

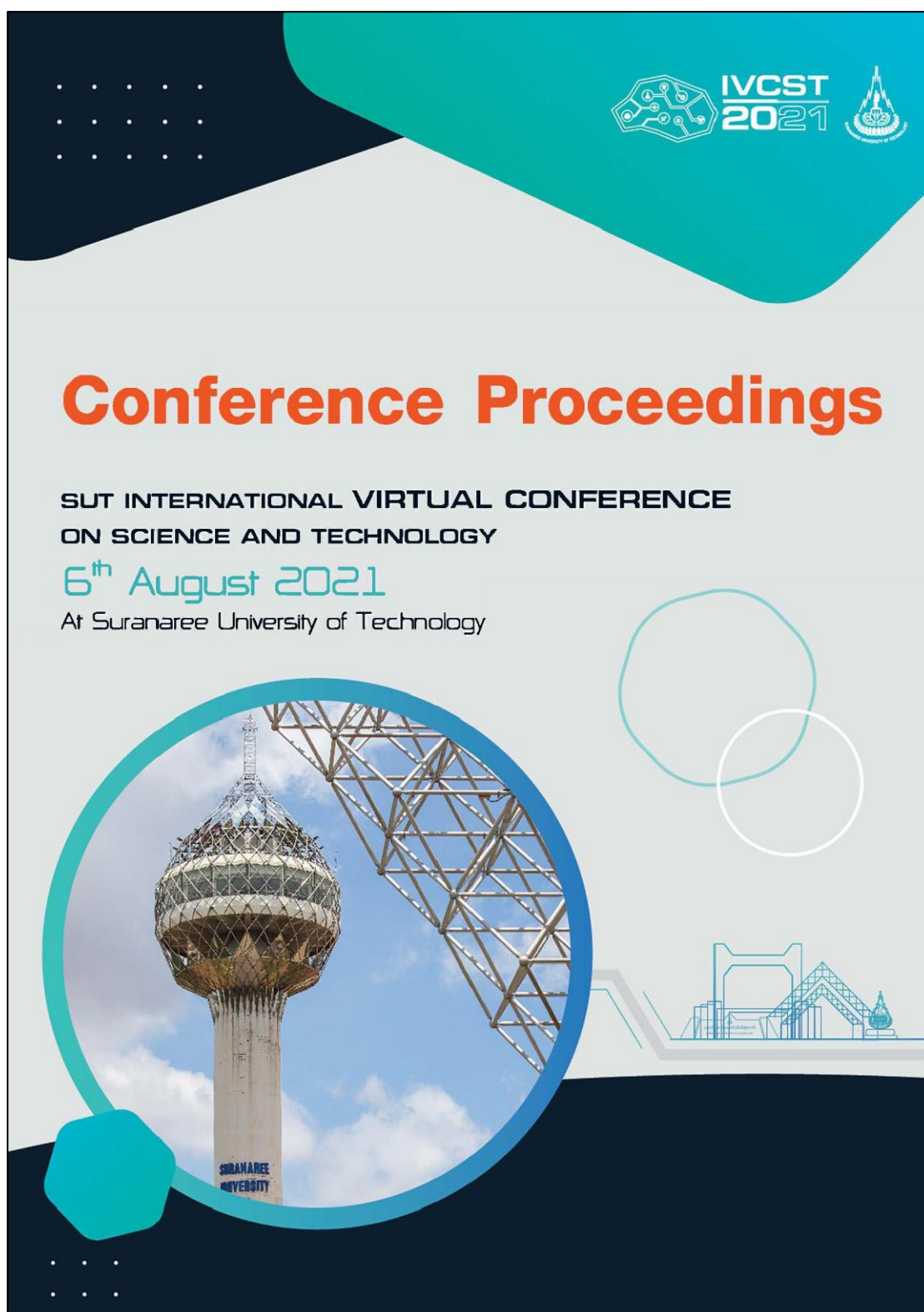
APPENDIX

LIST OF PUBLICATIONS

List of Publications

Seejuntuek, A., Suppakarn, N., Hamid, Z.A.A., Chaiwong, S., and Trongsatitkul, T. (2021), Microwave-assisted Grafting of Poly(*N*-isopropylacrylamide) (PNIPAM) onto Polyethylene Terephthalate (PET) Film. Proceeding of SUT International Virtual Conference on Science and Technology (SUT-IVCST 2021), Nakhon Ratchasima, Thailand, August 6

Seejuntuek, A., Kajornprai, T., Nam, S.Y., Chaiwong, S., Suppakarn, N. and Trongsatitkul, T. (2025), Development of Thermoresponsive PNIPAm-PET Composite Membranes Using Solvent- and Microwave-Assisted Techniques with Potential Applications in Smart Packaging. J Appl Polym Sci e57425. <https://doi.org/10.1002/app.57425>



EAT0035

Microwave-Assisted Grafting of Poly(*N*-isopropylacrylamide) (PNIPAM) onto Polyethylene Terephthalate (PET) Film

A Seejuntuek^{1,2}, N Supakarn^{1,2}, ZAA Hamid³, S Chaiwong⁴, and T Trongsatitkul^{1,2,*}

¹School of Polymer Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand

²Research Center for Biocomposite Materials for Medical Industry and Agricultural and Food Industry, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

³Biomaterials Research Niche Group, School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, Penang, 14300, Malaysia

⁴School of Agro-Industry, Mae Fah Luang University, Chiang Rai, 57100, Thailand

* Corresponding Author: tatiya@sut.ac.th

Abstract. This work, a novel fabrication technique was developed to graft PNIPAm onto PET film using solvent-assisted technique together with microwave-assisted polymerization. The parameters studied included microwave output power (450, 600, 850, and 1000 W), radiation time (1, 3, and 5 min), and monomers concentrations (5, 10, and 15 wt%). Fourier transform infrared spectroscopy (FTIR) results confirmed the success of this novel technique and also provided calculated grafting percentage (Pg). The change in contact angle at temperature below and above the lower critical solution temperature of PNIPAm was in a good agreement with FTIR results. It was found that the increased microwave output power, radiation time, and monomers concentration resulted in increased amount of PNIPAm grafted onto the PET and increased hydrophilic to PET films. The output power of 850 W at 5 min were found to be an optimum condition which gave the highest Pg above 80%. This study demonstrated that Thermoresponsive films of PNIPAm grafted PET film can be prepared using the novel technique of Microwave radiation and solvent-assisted polymerization.

Keywords: Polyethylene terephthalate (PET), Poly(*N*-isopropylacrylamide) (PNIPAm), Solvent-assisted polymerization, Microwave-assisted polymerization

1. Introduction

One of the most studied temperature-responsive materials is poly(*N*-isopropyl acrylamide) (PNIPAm). Physical changes with a lower solution critical temperature (LCST) of 32 °C are one of the most attractive properties of PNIPAm. The chain of this polymer collapses when it is exposed to temperatures higher than its LCST[1]. The polymer has been considered to be used in a variety of fields, including biosensing, artificial muscle[2], and smart gating[3]. The LCST of PNIPAm can be tailored to meet specific needs or used as a copolymer to improve temperature response capabilities in other

polymers. PNIPAm has been copolymerized with various polymers, such as PNIPAm-g-PP[4], PNIPAm-g-Nylon, and PNIPAm-g-PET[5], has recently been employed in investigations.

Polyethylene terephthalate (PET) is a commodity plastic that have used in form of films, fibers, and plastic resins for various industries. The properties of PET are excellent mechanical strength, good stability in the presence of body fluids, and high radiation resistance [6]. Adding or modifying the properties of PET can be done using graft copolymer. In generally, the monomers that are copolymerized with PET are vinyl monomers such as acrylic acid (AA), methyl methacrylate (MMA) [7], and acrylamide (AAm) [8]. NIPAm can also be copolymerized with PET as a vinyl monomer.

The grafted polymerization of PNIPAm of PET can be done by various techniques such as UV radiation induced grafting [9], transfer radical polymerization (ATRP) [10], and redox polymerization [11]. Each technique takes different grafting time and has different limitations. UV grafting is easy to control but gives a low radical yield and there is a problem of degradation of PET. ATRP and Redox polymerization takes a long reaction time and uses more ingredients.

Sanli and Pulat studied solvent-assisted grafted copolymerization of acrylamide on PET films using benzoyl peroxide initiator. The grafted polymerization in this study relied on the swelling of the PET, which allowed monomers to enter the PET's physical structure. The solubility parameter (δ) of the solvent was one of the factors that affected the swelling of the polymer. When the solubility of the solvent was close to that of the polymer, the chemical energy required to breakdown intermolecular cohesive interactions between polymer chains was sufficient to create significant chain mobility. Dimethyl sulfoxide (DMSO) was determined to be the most acceptable swelling agent and solvent-assisted graft copolymerization for PET. In this investigation. This graft copolymerization method was easy to synthesize and required less components. However, this method had long reaction time.

Katesripongs and Trongsatitkul studied an optimization of microwave-assisted grafting of poly(N-isopropylacrylamide) (PNIPAm) onto nylon-6 porous film for thermo-responsive gating membrane. Microwave radiation was used in this study to help with the grafted copolymerization process. Microwave-assisted grafting has a number of distinct advantages, including reduced energy usage and thermal homogeneity. They reported that a PNIPAm grafted Nylon membrane could be fabricated under only 5 minutes of microwave irradiation time.

In this study, we investigated parameters of a novel technique to graft PNIPAm onto PET film using solvent-assisted combined microwave-assisted copolymerization. The focus of this work was to optimize the essential parameters of microwave-assisted grafting. The effects of microwave output power and irradiation, and monomer content. The success of the grafting by the novel technique was verified using Fourier transform infrared spectroscopy (FTIR) and contact angle measurement.

