

Chapter III

EXPERIMENTAL

3.1 Materials

The circular PET TeMs with a diameter of 47 mm, a thickness of 12 μm , and an averaged pores diameter of 0.2 μm were purchased from Starlitech Co. Ltd., USA. DMSO as a swelling agent was obtained from RCI Lab Scan Co. Ltd., Thailand. *N*-isopropyl acrylamide (NIPAm) monomer and *N,N*-methylene bisacrylamide (BIS) crosslinker were obtained from TCI Co., Japan. The NIPAm was recrystallized in hexane to remove inhibitors. Ammonium persulfate (APS) with 75% remaining water as an initiator was obtained from Acros Organics Co., Ltd., USA. Calcium chloride 2-hydrate from KemAus Co., Australia, was used as a desiccant for water vapor permeability testing. Deionized (DI) water was used throughout the study.

3.2 Preparation of PNIPAm-PET composite membranes

Figure 3.1 displays the preparation process of pore-fulfilled PNIPAm-PET composite membranes. The PET TeM was first swollen in DMSO at 100 °C for 3 hours and then carefully blotted with tissue paper. NIPAm monomer was dissolved in DI water at different concentrations with a constant APS initiator concentration of 8.76×10^{-3} mmol. The swollen PET TeM was individually submerged in the 10 mL NIPAm solution for 10 minutes at room temperature, and then the solution containing PET TeM was placed into a microwave oven (Samsung, MS28J5255UB/ST, Thailand). The decomposed APS at a solution temperature beyond 70 °C began the free-radical polymerization process of the NIPAm monomer. After polymerization, the PNIPAm-PET composite membrane was 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. In the case of crosslinked PNIPAm, the constant BIS crosslinker ratio with PNIPAm of 50:800 was added and coupled with a NIPAm solution. For the vacuum-assisted technique, the swollen PET TeM was clamped in the vacuum filtration device, followed by the flushing of 10 mL of NIPAm water through vacuum filtration before being led to the microwave oven. The weight gain (WG), based on Minghui, G. et al. [30], was defined as the ratio of the dry weight difference through the PNIPAm PET composite membrane to the weight of PET TeM and calculated according to equation (1).

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

Where W_0 and W_1 was the weight of the membrane before and after functionalization

Table 1 summarized the conditions for the fabrication of the PNIPAm-PET composite membrane, including monomer concentration (wt%), microwave output power (Watt, W), and irradiation time (min). The microwave irradiation conditions were first investigated to determine an optimum condition for weight gain, and the influences of monomer concentration on the weight gain of the composite membrane were then investigated. For the nomenclature, the sample name was designed as MxPyTz where x, y, and z referred to the concentration of NIPAm monomer, microwave output power, and irradiation time respectively. For instance, M10P300T5 indicated the composite membrane was functionalized with a NIPAm monomer concentration of 10 wt%, microwave output power of 300 W, and irradiation time of 5 min. For crosslinked PNIPAm and vacuum-assisted techniques, the sample name has added a letter next to MxPyTz with “C” and “VA”, respectively.

