- (i) Fabricate smart membranes of PNIPAm grafting PET using solvent-assisted coupled with microwave-assisted polymerization
- (ii) Investigate microwave irradiation parameters including output power and irradiation time on weight gain efficiency.
- (iii) Study effects of the presence of cross-linker and monomer solution concentration on weight gain and structure of the PNIPAm PET composite membranes.
- (iv) Study the thermo-responsive performance of the grafted PET porous membranes in controlling of gas (H_2O , O_2 , and CO_2) permeability.

1.3 Scope and limitation of the study

The circular PET track-etched membranes were physically coating with poly (*N*-isopropyl acrylamide) (PNIPAm) using solvent-assisted coupled with microwave-assisted polymerization. Dimethyl sulfoxide (DMSO) is the selected solvent to swell the PET membrane. The PET membrane is swollen with 10 ml of DMSO. The swollen membrane is immersed in NIPAm aqueous solution and then polymerized in the commercial microwave. The investigational parameters are output power and irradiation time of the microwave. Output power of 300-1,000 W and irradiation time of 5-15 min are selected to optimize grafting conditions. The optimum grafting condition is first determined using a constant monomer percentage concentration of 10 wt%. The monomer solutions with and without the presence of *N*, *N'*-Methylene bis (acrylamide) (BIS), as a cross-linker, are also investigated in the first study. The second study is to investigate the effect of the monomer solution concentration on the grafting yield. Aqueous solutions containing different concentrations of the NIPAm monomer (5, 10, and 15 wt %) are prepared and used for grafting using the optimum condition obtained for the first step. After grafting, the grafted membranes are characterized for their grafting efficiency, thermal properties, hydrophobicity, and thermo-responsive properties. The first characterization is to confirm the success of the grafting technique. This is done using Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR). The data of ATR-FTIR result is used to calculate a grafting yield. The grafting yield is also validated by determining the increase in the sample mass after grafting. A scanning electron microscope (SEM) is used to observe the microstructure of the grafted membranes. Thermal properties are determined using differential scanning calorimetry (DSC). The hydrophilic-hydrophobic of the grafted membrane is analyzed using contact angle measurement. The thermo-responsive performance of the PNIPAm grafted PET membranes is investigated by using water vapor transmission rate (WVTR) and gas transmission measurements at two different temperatures. The water vapor transmission rate is determined using the dry

cups method. Oxygen (O_2) and carbon dioxide (CO_2) transmission rate measurements are carried out using a bubble flow meter. The WVTR, O_2 TR, and CO_2 TR are measured at temperatures of 25 and 40 °C.