2. Experimental

2.1. Materials

The PET used in this study were thickness 170 -190 μm . and purchased from Polyplex Co. Ethanol (99.9%), used for washing the PET base film, was from Duksan Pure Chemicals. I-isopropylacrylamide (NIPAm) (98%) used as monomer were purchased from TCI Co. Dibenzoyl peroxide (Bz_2O_2) (75% remainder water) used as initiator were purchased Acros Organics. Dimethyl sulphoxide (DMSO) (99.9%) used as solvent for polymerization were purchased from RCI Labscan Ltd. and Deionized water was used in all experiment throughout the study.

2.2. Preparation PET films

PET films were cut into small square pieces of $20 \times 20 \text{ mm}^2$. They then were immersed in ethanol sonicated for 15 minutes to remove contaminants from the PET surface. The treated PET films were dried in a vacuum desiccator under ambient temperature overnight.

2.3. Grafted PNIPAm on PET film via microwave

The NIPAm monomers were dissolved in DMSO solvent in the first step. Bz_2O_2 was added to the NIPAm monomer solution at a concentration of 0.159 g/mL. The treated PET films were then placed on a petri dish and submerged in the prepared solutions in the second step. After that, microwave irradiation was used to initiate grafting polymerization through heating. The various optimization conditions used in this study are summarized in table 1. After grafting polymerization with microwave, a residual solvent, monomer, and unstably bound oligomers were removed from the film substrates by washing the films in boiling water for 1.5 hours. Washing water was changed at least four times. After that, the films were dried and stored in a desiccator.

Table 1. Conditions for the fabricating of PNIPAm-g-PET Films via microwave and solvent assisted polymerization.

Condition no.	NIPAm concentration (wt%)	Output Power (W)	Irradiation time (min)
1	10	450	1
2			3
3			5
4	10	600	1
5			3
6			5
7	10	850	1
8			3
9			5
10	10	1000	1
11			3
12			5
13	5	600	5
14	15		

2.4. Characterization

2.4.1. Fourier Transform Infrared Spectrometer (FT-IR)

The grafting of PNIPAm onto PET film was confirmed using Fourier Transform Infrared Spectrometer (FT-IR) (Tensor27, Bruker, Billerica, MA, USA). For all of the samples, the attenuated total reflection (ATR) mode was used. FT-IR microscopic spectrometer was used to acquire the spectra at 4 cm^{-1} resolutions over 64 scans. The information obtained was the relationship between Transmittance and wavenumber.

The percentage of grafting, P_g (%) could be calculated from FT-IR spectra by estimating the specific absorbance peak [12], which could be used to convert transmittance to absorbance using the equation following (1)

$$A = -\log_{10} T \quad (1)$$

Where; A is absorbance (a.u.)
T is transmittance (a.u.)

The following equation could be used to determine Pg (%) (2)

$$Pg (\%) = \frac{A_{\text{sample}} - A_{\text{ungrafted}}}{A_{\text{ungrafted}}} \times 100 \quad (2)$$

Where; Pg (%) is percentage of grafting
 A_{sample} is absorbance of sample specimen (a.u.)
 $A_{\text{ungrafted}}$ is absorbance of ungrafted specimen (a.u.)

2.4.2. Contact angle measurement

The PNIPAm grafting onto the PET film was carried out at room temperature ($23 \pm 2^\circ\text{C}$). The water contact angle was measured with a microscope (Dino-Lite Digital Microscope, Taiwan) using the sessile drop method. Using a micro syringe, a droplet of deionized water ($5 \mu\text{L}$) was placed on the sample's surface. Using the ImageJ software, the contact angle was determined immediately after droplet placement. DI water at two different temperatures (28°C and 68°C) was used in this experiment. The contact angle reported was the average of five readings taken from different places on the same sample.

3. Results and discussion

Three parameters for grafted PNIPAm on PET films using microwave assisted were investigated in this study. These parameters were output power, radiation time, and NIPAm concentration. The effects of each effect parameter on physical appearance, chemical change (FTIR analysis), and surface hydrophobic-hydrophilic behaviour (contact angle) were described in the data presented here.

3.1. Physical analysis

The NIPAm monomers was grafting copolymerization on PET films using microwave-assisted radiation. Figure 1 shows the temperatures measured in the NIPAm solution immediately after microwave irradiation. The increases of output power and radiation time resulted in the increase of the measured temperature. The increased temperature affected the shape and transparency of PET films. Figure 2 shows samples after grafted polymerization using microwave radiation. When higher temperature was used, the swell ability of the film and the rate of diffusion of monomer and initiator into the film matrix was increased [14]. This causes the specimen to become cloudy and swell. At high output power of 1000 W and irradiation time of 5 min, the film broke into small pieces. This was account as an unusable condition for this grafting technique.

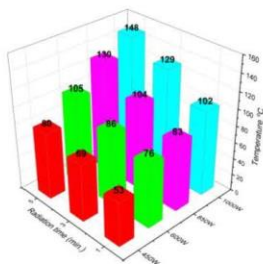


Figure 1 The temperatures measured in the NIPAm solution after microwave irradiation.

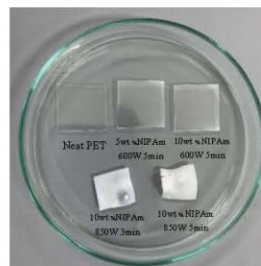


Figure 2 Appearance of the samples after grafted polymerization using microwave radiation using different conditions.

3.2. FTIR analysis

Figure 3 shows the confirmation of grafted PNIPAm on PET films using the ATR-FTIR methodology. The PNIPAm peaks were identified on FTIR spectra at $3,300\text{ cm}^{-1}$ (N-H stretching), $3,070\text{ cm}^{-1}$ (N-H stretching resonant with Amide II overtone, also known as Amide B band), $1,650\text{ cm}^{-1}$ (Amide I) and $1,550\text{ cm}^{-1}$ (Amide II). The peaks of $1,650\text{ cm}^{-1}$ and $1,550\text{ cm}^{-1}$ could be clearly observed. Figure 3(a) shows the increasing amounts of the grafted PNIPAm with increasing output power and radiation time. Increased NIPAm concentrations, as well as increased reaction medium viscosity, slowed monomer diffusion into the film illustrated in Figure 3(b).

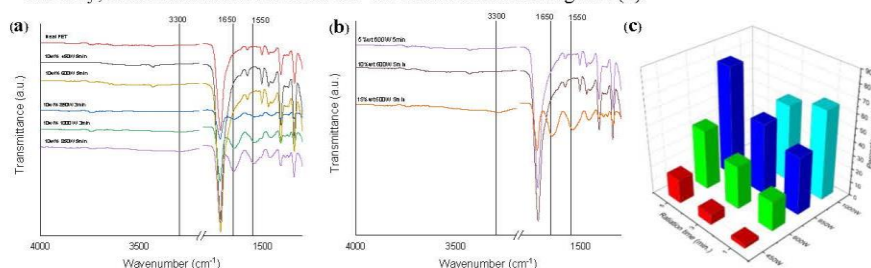


Figure 3 FTIR spectra of the films prepared the effects of (a) output power and radiation time and (b) Monomer content on the degree and success of grafting. (c) Percentage of grafting from FTIR spectra using varied output power and radiation time at 10wt% NIPAm concentration

The 1550 cm^{-1} transmittance peak was transformed to an absorbance peak using Equation 1. Figure 3(c) shows Percentage (Pg), estimated from Equation 2, of grafting from FTIR spectra using various output power and radiation time at 10wt%NIPAm concentration. With increasing output power and radiation time, the result shows an increase in Pg. The best condition was found to be 850 W for 5 minutes, which yielded the highest Pg of over 80%.

3.3. Contact angle (CA) measurement

PET film was a hydrophobic polymer that gave water contact angle to be closer to 90° . Figure 4(a) shows relationship of water contact angles of grafted PNIPAm on PET films and different condition of grafting and structures at temperature below and above PNIPAm's LCST at 25 and 63°C , respectively. The condition with monomer concentration of 10 wt%, irradiation power 450W for 1min was assigned default condition and was given a code as 10-450-1. It was found that the film prepared using the default condition gave the CA at 25°C higher than that of at 63°C . This result was similar that observed in the neat PET film and with the condition of 5-600-5 indicating that these conditions may give little to no grafting yield. It was also plausible that the surface coverage of the grafted PNIPAm molecules was more or less limited. It should be also point out that temperature is one of critical parameter in measuring CA. Higher temperature usually gave lower water CA. Interestingly, when greater grafting yield film was measured, the hydrophobic-hydrophilic behavior reversed. This could be the evident that PNIPAm was successfully grafted onto the PET film's surface. Also, the surface coverage was sufficient the film showed the Thermoresponsive behavior of PNIPAm. The increased output power, radiation time and NIPAm concentrations resulted in the deceased contact angle at 25°C because with more amount of PNIPAm, the stretching PNIPAm chains were wrapped by the water molecules, showing hydrophilicity. While at above LCST, the contact angle of grafted PNIPAm film was increased because the collapsed PNIPAm chains were wrapped by isopropyl groups, showing hydrophobicity. Therefore, the increased output power, radiation time, and NIPAm concentrations enhanced hydrophilicity. For the film prepared with the condition using monomer concentration of 10 wt%, Power output of 1000W, and time of 1min clearly showed the difference in contact angle at two temperatures in figure 4(b) and 4(c) that corresponded to their %Pg value.