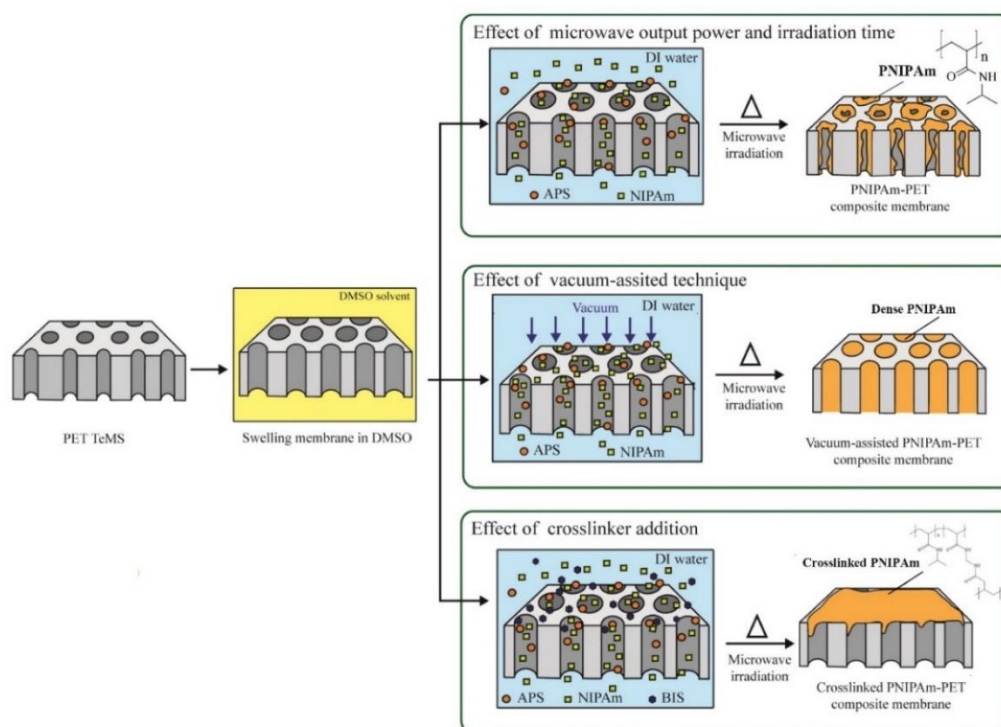


Figure 3.1 Schematic illustration of the preparation process of pore-fulfilled PNIPAm on PET

Table 3. 1 Conditions of PNIPAm-PET composite membrane

Effect	Output Power (W)	Irradiation time (min)	NIPAm concentration(%wt)	Aero-press and Vacuum technique use	NIPAm:BIS
Microwave output power and Irradiation time	300-1000	5-15	10	-	-
NIPAm concentration	Optimum condition		1-15	-	-
Aero-press and Vacuum-assisted technique	Optimum condition		-	Aero-press	-
	Optimum condition		-	Vacuum technique	-
Crosslinker addition	Optimum condition		-	-	0.41: 8.81

3.3 Characterizations

3.3.1 Quantitative and qualitative analysis of Fourier transform infrared (FT-IR) spectroscopy measurement.

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

3.3.2 Morphological analysis

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

3.3.3 Hydrophobic-Hydrophilic measurement

The water contact angle measurement was performed on the composite membranes at room temperature by the sessile drop method using a goniometer (Dino-Lite Digital Microscope, AnMo Electronics Corp., Taiwan). A droplet of DI water (3 μL) at temperatures of 25 and 40 °C was placed on the sample's surface using a syringe. The contact angle was measured from a photograph taken immediately after the water was dropped on the sample's surface and then determined with the axisymmetric drop shape analysis (ASDA) method by ImageJ software. The reported contact angle was averaged from five readings with different observation locations.

3.3.4 LCST analysis by differential scanning calorimetry (DSC)

The thermal properties of the samples were investigated using DSC (Q20, TA Instruments, USA). A composite membrane was cut into small pieces with a weight

of about 5–10 mg. The small piece of the sample was hermetically sealed in an alumina pan and then wetted with a constant volume of DI water (20 μL) before closing the lid. The sample was kept at room temperature for 24 hours before characterization to ensure the fully swollen state of PNIPAm. The test was performed using a scanning rate of 3 $^{\circ}\text{C}$ /min under a nitrogen atmosphere. The heat-cool-heat cycle was used, and the results from the first heating were used for analysis.

3.3.5 Thermoresponsive water vapor permeability

Measurement of water vapor transmission rate was based on the Dye-cup method (ASTM 96-95)¹⁶. The measurement was performed at 25 and 40 $^{\circ}\text{C}$, which were respectively below and above the LCST of PNIPAm, with a humidity of 90% RH. The sample was placed on the top lid of a Polytetrafluoroethylene (PTFE) cup, containing 5 g of calcium chloride (CaCl_2) as desiccant. The prepared cups were placed in a temperature- and humidity-controlled chamber. The samples were consecutively weighed every hour. The water vapor transmission rate (WVTR) was calculated using equation (2).

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

Where WVT was water vapor transmission rate (g/h.m^2). A was the permeable area (m^2). ΔG and Δt were the weight difference (g) and time difference (h) of the tested sample, respectively.