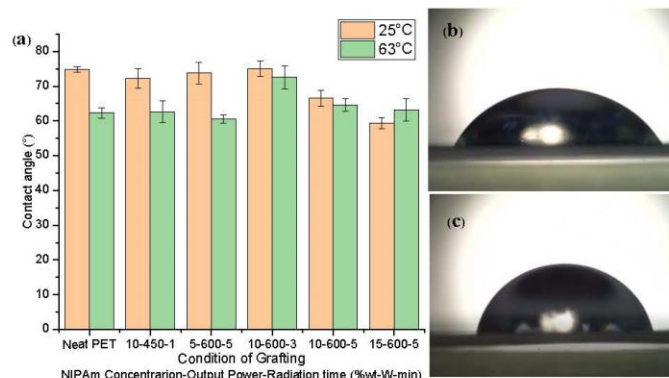


Figure 4 (a) Relationship of water contact angles of grafted PNIPAm on PET films and different condition of grafting and structures at 25 and 63 °C

(b) and (c) Water contact angle of 10%wt 1000W 1min at 25 °C and 63 °C respectively

4. Conclusions

Poly(N-isopropyl acrylamide) have been successfully grafting on PET films using solvent-assisted together with microwave-assisted polymerization method. The PNIPAm grafted on PET resulted in a change in the film's transparency and shape. The success of grafting was confirmed and calculated percentage of grafting (P_g) were done through the appearance of the specific peak of PNIPAm in FTIR spectra. The increased microwave output power, radiation and monomers concentration resulted in increased amounts of PNIPAm grafted onto the PET and increased hydrophilic to PET films. Finally output power 850 W at 5 min were found to be an optimum condition which gave the highest P_g above 80%. The results of this work could bring about the possibility to create smart films with tailorable surface properties in small amounts of time and energy.

Acknowledgments

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RESEARCH ARTICLE

Development of Thermoresponsive PNIPAm-PET Composite Membranes Using Solvent- and Microwave-Assisted Techniques With Potential Applications in Smart Packaging

Anucha Seejuntuek¹  | Todsapol Kajornprai²  | Sang Yong Nam³  | Saowapa Chaiwong^{4,5}  | Nitinat Suppakarn^{1,2}  | Tatiya Trongsatitkul^{1,2,6} 

¹School of Polymer Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand | ²Research Center for Biocomposite Materials for Medical Industry and Agricultural and Food Industry, Suranaree University of Technology, Nakhon Ratchasima, Thailand | ³Department of Materials Engineering and Convergence Technology, Gyeongsang National University, Jinju, Republic of Korea | ⁴School of Agro-Industry, Mae Fah Luang University, Chiang Rai, Thailand | ⁵Integrated Agri-Tech Ecosystem Research Group, Mae Fah Luang University, Chiang Rai, Thailand | ⁶Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok, Thailand

Correspondence: Tatiya Trongsatitkul (tatiya@sut.ac.th)

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Keywords: coatings | membranes | packaging | stimuli-sensitive polymers | synthesis and processing techniques

ABSTRACT

This study presents a simple and scalable process for fabricating thermoresponsive membranes by physically coating poly(*N*-isopropyl acrylamide) (PNIPAm) onto a track-etched polyethylene terephthalate (PET) substrate. Dimethyl sulfoxide (DMSO), used as a swelling agent, enhanced monomer penetration into PET pores, while microwave-assisted polymerization reduced fabrication time to 30 min, achieving uniform polymer deposition. Key parameters—microwave power (300–850 W), irradiation time (5–15 min), and crosslinker addition—were systematically studied. Weight gain (WG) increased by 195%, with crosslinker addition further enhancing incorporation fourfold. Vacuum-assisted techniques improved PNIPAm coverage, confirmed by scanning electron microscopy (SEM). Fourier-transform infrared spectroscopy (FT-IR) verified PNIPAm incorporation, with peak intensity correlating to WG. The membrane exhibited thermoresponsive hydrophilic-hydrophobic transitions, with contact angles shifting from 40°–67° (below 25°C) to 56°–72.8° (above 40°C), enabling “on–off” permeability control. In a shelf-life simulation, membranes fabricated at 600 W and 15 min irradiation effectively regulated O₂ and CO₂ concentrations in asparagus packaging, extending shelf life. These results demonstrate the potential of this scalable fabrication method for smart packaging and industrial applications.

1 | Introduction

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 [1–3].

Among the stimuli-responsive materials, poly(*N*-isopropyl acrylamide) (PNIPAm) has emerged as one of the most extensively studied and widely applied in recent years. PNIPAm is a

thermosensitive polymer characterized by its unique ability to undergo a coil-to-globule phase transition at its lower critical solution temperature (LCST), approximately 32°C [4]. Below the LCST, the PNIPAm chains expand as hydrogen bonds form between the hydrophilic amide ($-\text{CONH}-$) 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 ($-\text{CH}(\text{CH}_3)_2$). This transition causes the PNIPAm chains to collapse and expel water, resulting in dehydration [5, 6]. This unique property of PNIPAm has made it an attractive material for applications such as drug delivery, tissue engineering, and biosensors [7–9]. When incorporated with a membrane, PNIPAm can transform a passive membrane into a smart membrane that can regulate transport properties, making it ideal for advanced applications in drug delivery, tissue engineering, and biosensors.

PNIPAm-based composite membranes have been synthesized on various substrates [10–12]. Among the substrates, polyethylene terephthalate (PET) has been extensively utilized in various forms, such as films, fabrics, and membranes [10, 13, 14]. The exceptional advantages of PET-based support membranes include high chemical resistance, superior mechanical properties, and excellent permeability [15, 16]. In addition, their inherent hydrophobic nature further enhances their performance, preventing unwanted moisture absorption [17].

The PNIPAm-PET composite membranes have been developed to leverage these unique properties, finding applications in smart-gating systems, bio-separation, and cell culture [18–20]. 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 membranes 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 [21, 22]. 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 a Nylon membrane to just 30 min—compared to several hours with traditional oil-bath heating—while achieving high grafting yields of approximately 83% [23]. This acceleration significantly enhances productivity and aligns with sustainable and energy-efficient manufacturing goals [24]. However, the plasma-activated technique used for initiating the polymerization process was expensive and it limited scalability. An alternative method was needed to improve 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 [25–27]. Hsieh et al. [25] 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: 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. [28] demonstrated that the vacuum-suction filtration assisted in the pervaporation dehydration of aqueous isopropanol solutions 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, simple 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 (300–850 W), irradiation time (5–15 min), vacuum-assisted technique, and crosslinker addition on weight gain (WG) 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°C 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.

2 | Experimental Section

2.1 | Materials

Circular PET membranes with a diameter of 47 mm, a thickness of 12 μm , and an average pore diameter of 0.2 μm were purchased from Starlitech Co. Ltd. DMSO and *n*-hexane, used as swelling and recrystallization agents, respectively, were obtained from

RCI Lab Scan Co. Ltd. *N*-isopropyl acrylamide (NIPAm) monomer and *N,N*-methylene bisacrylamide (BIS) crosslinker were obtained from TCI. The NIPAm was recrystallized in *n*-hexane to remove inhibitors. Ammonium persulfate (APS) with 75% remaining water was used as an initiator and obtained from Acros Organics Co. Ltd. Calcium chloride 2-hydrate, procured from KemAus Co. Ltd., served as a desiccant for water vapor permeability testing. Deionized (DI) water was used throughout the study.

2.2 | Preparation of PNIPAm-PET Composite Membranes

Figure 1 shows the preparation process for PNIPAm-PET composite membranes. The PET membrane was first swollen in DMSO at 100°C for 3 h and then carefully blotted with tissue paper to remove excess solvent. A NIPAm monomer solution was prepared by dissolving 8.80 mmol NIPAm monomer and 8.76×10^{-3} mmol of APS initiator in 10 mL DI water. After that, the swollen PET membrane was individually submerged in the prepared NIPAm solution for 10 min at room temperature. Subsequently, the membrane was irradiated in a microwave oven (Samsung, MS28J5255UB/ST, Thailand). During the microwave irradiation, the APS initiator decomposed at solution

temperatures exceeding 70°C and initiated the free-radical polymerization of the NIPAm monomer [29]. Table 1 summarizes the microwave irradiation conditions employed for synthesizing the PNIPAm-PET composite membranes.

The microwave output power (300, 600, and 800 W) and irradiation time (5, 10, and 15 min) were varied to optimize the synthesis conditions. For membranes prepared using the vacuum-assisted technique, the swollen PET membrane was clamped in the vacuum filtration device, and the NIPAm solution was flushed through the membrane before being irradiated in the microwave oven. To investigate the effect of crosslinker addition, the mol ratio of BIS: NIPAm was fixed at 0.41: 8.81 mmol. The BIS crosslinker was added to a NIPAm solution, and the same procedure was followed for preparing the non-crosslinked or linear PNIPAm-PET composite membrane.

The smart membranes were labeled based on the synthesis conditions to streamline identification. The effects of key parameters, including microwave output power, irradiation time, additional vacuum-assisted technique, and crosslinker addition, were abbreviated as P, T, Va, and C, respectively. For instance, P600T15VA was synthesized under microwave power output of 600 W, irradiation time of 15 min, and with the use of a vacuum-assisted technique.

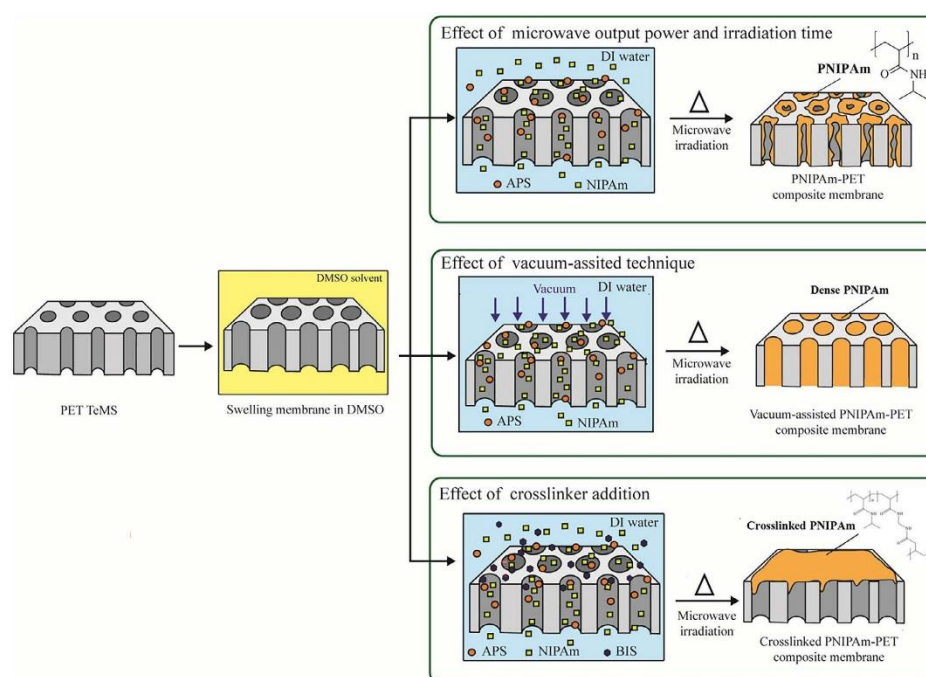


FIGURE 1 | Schematic illustration of the preparation process of PNIPAm-PET composite membranes. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)] [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)

TABLE 1 | The PNIPAm-PET composite membrane codenames and preparation conditions.

Effect	Codename	Output Power (W)	Irradiation time (min)	Vacuum technique use	NIPAm:BIS
Microwave output power	P300T15	300	15	—	—
	P600T15	600	15	—	—
	P850T15	850	15	—	—
Irradiation time	P600T5	600	5	—	—
	P600T10	600	10	—	—
Vacuum-assisted technique	P600T15Va	600	15	✓	—
Crosslinker addition	P300T15C	300	15	—	0.41:8.81

After completing the polymerization process, the PNIPAm-PET composite membrane was then thoroughly washed with DI water and subsequently immersed in 20 mL of DI water in a water-shaking bath overnight to remove the nonreacted monomer before being stored in a desiccator at room temperature. The percentage WG—defined as the dry weight difference between the PNIPAm-PET composite membrane and the original PET membrane using the gravimetric method—was calculated according to Equation (1).

$$WG(\%) = \frac{W_0 - W_1}{W_1} \times 100 \quad (1)$$

wherein W_0 is the weight (g) of the original PET membrane and W_1 is the weight of the membrane after microwave-assisted polymerization of PNIPAm.

For chemical structure and thermal character comparison, PNIPAm hydrogel was prepared by microwave-assisted polymerization at the microwave output power of 600 W and the irradiation time of 15 min with the same concentration of NIPAm monomer and APS initiator in fabricating PNIPAm-PET composite membranes. Then, the film of PNIPAm hydrogel was acquired by solution-casting in a petri dish at room temperature.

2.3 | Characterizations

Fourier-transform infrared spectroscopy (FT-IR) analysis of the PNIPAm-PET composite membranes was carried out using an FT-IR spectrometer (Tensor 27, Bruker, USA) equipped with attenuated total reflectance (ATR) mode to confirm the presence of PNIPAm functional groups. The FT-IR spectra were collected in the wavenumber range of 4000 to 400 cm^{-1} with 64 scans in the resolution of 2 cm^{-1} .

The morphology of the PNIPAm-PET composite membranes was examined using a scanning electron microscope (SEM) (JEOL JSM-6010LV, JEOL Ltd., Japan). The samples were cryo-fractured in liquid nitrogen and sputter-coated with gold for 120 s before observation. Morphological analyses were performed on both the top surface and cross-sectional areas with a rotating angle of 45° tilt angle with an accelerating voltage of 10 kV.

Water contact angle measurement was performed on the composite membrane at room temperature using the sessile drop method and a goniometer (Dino-Lite Digital Microscope, AnMo Electronics Corp., Taiwan). A 3 μL droplet of deionized (DI) water was placed on 5 different surfaces for 3 sample repetitions of the composite membrane using a syringe at temperatures of 25°C and 40°C. The contact angle was determined immediately after the droplet was applied by analyzing photographs of five different areas on the sample surface. The axisymmetric drop shape analysis (ASDA) was performed using ImageJ software.

2.4 | Thermoresponsive Performance Measurement

Water vapor transmission rate (WVTR) measurement was conducted using the dry-cup method (ASTM 96–95) [30]. The PNIPAm-PET composite membrane with an effective area of 176.71 mm^2 was secured on the lid of a polytetrafluoroethylene (PTFE) cup, which contained 5 g of calcium chloride (CaCl_2) as desiccant. The assembled cups were placed in a temperature- and humidity-controlled chamber maintained at a relative humidity (RH) of 90%, and tested at temperatures of either 25°C or 40°C. Mass measurements were recorded at hourly intervals. The WVTR was calculated based on the water vapor flux, defined as the rate of mass change over time normalized by the effective area of the membrane, as described by Equation (2).

$$WVTR = \frac{\text{Flux}}{\text{Area}} = \frac{\Delta G}{\Delta t \times A} \quad (2)$$

where WVTR is the water vapor transmission rate ($\text{g}/\text{h}\cdot\text{m}^2$). A is the permeable area (m^2). ΔG and Δt are the weight difference (g) and time difference (h) of the tested sample, respectively [30].

The ratio of water vapor transmission rate (R_{WVTR}) was calculated by using Equation (3).

$$R_{WVTR} = \frac{WVTR_{\text{at } 40^\circ\text{C}}}{WVTR_{\text{at } 25^\circ\text{C}}} \quad (3)$$

The gas permeability measurements were conducted following the methodology described in the previous study [23]. In short,

the PNIPAm-PET composite membrane was immersed in DI water for 20 min at room temperature to allow the PNIPAm to swell. The swollen PNIPAm-PET composite membrane was then placed over the opening of a chambered acrylic cylindrical container with a volume capacity of 1179 cm³. The membrane was secured with an acrylic cover that featured a 5 mm perforated hole. The chamber was evacuated with a high-vacuum pump for 3 min to remove air, followed by flushing with a gas mixture containing 21% CO₂-balanced N₂. This flushing process was repeated twice to ensure consistent gas composition. The container was then stored under controlled conditions: either in an air-conditioned room at 25°C or in an oven at 40°C.

Gas sampling was performed by extracting 5 cm³ of gas from the chamber hourly, replacing the sampled volume with N₂ to maintain chamber pressure. The gas composition was analyzed using a gas chromatograph (7890A, Agilent Technologies, USA). The data were processed by plotting the logarithm ratio of gas concentrations $\ln\left(\frac{C_{I,as}(t) - C_{I,as}(0)}{C_{I,as}(0) - C_{I,as}(t)}\right)$ against time, where and represent the volumetric fractions of gas *I* inside and outside the container at the initial time (0) and at a determined time (t). This analysis determined the CO₂ and O₂ transmission rates per volume.

2.5 | Shelf-Life Analysis of Green Asparagus Under Simulated Storage and Transportation Conditions Using PNIPAm-PET Composite Membranes

The PNIPAm-PET composite membrane was evaluated for its suitability in simulating the transportation conditions of fresh produce, characterized by immediate temperature changes. Figure 2a illustrates the temperature profile during storage and transportation. Green asparagus was stored in airport cargo at 5°C for 48 h (hours 0–48), followed by exposure to 35°C during a tarmac process for 2 h (hours 49–50), and then returned to storage at 5°C (hours 51–216) [31].

The PNIPAm-PET composite membrane was chosen for its high β value to accommodate the high respiration rate of the green asparagus. The composite membrane was compared to commercial LDPE film. Green asparagus was chosen for this study due

to its high respiration rate and sensitivity to temperature fluctuations. The asparagus was sourced from Stang Farm Fresh Vegetable Ltd. (14.927042°N, 102.109524°E), washed twice with distilled water to remove soil, and trimmed to a length of 140 mm. Uniform spears with straight profiles and diameters ranging from 7 to 12 mm were selected, with 100 g batches weighed for the experiment. The chosen asparagus batches were placed in acrylic containers (1179 cm³ capacity), as shown in Figure 2b. The containers were covered using three configurations: an open control condition with a perforated acrylic lid (5 mm diameter hole), a lid covered with the PNIPAm-PET composite membrane (CM) over the 5 mm diameter hole, and a lid covered with commercial LDPE film (LDPE) 5 mm diameter hole. Each configuration was further covered with the perforated lid. The asparagus containers were tightly sealed with binder clips and stored under the temperature profile illustrated in Figure 2a. Gas concentrations (CO₂ and O₂) were monitored every 24 h. Due to the dynamic storage profile, actual internal temperatures increased over the measurement period.