3.3.6 CO_2 and O_2 transmission rates analysis

The gas permeability measurement was described in the previous study (Todsapol Kajornprai et al., 2023). The PNIPAm-PET composite membrane was immersed in DI water for 20 minutes at room temperature to swell the PNIPAm. The immersed PNIPAm-PET composite membrane was covered on a chambered acrylic cylindrical container (1,179 cm^3 capacity) and placed over with an acrylic cover with a

5 mm perforated diameter hole. The gas in the chamber was evacuated with a high vacuum pump for 3 min before being replaced with a mixing gas containing 21% CO₂ and balanced N₂ which was repeated 2 times. After finishing two replications, the container was stored at a room temperature of 25 °C. In the case of 40 °C, the chamber was stored in an oven with a temperature of 40 °C. The gas in the chamber was collected with the syringe in a volume of 5 cm³ along with added N₂ into the chamber for space replacement. The gas sampling was measured every hour to analyze gas composition using a gas chromatograph (7890A, Agilent Technologies, USA). The retained gas composition was analyzed to gas transmission rate which can be obtained from the slope of the plot of $\ln \frac{(C_{i,in}(t)-C_{i,out})}{C_{i,in}(0)-C_{i,out}}$ over time, where **C_{i,in}** and **C_{i,out}** were the volumetric fraction of gas i inside and outside the container at the initial time (0) and at a determined time (t), were constructed to calculate CO₂ and O₂ transmission rate per volume.

3.4 Shelf-Life Analysis of Green Asparagus Under Simulated Storage and Transportation Conditions

3.4.1 Gas concentration analysis

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

The PNIPAm-PET composite membrane was chosen from its high β 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 release soil and trimmed to a length of 140 mm. Uniform spears with straight profiles and diameters ranging from 7 to 12 mm asparagus were selected, with 100 g batches weighed for the experiment. The chosen asparagus batches were placed in acrylic containers (1,179 cm³ capacity), as shown in figure 2(b). 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 3.2(a).

Shelf-life study, the concentrations of O₂ and CO₂ in the container headspace were monitored using a gas analyzer (900141, Bridge Analyzers Inc., USA). During sampling, N₂ was added to the chamber to maintain pressure balance and compensate for the removed volume.

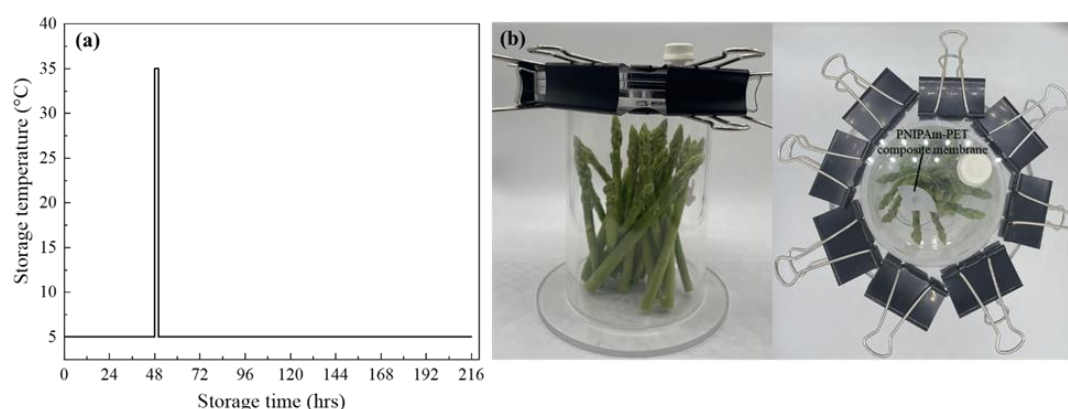


Figure 3.2 (a) Temperature profile for simulated storage and transportation and
(b) Setup of the PNIPAm-PET composite membrane preparation for shelf-life simulation

3.4.2 Green asparagus quality analysis

Images of green asparagus in each container were taken before and after 264 hours (11 days) of storage using a digital camera. The percentage of soft rot was determined by calculating the ratio of bruised or spoiled spears to the total number of spears within each chamber. Samples were weighed before and after storage to determine the percentage of weight loss. Furthermore, the textural properties of the asparagus were analyzed using a TA-XTplusC texturometer (Stable Micro Systems, UK). Shear force measurements were conducted by cutting the spears at two positions—50 mm and 100 mm from the tips—at a test speed of 10 mm/min. These analyses provided quantitative insights into the mechanical integrity of the asparagus following storage under the specified conditions.