In a shelf-life study, the concentrations of O₂ and CO₂ in the container headspace were monitored using a gas analyzer (900,141, Bridge Analyzers Inc., USA). During sampling, N₂ was added to the chamber to maintain pressure balance and compensate for the removed volume. The asparagus in each container was weighed before and after storage to determine the percentage of weight loss. Additionally, the textural properties of the asparagus were assessed using a TA-XTplusC texturometer (Stable Micro Systems, UK). Shear force tests were performed by cutting the asparagus at two positions—50 mm and 100 mm from the tips—at a test speed of 10 mm/min. These measurements provided insights into the mechanical integrity of the asparagus after storage under the specified conditions.

2.6 | Statistical Analysis

Most experimental results were analyzed using one-way ANOVA based on three replicates. Post hoc comparisons were conducted using Tukey's HSD test at a significance level of $\alpha = 0.05$.

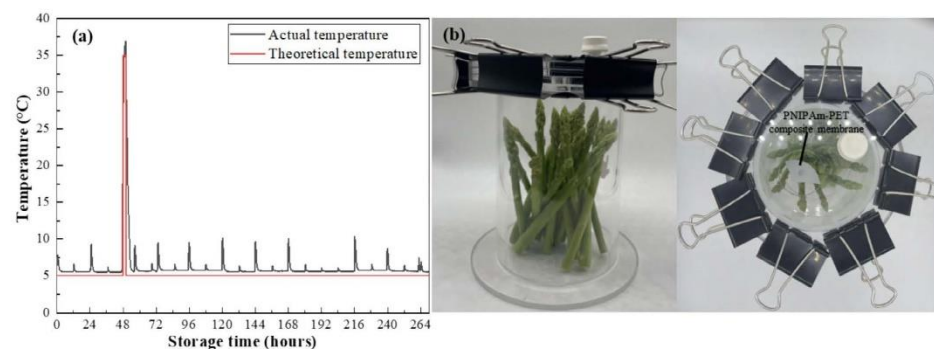


FIGURE 2 | (a) Theoretical and actual temperature profile for simulated storage and transportation and (b) Setup of the PNIPAm-PET composite membrane preparation for shelf-life simulation. [Color figure can be viewed at wileyonlinelibrary.com]

3 | Results and Discussion

3.1 | Effects of Synthesis Conditions on the Weight Gain of PNIPAm-PET Composite Membranes

Table 2 presents the WG of the PNIPAm-PET composite membranes synthesized under various conditions. To examine the effect of microwave output power, the irradiation time was fixed at 15 min. It could be seen that the WG increased as the microwave output power increased from 300 to 600 W, showing that the WG of 44.21 and 191.74% corresponded to the samples P300T15 and P600T15, respectively. However, at a higher output power of 800 W, the WG decreased to 93.35% for sample P800T15. The increased microwave output power enhanced the activity of the reaction system and the propagation rate of the NIPAm monomer [32]. Nevertheless, excessive microwave power led to rapid and excessive heating, which accelerated the termination phase of the monomer polymerization reaction [22].

On the other hand, at a fixed microwave output power of 600 W—which yields the maximum WG, the WG increased linearly with the extended irradiation times. The WG of the samples P600T5, P600T10, and P600T15—corresponding to the irradiation times of 5, 10, and 15 min—was 36.25, 121.73, and 191.74, respectively. The increase in WG was attributed to the prolonged propagation process in the reaction system, allowing more monomer incorporation [33].

The effect of the vacuum-assisted technique was evaluated by comparing sample P600T15Va, which utilized vacuum assistance, to sample P600T15, prepared under normal conditions; both used a microwave output power of 600 W and an irradiation time of 15 min. The vacuum-assisted technique enhanced the WG of the CM from 191.74 to 210.25%, because the pressure facilitated the penetration of monomers and initiator into the surface and pore of the PET membrane before microwave-assisted polymerization.

Furthermore, the addition of a crosslinker was also investigated. Preliminary results showed that at the microwave output power of 600 W with an irradiation time of 15 min, the PNIPAm layer became too thick for the PET membrane to maintain its shape. Therefore, the reduced microwave output power and irradiation time of 300 W and 15 min were used. The sample P300T15C had a WG of 184.03%, which was approximately 4 times higher

than P300T15 (44.21%). This result was because the BIS crosslinker reacted with the PNIPAm monomers to form covalent bonds between the polymer chains. This reaction results in a three-dimensional network structure that prevents the polymer chains detaching from the membrane [34].

In the previous study [23], the surface of the Nylon membrane was modified by plasma treatment before grafting with PNIPAm using microwave-assisted polymerization. These coupled methods could fabricate the grafted PNIPAm on the Nylon membrane with a grafting yield of 6–154%, which is less than the solvent and microwave-assisted method. The solvent and microwave-assisted polymerization were alternative methods to fabricate the CM.

In summary, the study highlighted the effects of microwave output power, irradiation time, vacuum-assisted technique, and crosslinker addition on the WG of PNIPAm-PET composite membranes. WG increased with higher output power and extended irradiation times due to the enhanced reaction activity. The vacuum-assisted technique improved WG by facilitating monomer penetration, while crosslinker addition further enhanced WG by forming a robust three-dimensional polymer network.

3.2 | Effects of Synthesis Conditions on the FT-IR Spectra of PNIPAm-PET Composite Membranes

Figure 3a shows the FT-IR spectra of PNIPAm film and PNIPAm-PET CMs. The absorption bands at 3285 cm⁻¹ (N–H stretching), 3080 cm⁻¹ (C–H stretching resonant with Amide II overtone), 2973 cm⁻¹ (asymmetric C–H stretching), 1638 cm⁻¹ (Amide I), and 1540 cm⁻¹ (Amide II) belonged to the characteristic absorption peaks of PNIPAm film [29, 35]. The PET membrane displayed the characteristic bands at 1715 cm⁻¹ (C=O stretching), 1250 cm⁻¹ (C–C–O stretching), 1100 cm⁻¹ (C–O stretching), and 724 cm⁻¹ (C–H bending) [36, 37]. The FT-IR spectra of the PNIPAm-PET CM presented the characteristic absorption bands of both the PNIPAm and PET membranes, confirming that the PNIPAm-PET CM comprised components from both materials. The FT-IR spectra of PNIPAm-PET CMs with and without BIS crosslinker addition were similar. This similarity was due to the characteristic NIPAm peaks and the H-bond between isopropyl groups, as

TABLE 2 | WG of PNIPAm-PET composite membranes.

Codename	Microwave output power (W)	Irradiation time (min)	Additional technique	Weight gain (%)
P300T15	300	15	—	44.21 ± 3.70 ^c
P600T15	600	15	—	191.74 ± 10.56 ^a
P850T15	850	15	—	93.35 ± 12.28 ^b
P600T5	600	5	—	36.25 ± 5.23 ^c
P600T10	600	10	—	121.73 ± 18.98 ^b
P600T15Va	600	15	Vacuum-assisted technique	210.25 ± 11.95 ^a
P300T15C	300	15	Crosslinker addition	184.03 ± 13.89 ^a

Note: Significant differences at $p < 0.05$ are indicated by different letters. Data are presented as mean ± standard error (S.E.) based on three replicates.

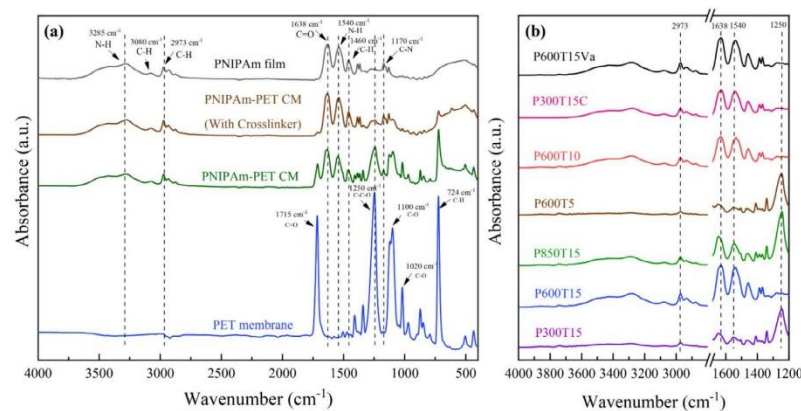


FIGURE 3 | (a) FT-IR spectra of PNIPAm film, PET membrane, and PNIPAm-PET composite membrane (without and with crosslinker), (b) FT-IR spectra of the PNIPAm-PET composite membrane fabricated under various conditions. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/polb.25251)]

reported in the literature [29, 38]. Moreover, no shifts were observed in the characteristic PET peaks within the FT-IR spectra of the PNIPAm-PET CM. This indicates that the microwave irradiation process did not chemically alter the PNIPAm or PET molecular structures.

Figure 3b presents the FT-IR spectra of PNIPAm-PET composite membranes prepared under varying synthesis conditions. A comparison of the microwave power outputs for samples P300T15, P600T15, and P850T15 (300, 600, and 850 W, respectively, with a constant irradiation time of 15 min) reveals differences in the intensities of characteristic absorption peaks. These include peaks at 1638 cm^{-1} (Amide I), 1540 cm^{-1} (Amide II), and 3285 cm^{-1} (N-H stretching) [39]. The intensities of these peaks increased as the microwave power output rose from 300 W to 600 W, indicating the enhanced incorporation of PNIPAm onto the PET membrane. It had been reported that the reaction rate enhancement depended on the microwave output power [22, 40]. Furthermore, the characteristic peaks at 1250 cm^{-1} of PET gradually decreased and disappeared due to the dense PNIPAm on the PET membrane, so that the infrared ray cannot penetrate the substrate [41]. However, applying excessively high microwave power to the reaction system could result in overheating [42]. In this study, at a higher output power of 850 W, the peak intensities associated with PNIPAm decreased while the characteristic PET peak (1250 cm^{-1}) reappeared. This suggests that overheating caused the polymerization process to terminate prematurely. Therefore, selecting optimal microwave conditions was crucial to achieving the maximum WG.

It was noticeable that the intensity of the characteristic absorption peak of PET at 1250 showed a decreasing trend with the WG obtained from different synthesis conditions. Similarly, the effect of irradiation time (P600T5, P600T10, and P600T15) showed an improvement in the intensity of PNIPAm-related peaks. This trend was consistent with the effects of the vacuum-assisted

technique and crosslinker addition. This phenomenon could be attributed to the increased WG, indicating a greater PNIPAm deposition over the PET surface. Therefore, the results confirmed that microwave-assisted did not chemically alter the substrate. Instead, the intensity of the composite's characteristic peak depended on the synthesis condition, which influenced the amount of PNIPAm incorporated into the substrate. In the case of crosslinker addition, the spectra predominantly resembled those of the PNIPAm-PET composite membrane, with only faint PET characteristic peaks detected. This reduction in PET peak intensity is likely due to the formation of a thicker PNIPAm layer on the membrane surface.

3.3 | Effects of Synthesis Conditions on the Morphology of PNIPAm-PET Composite Membranes

Figure 4 presents SEM images of PNIPAm-PET composite membranes, illustrating the top surface (top row) and cross-sectional views (bottom row) under different synthesis conditions. The pristine PET membrane (Figure 4a) exhibited uniformly distributed pores with vertically aligned cylindrical structures and no polymer coverage.

Under microwave-assisted polymerization at lower power and irradiation time (P300T15; Figure 4b), partial membrane surface coverage and pore infiltration by PNIPAm were observed, with some polymer localized on the surface and within the pores. Randomly distributed PNIPAm clusters were also seen on the surface. As microwave output power and irradiation time increased (P600T15; Figure 4c), the extent of pore coverage improved significantly, and the frequency and size of surface clusters increased. This behavior is attributed to the higher energy, facilitating rapid polymerization and localized accumulation of PNIPAm, particularly in areas where monomer concentration may have been higher during the synthesis process. These

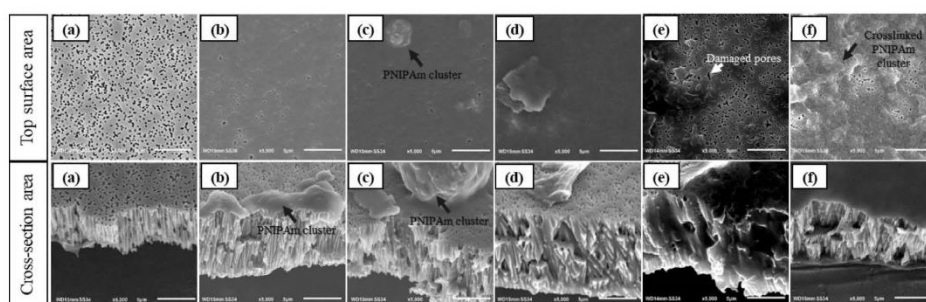


FIGURE 4 | SEM micrographs of the top surface (top) and cross-sectional area (bottom) of: (a) original PET membrane and PNIPAm-PET composite membranes with different conditions: (b) P300T15, (c) P600T15, (d) P850T15, (e) P600T15Va, and (f) P300T15C.

observations align well with the WG results, which showed a higher WG value for P600T15 compared to P300T15, confirming the role of synthesis conditions in influencing both polymer coverage and cluster formation. At the high output power (P850T15; Figure 4d), PNIPAm clusters appeared to be larger than those of P600T15 because of the rapid polymerization induced by the high-energy condition. However, the PET membrane pores also became visible, suggesting that the overheating caused the polymerization in some areas, which aligns with WG and FT-IR results.

The application of the vacuum-assisted technique (Figure 4e) further enhanced PNIPAm dispersion and pore infiltration. The vacuum promoted monomer penetration and polymerization within the pores, creating a more consistent polymer layer. However, excessive vacuum pressure caused slight pore deformation and aggregation of PNIPAm into clusters, as observed in the SEM images. These clusters may result from local increases in monomer population during synthesis under high-vacuum conditions.

The addition of a crosslinker (Figure 4f) produced the most extensive surface and pore coverage, forming a thick, cohesive polymer layer. The crosslinker facilitated stronger intermolecular interactions, which enhanced polymer uniformity but also promoted the formation of larger PNIPAm clusters. These clusters enveloped the pores and surface, contributing to the higher WG observed under these conditions.

The random distribution of PNIPAm clusters and their increased occurrence at higher microwave energies suggest that synthesis parameters strongly influence the morphology of the composite membranes. The clusters are likely formed due to the rapid polymerization and localized accumulation of polymer in high-concentration regions, particularly during microwave-assisted synthesis. These observations, coupled with the WG results, demonstrate the interplay between synthesis conditions, polymer morphology, and functional properties. The extent of pore coverage and cluster formation plays a crucial role in determining the gas permeability and thermoresponsive behavior of the membranes.

3.4 | Hydrophilicity and Hydrophobicity Analysis of PNIPAm-PET Composite Membranes

The thermoresponsive hydrophilic-hydrophobic properties of PNIPAm-PET composite membranes were evaluated through water contact angle measurements. To ensure accurate analysis, the PET sheet was used in place of the PET support membrane to avoid interference from pore-connecting channels that could cause water droplets to migrate. Figure 5 presents the water contact angles of PNIPAm-PET composite sheets prepared under various conditions.

The water contact angles of the PET sheet showed a minimal change, from 77° to 75°, when the temperature changed from 25°C to 40°C, indicating that there were no thermoresponsive “hydrophilic-hydrophobic” switching properties. In contrast, PNIPAm-PET composite membranes prepared using microwave-assisted polymerization demonstrated a significant change, with the water contact angle of 40° and 80° at 25°C and 40°C, respectively. At 25°C, the influence of microwave output power was assessed for samples P300T15, P600T15, and P850T15, which exhibited water contact angles of 58°, 40°, and 61°, respectively. Additionally, the effect of irradiation time was evaluated for samples P600T5, P600T10, and P600T15, which showed contact angles of 67°, 53°, and 40°, respectively. The observed decrease in water contact angle with increased microwave output power and irradiation time was attributed to enhanced WG of the composite sheets, resulting in greater hydrophilicity. This phenomenon occurs as the hydrophilic groups ($-\text{NH}_2-\text{C}=\text{O}$) form hydrogen bonds with water molecules.

At 40°C, the contact angles of the composite sheets were generally higher than those at 25°C, consistent with the thermoresponsive properties of PNIPAm. For example, as shown in Figure 5b, the water contact angle of P600T15 increased from 55.9° at 25°C to 72.8° at 40°C. This temperature-dependent behavior was attributed to the interaction of hydrophilic groups ($-\text{NH}_2-\text{C}=\text{O}$) and hydrophobic groups ($-\text{CH}(\text{CH}_3)_2$) in PNIPAm [39]. The WG played a significant role in the water contact angle changes, as increased PNIPAm content

on the PET surface enhanced its unique thermoresponsive properties.

The effect of crosslinker addition was further compared between sample P300T15C and the P600T15Va, which has similar WGs. It was observed that the difference in water contact angles at 40°C and 25°C was smaller for P300T15C compared to P600T15Va. This suggests that the BIS crosslinker restricted the free movement of PNIPAm chains, limiting their swelling ability, a phenomenon consistent with previous reports [23].

3.5 | Water Vapor Permeability of PNIPAm-PET Composite Membranes

Fresh-produce packaging relies heavily on water vapor permeability due to its connection to transpiration. Moreover, water vapor permeability plays a critical role in humidity optimization to restrict bacterial growth and prolong shelf life [43]. Table 3 shows the relationship between the WVTR of various PNIPAm-PET composite membranes at 25°C and 40°C and the water vapor transmission ratio (R_{WVTR}), denoted as $WVTR_{40^\circ C}/WVTR_{25^\circ C}$.

Firstly, the WVTR of the PET membrane was 134 g/(h m²) at 25°C and 268 g/(h m²) at 40°C, indicating that temperature

significantly influences water vapor permeability. This increase in WVTR at higher temperatures is due to the enhanced molecular motion, allowing more water vapor molecules to permeate through the membrane material [44]. The WVTR of composite membranes P300T15, P600T10, and P600T15 reflected the impact of microwave output power and irradiation time. P300T15, with low WG, showed WVTR values comparable to the PET membrane at 25°C, suggesting insufficient PNIPAm coverage on the pores to fully exhibit thermoresponsive behavior. In contrast, P600T10 and P600T15, which had higher WG, exhibited decreased WVTR at 25°C due to the increased PNIPAm coverage, which effectively restricted water vapor transmission.

The application of the vacuum-assisted technique (P600T15Va) resulted in a WVTR of 83 g/(h m²) at 25°C, slightly higher than P600T10, likely due to the differences in membrane morphology caused by vacuum processing. Similarly, the addition of a crosslinker (P300T15C) yielded a WVTR of 83 g/(h m²) at 25°C.

At 40°C, the WVTR of all composite membranes increased significantly, approaching but remaining slightly lower than that of the PET membrane, compared to their values at 25°C, except for the crosslinked membrane (P300T15C). This trend suggests the temperature-dependent behavior of smart membranes. The slightly lower WVTR at elevated temperatures indicates that

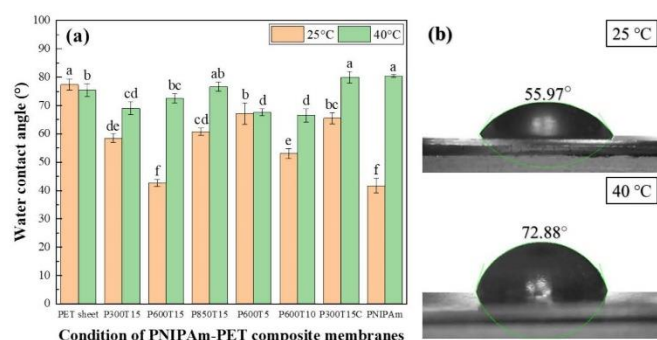


FIGURE 5 | (a) Water contact angles at 25°C and 40°C of the PNIPAm composite membrane prepared under various conditions (b) Water contact angle measurement of PNIPAm composite membrane (P600T15), showing values of 55.9° at 25°C and 72.8° at 40°C. Significant differences at $p < 0.05$ are indicated by different letters. Data are presented as mean $\pm$ SE based on three replicates. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 | Water vapor transmission rate at 25°C and 40°C of the PNIPAm-PET composite membranes prepared under various conditions.

Effect	Codename	%WG	WVTR (g/(h·m ²))		R_{WVTR}
			25°C	40°C	
PET membrane	—	—	134 $\pm$ 3 ^a	268 $\pm$ 4 ^a	2.0
Output power and irradiation time	P300T15	44	104 $\pm$ 22 ^{ab}	219 $\pm$ 8 ^c	2.1
	P600T10	121	80 $\pm$ 9 ^b	231 $\pm$ 19 ^{bc}	2.8
	P600T15	191	46 $\pm$ 10 ^c	214 $\pm$ 3 ^c	4.7
Vacuum-assisted technique	P600T15Va	210	83 $\pm$ 7 ^b	247 $\pm$ 10 ^{ab}	3.0
Crosslinker addition	P300T15C	184	83 $\pm$ 14 ^b	88 $\pm$ 4 ^d	1.1

Note: Significant differences at $p < 0.05$ are indicated by different letters. Data are presented as mean $\pm$ standard error (SE) based on three replicates.

the presence of PNIPAm polymer within the membrane pores may partially restrict water vapor mobility through the membrane, even when the polymer chains collapse above the LCST. The increased WG in these membranes enhanced their ability to regulate water vapor permeability, demonstrating that higher PNIPAm content improves the “on-off” gating mechanism for water vapor. However, despite its high WG of 184%, P300T15C achieved a WVTR of 88 g/(h m²) at 40°C, closely resembling its value at 25°C. This outcome is likely due to the obstruction of chain movement caused by crosslinking, which restricted the polymer's thermoresponsive behavior and hindered the “on-off” gating effect.

R_{WVTR} was analyzed to reveal the thermoresponsive characteristics of the composite membranes. According to Darcy's law, the theoretical R_{WVTR} for a membrane at 25°C, 90% RH, and at 40°C, 90% RH, is 2.32 [45]. The R_{WVTR} of the PET membrane and P300T15 is lower than 2.32, likely due to their porous structures, which allowed unrestricted water vapor transmission. Conversely, the composite membranes with high WG exhibited an R_{WVTR} greater than 2.32, suggesting the presence of additional mechanisms beyond Darcy's law. These mechanisms include enhanced diffusion through PNIPAm polymers and structural changes in the pores at 40°C. However, the cross-linked membrane exhibited an R_{WVTR} lower than 2.32, likely due to the restricted chain mobility caused by crosslinking. This limitation reduced diffusion, caused pore blockage, and hindered gate opening at elevated temperatures.

3.6 | Gas Permeability Performance of Composite Membranes

Gas permeability is a critical property of packaging materials for extending the shelf life of fresh produce. Properly aligning the gas permeability of the packaging with the respiration rate of the produce can suppress respiration, reduce weight loss, and slow down aging, thereby preserving quality. Gases such as oxygen (O₂) and carbon dioxide (CO₂) play an essential role in modulating internal gas concentrations, which are vital for shelf-life

extension. However, as temperature increases, the respiration rate of fresh produce also rises, requiring higher O₂ concentrations and greater CO₂ release from the packaging. This variability underscores the need for self-regulating gas permeability systems in fresh-produce packaging. Furthermore, permselectivity, defined as the permeability ratio between CO₂ and O₂ (denoted as β), is a crucial parameter in modified atmosphere packaging (MAP) systems. A high β value supports the maintenance of reduced oxygen levels, thereby decreasing respiration rates and metabolic activity in fresh produce, significantly contributing to extended shelf life and quality preservation [46].

The smart-gating membrane concept for fresh-produce packaging operates via temperature-responsive behavior mediated by water. During storage, transpiration induces water vapor condensation, which becomes trapped on the film or CM surface. This moisture facilitates the hydration of PNIPAm, enabling its thermoresponsive phase transition in response to temperature fluctuations.

Table 4 presents the O₂ transmission rate (O₂TR), CO₂ transmission rate (CO₂TR), and β values for the PET membrane and PNIPAm-PET composite membranes under various synthesis conditions at 25°C and 40°C. The PET membrane exhibited CO₂TR, O₂TR, and β values at 25°C of 60.65 cm³/h, 74.57 cm³/h, and 0.82, respectively. In general, the O₂TR was higher than the CO₂TR due to the differences in the molecular sizes and diffusivities of oxygen and carbon dioxide [46, 47]. When the temperature increased to 40°C, CO₂TR and O₂TR values also increased, consequently influencing the β value. This behavior can be attributed to the enhanced molecular motion at higher temperatures, driven by increased kinetic energy, which facilitates the ability of gas molecules to overcome barriers and permeate through the membrane pores more readily [48].

The composite membrane P300T15, with a WG of 44%, exhibited O₂TR and CO₂TR at 25°C and 40°C similar to those of the PET membrane, reflecting the insufficient PNIPAm coverage on the PET surface. Increased microwave output power and irradiation time enhanced WG, leading to improved PNIPAm

TABLE 4 | Gas transmission rates (O₂, CO₂) of PET membrane and PNIPAm-PET composite membranes prepared under various conditions.

Effect	Condition	%WG	25°C			40°C		
			CO ₂ TR (cm ³ /h)	O ₂ TR (cm ³ /h)	β	CO ₂ TR (cm ³ /h)	O ₂ TR (cm ³ /h)	β
PET membrane	—	—	60.65 ± 3.89 ^a	74.57 ± 7.43 ^a	0.82 ± 0.05 ^b	74.93 ± 1.70 ^a	91.02 ± 1.27 ^a	0.82 ± 0.01 ^{ab}
Output power and irradiation time	P300T15	44	55.29 ± 2.13 ^{ab}	73.68 ± 0.44 ^a	0.75 ± 0.03 ^b	78.72 ± 2.71 ^a	92.32 ± 6.00 ^a	0.85 ± 0.03 ^a
	P600T10	122	19.80 ± 2.19 ^e	14.50 ± 1.27 ^d	1.38 ± 0.24 ^a	56.59 ± 1.12 ^{bc}	77.46 ± 3.27 ^b	0.73 ± 0.02 ^{bc}
	P600T15	191	51.88 ± 3.36 ^{bc}	43.05 ± 1.75 ^c	1.20 ± 0.03 ^a	61.43 ± 2.08 ^b	84.42 ± 2.65 ^b	0.73 ± 0.01 ^{bc}
Vacuum-assisted technique	P600T15Va	210	44.09 ± 3.22 ^c	54.82 ± 3.36 ^b	0.80 ± 0.01 ^b	61.43 ± 9.85 ^b	84.42 ± 7.83 ^{ab}	0.73 ± 0.07 ^c
Crosslinker addition	P300T15C	184	31.95 ± 2.11 ^d	41.48 ± 2.17 ^c	0.77 ± 0.01 ^b	48.10 ± 2.90 ^c	78.05 ± 0.24 ^b	0.62 ± 0.04 ^d

Note: Significant differences at $p < 0.05$ are indicated by different letters. Data are presented as mean ± standard error (SE) based on three replicates.

coverage and significant changes in gas transmission behavior. Membranes P600T10 and P600T15, with WG of 121% and 191%, respectively, demonstrated decreased O_2 TR and CO_2 TR at 25°C. This reduction indicates that the swelling of PNIPAm chains below the LCST restricts gas transmission by effectively blocking the pores.

At 40°C, above the LCST, the PNIPAm chains collapsed, exposing more of the PET membrane to air and facilitating greater gas transport. This transition resulted in increased O_2 TR and CO_2 TR values, approaching those of the PET membrane. These findings highlight the temperature-dependent behavior of PNIPAm-PET CMs and their ability to regulate gas permeability through a thermoresponsive “on-off” gating mechanism.

In order to enhance PNIPAm uniformity on the PET membrane, the effects of the vacuum-assisted technique were examined. At 25°C, the O_2 TR, CO_2 TR, and β values of P600T15Va were 44.09, 54.82, and 0.80, respectively. In comparison to the P600T15, the vacuum-assisted sample demonstrated increased O_2 TR and CO_2 TR values, while presenting a reduced β value. This suggests that the pressure applied during the vacuum-assisted technique may have caused pore damage, which notably impacts gas transmission rates. The resulting membrane exhibited larger, interconnected pores that facilitated increased gas permeation through the membrane.

A previous study reported that the grafted PNIPAm on a Nylon porous membrane with high grafting yields showed β at 25°C close to 1.1 [23]. In contrast, the PNIPAm-PET composite membrane prepared under P600T15 conditions demonstrated the potential to achieve a β value exceeding 1.1, highlighting its superior gas permselectivity. The increased β value makes P600T15 a promising alternative due to its simple fabrication process and reduced reliance on chemical ingredients. Additionally, designing atmosphere-controlling packaging systems that effectively extend shelf life depends on choosing a gas permselectivity that is compatible with the specific respiration rates of different species of fresh produce.

3.7 | Fresh-Produce Storage and Transportation Simulation Analysis

The CM P600T15 was selected for the simulation and compared to commercial LDPE film due to its high β value. Figure 6 (a) illustrates the gas composition (O_2 and CO_2) within the asparagus packaging headspace during storage. The optimal ranges for O_2 (15%–20%) and CO_2 (5%–10%) at 5°C are indicated by the green and gray bands on the graph, respectively [49].

For O_2 concentration monitoring, the open (control) condition maintained a constant concentration of 20%, whereas the CM and LDPE conditions decreased to approximately 17%. When the asparagus chambers were exposed to 35°C for 2 h (hours 49–50), O_2 concentrations declined sharply across all three conditions due to the accelerated respiration of the asparagus. Upon returning to 5°C for 9 days (hours 51–216), the respiration rate of the fresh produce decreased. By hour 72, the open condition returned to equilibrium at 20%, maintaining a stable O_2 concentration throughout the storage period. In contrast, the CM and

LDPE conditions stabilized at 11%–12% O_2 after the temperature abuse and showed a slight increase upon returning to 5°C. Both conditions reached equilibrium around hour 140, with the O_2 concentration for the CM remaining within the optimal range for asparagus storage.

The CO_2 concentration across all three conditions remained within the range of 0%–3% during the initial 2 days. Exposure to 35°C for 2 h caused a sharp increase in CO_2 concentration, which was followed by a gradual decline until equilibrium was achieved. Both the LDPE film and the PNIPAm-PET CM effectively regulated CO_2 levels, maintaining concentrations suitable for asparagus storage throughout the experiment.

From these results, it is evident that the gas concentrations in the package headspace for the smart packaging (CM) were comparable to those of the commercial LDPE film during the 10-day experiment. However, as shown in Figure 6a, the gas concentrations for the smart packaging consistently fell within the optimal range for asparagus storage (indicated by the green and gray bands on the graph), demonstrating comparable performance over the full storage duration. This highlights the effectiveness of the responsive properties of the PNIPAm-PET CM in maintaining favorable storage conditions.

Figure 6b further supports the effectiveness of the PNIPAm-PET CM in restricting asparagus transpiration, as indicated by reduced weight loss. The weight loss for the CM was 2.85%, slightly higher than the LDPE film (2.73%) but significantly lower than the open control (3.13%). Although the differences in weight loss were not statistically significant within the 10-day experiment, the results highlight the CM's ability to regulate water vapor and maintain produce freshness. Given the thermoresponsive properties of the CM, it is hypothesized that over extended storage periods, the CM may demonstrate even better performance in reducing weight loss compared to the LDPE film. The CM's dynamic regulation of water vapor permeability, especially under fluctuating temperature conditions, could provide cumulative benefits in preserving asparagus quality over time. Future studies could further validate this by examining its performance in longer storage trials.

Figure 6c presents the firmness of asparagus before and after storage under the open (control), commercial LDPE film, and PNIPAm-PET CM conditions. Measurements taken 5 cm from the tips showed an increase in asparagus firmness after storage across all conditions, attributed to enhanced fiber content and fiber lignification [50]. Notably, both the LDPE and CM conditions exhibited firmness values approximately 180 N higher than the open condition, primarily due to reduced moisture loss.

Additionally, firmness measurements taken at 10 cm from the tips were consistently higher than those at 5 cm across all conditions prior to storage, reflecting variations in fiber content along the asparagus spears. Despite these non-significant differences, the overall firmness trends at both 5 cm and 10 cm from the tips were similar, reinforcing the effectiveness of both the LDPE and CM in maintaining asparagus quality during storage.

Given the responsive nature of the CM, it is anticipated that during extended storage periods, the smart packaging would

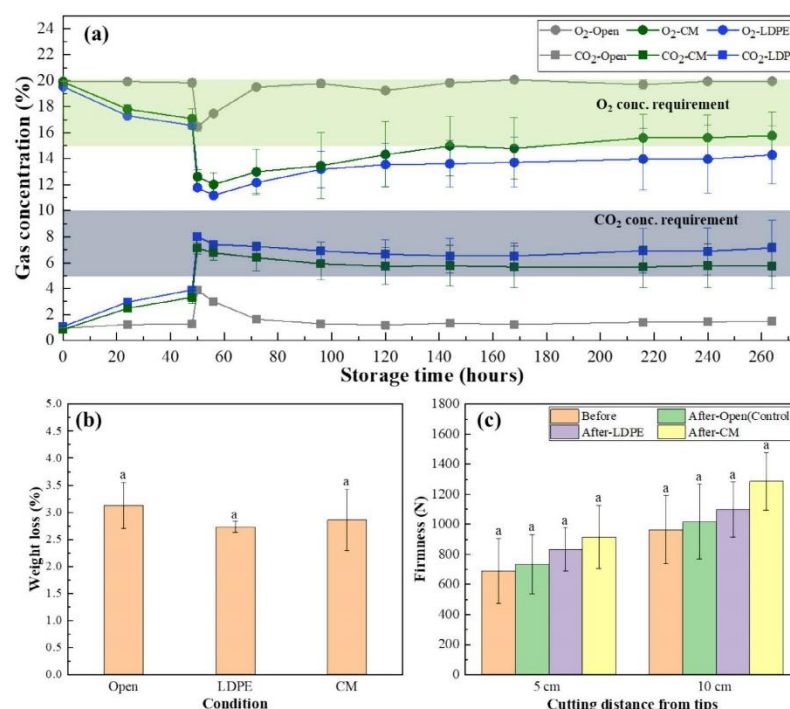


FIGURE 6 | (a) Gas composition (O₂ and CO₂) of the headspace, (b) weight loss, and (c) the firmness of the asparagus during the storage time of the open (control), commercial LDPE film, and PNIPAm-PET composite membrane (P600T15). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

demonstrate superior performance in preserving the quality of fresh asparagus. Moreover, as a responsive packaging system, the CM is expected to perform even better in extending shelf life when used with larger quantities of fresh produce, leveraging its self-regulating properties to adapt to the respiration rates of the stored produce.

It is important to note that this study represents a preliminary experiment designed to demonstrate the potential application of the CM for extending the shelf life of fresh produce. While these results are promising, a more extensive investigation is required to validate the effectiveness of the CM. Future studies should include a larger sample size and incorporate more rigorous and comprehensive quality assessments of asparagus, such as sensory evaluation, nutritional content, and microbial analysis. However, this work focused not on extensive quality testing but on showcasing the potential utility of the CM as a responsive packaging material.

In summary, the PNIPAm-PET CM exhibited comparable properties to the LDPE film, with the added advantage of regulating water and gas transport based on temperature, making it a promising alternative for advanced packaging applications.

4 | Conclusions

Smart PNIPAm-PET CMs were successfully fabricated using solvent- and microwave-assisted polymerization techniques, providing a simple, scalable, and efficient method for advanced membrane production. Among the fabrication parameters, microwave power and irradiation time had significant effects on WG, with optimal conditions (600 W, 15 min) achieving a WG of 192%. The addition of a crosslinker further increased WG by up to four times through covalent bonding between polymer chains, enhancing the functional properties of the membranes.

Morphological and chemical analyses confirmed the successful incorporation of PNIPAm, with vacuum-assisted polymerization improving monomer penetration and distribution on the PET surface. The membranes exhibited thermoresponsive behavior, with water contact angles shifting from 55.9° at 25°C to 72.8° at 40°C, demonstrating hydrophilic-to-hydrophobic switching near the LCST. Membranes with WG greater than 120% enabled effective “open-closed” pore switching for selective water vapor and gas transmission. Despite the crosslinker's restriction of PNIPAm chain mobility, high thermoresponsive performance and permselectivity were maintained. The CM

fabricated under optimal conditions exhibited a permselectivity of 1.36 at 25°C, indicating efficient gas barrier performance at lower temperatures, and a reduced permselectivity of 0.73 at 40°C, corresponding to increased gas permeability due to the thermoresponsive pore opening behavior.

The optimized CM demonstrated effective shelf-life extension for green asparagus by regulating O₂ and CO₂ concentrations to meet storage requirements, achieving quality comparable to commercial LDPE film. Solvent- and microwave-assisted polymerization thus offers a versatile approach to fabricating thermoresponsive membranes for gas separation and smart packaging applications. Future studies should focus on validating these membranes' performance in extended storage periods and with different produce types to fully explore their industrial potential. In addition to extending the shelf life of fresh produce by preserving their quality, smart packaging can also be reused multiple times, owing to the reversibility of PNIPAm [29]. This characteristic contributes to more sustainable material utilization.

Author Contributions

Tatiya Trongsatitkul: conceptualization (equal), formal analysis (equal), funding acquisition (lead), project administration (lead), resources (supporting), supervision (lead), writing – review and editing (lead). **Anucha Seejuntuek:** conceptualization (equal), formal analysis (equal), methodology (equal), writing – original draft (lead). **Todsapol Kajornprai:** conceptualization (equal), formal analysis (equal), investigation (equal), writing – original draft (supporting). **Sang Yong Nam:** supervision (supporting), writing – review and editing (supporting). **Saowapa Chaiwong:** formal analysis (supporting), writing – review and editing (supporting). **Nitinat Suppakarn:** formal analysis (supporting), supervision (lead), writing – review and editing (supporting).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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