

CHAPTER IV

RESULTS AND DISCUSSIONS

In this chapter, there are four sections, as follows: Section 4.1 describes the effect of solvent-assisted polymerization on the swelling of the membrane. Section 4.2 demonstrated the influence of microwave output power and irradiation time on membrane properties to determine the optimized condition. The effect of added techniques such as crosslinker addition, aerosol pressure, and vacuum-assisted membrane properties was described in Section 4.3, and the application of composite membrane to simulate fresh produce storage and transportation was revealed in Section 4.4.

4.1 Solvent-assisted polymerization

4.1.1 Effect of temperature of percentage on swelling

The changes in the physical properties of the PET membrane, specifically thickness and weight, were quantified following swelling to determine the percentages of swelling and solvent uptake. Temperature was identified as a key factor influencing membrane swelling, as elevated temperatures increase the mobility of polymer chains, thereby facilitating greater solvent diffusion into the polymer matrix (Luna et al., 2024; Rahman et al., 2014). For instance, treatment of PET films in DMSO at 100–140 °C enhanced DMSO uptake, likely due to improved interaction between PET and DMSO at higher temperatures.

Table 4.1 presents the physical changes in PET membranes after one hour of swelling in DMSO at various temperatures. Raising the temperature resulted in more pronounced alterations—greater swelling—indicating accelerated intermolecular

kinetics within the PET matrix. Membrane swelling also increased the likelihood of monomer infiltration into the internal pore network. The highest swelling after one hour was observed at 100 °C; however, at 110 °C, the membrane exhibited defects due to excessive thermal stress, as depicted in Figure 4.1a. Consequently, 100 °C was selected as the optimized swelling temperature for further investigation of swelling time effects.

Swelling time was subsequently varied from one to four hours under the optimized temperature (100 °C). The results demonstrated augmented physical changes with prolonged immersion: extended exposure allowed continuous diffusion of DMSO molecules into the polymer matrix, enabling further absorption and expansion until equilibrium was reached.

Table 4.1 The percentage of swollen PET membranes of on the various temperature and time

Temperature (°C)	Time (hours)	Thickness change (ΔH) (μm)	Weight before swelling (g)	Weight after swelling (g)	Solvent uptake
RT	1	0	0.0234	0.0234	0
80	1	0.2	0.0234	0.0244	4.13
90	1	0.4	0.0234	0.0247	5.45
100	1	0.2	0.0234	0.0249	6.45
	2	0.3	0.0234	0.0254	8.55
	3	0.5	0.0235	0.0260	10.84
	4	0.5	0.0234	0.0256	9.45
110	1	0.3	0.0235	0.0253	7.45
120	1	n.d.	0.0234	n.d.	n.d.

Note: Not determined (n.d.) because the PET membrane damage until not retain form

4.2 The effect of microwave-assisted polymerization under various parameter

4.2.1 Microwave output power and irradiation time

Table 4.1. illustrated the percentage of weight gain (%WG) of PNIPAm-PET composite membranes prepared under varying microwave output powers and irradiation times. It could be seen that the WG increased as the microwave output power increased from 300 to 1000 W in irradiation time of 5 min, showing the WG of 0 to 73.54 %. However, the WG was found to decrease on the applied higher microwave output power of 850 W and 1000 W at the irradiation time of 10 and 15 min. The increased microwave output power enhanced the activity of reaction system and propagation rate of NIPAm monomer (Li et al., 2006). Nevertheless, the high output power made overheating and rapid heating which accelerate time in the terminal process of monomer (Katesripongsa & Trongsatitkul, 2019).

On the other hand, at a fixing microwave output power of 600 W—a maximum obtained WG, the WG linearly increased as extending the irradiation times. The WG of the synthesized samples at microwave output power 600W and the irradiation time of 5, 10, and 15 min—was 36.25, 121.73, and 191.74, respectively. The WG increased with the irradiation time because caused by the allowing more propagation process in the reaction system ("Front Matter," 2015).

The optimal synthesis condition for PNIPAm-PET composite membranes was identified at 600 W microwave output power with 15 minutes irradiation, The highest WG of 191.74%. This condition promotes effective polymer propagation without overheating, unlike higher powers which cause premature termination and reduce water absorption. Thus, 600 W and 15 minutes irradiation provide the best balance for maximizing membrane hydrophilicity.

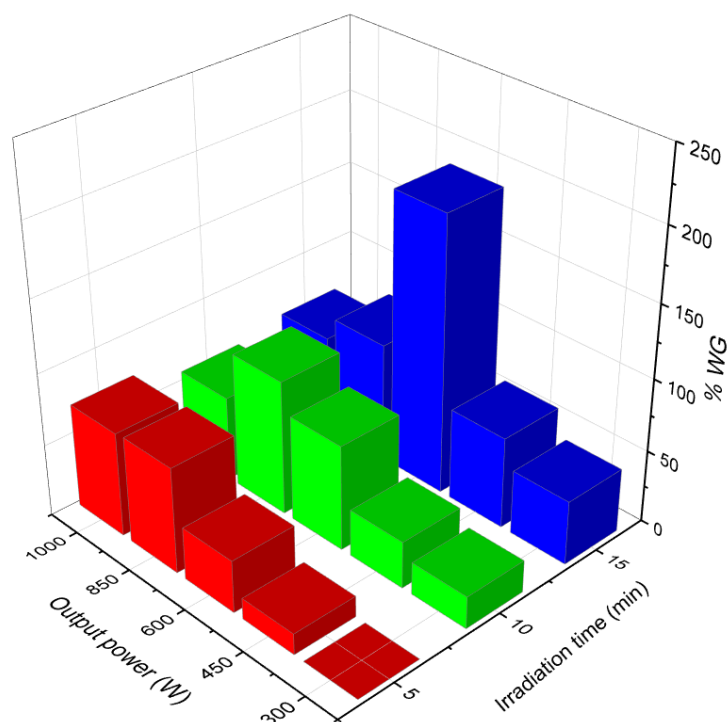


Figure 4.1 The effect of microwave output power and irradiation time on WG of composite membrane

4.2.1 Cosolvent

Dimethyl sulfoxide (DMSO) is an effective swelling agent for polyethylene terephthalate (PET) due to the similarity in their solubility parameters. The close match in solubility parameters facilitates the penetration of DMSO molecules into the polymer matrix, causing polymer chain relaxation and swelling. (Hansen, 2007; Rahman et al., 2014) This property makes DMSO a crucial variable in studies involving solvent systems for PET-based composites, especially when combined with water as a co-solvent. Investigating the effects of varying DMSO-water fractions enables a better understanding of the swelling behavior and structural modification of PNIPAm-PET composite membranes during microwave-assisted polymerization.

Figure 4.2 illustrates the effect of the DMSO/water cosolvent system on the water gain (%WG) of PNIPAm-PET composite membranes. At a fixed microwave output power of 600 W and an irradiation time of 15 min, the membrane exhibited a %WG of 191.45% when the DMSO fraction was 0 (pure water). As the DMSO fraction increased, a gradual decrease in %WG was observed. Beyond a DMSO fraction of 0.3, the membrane integrity was compromised, and accurate %WG measurements could not be obtained due to membrane damage.

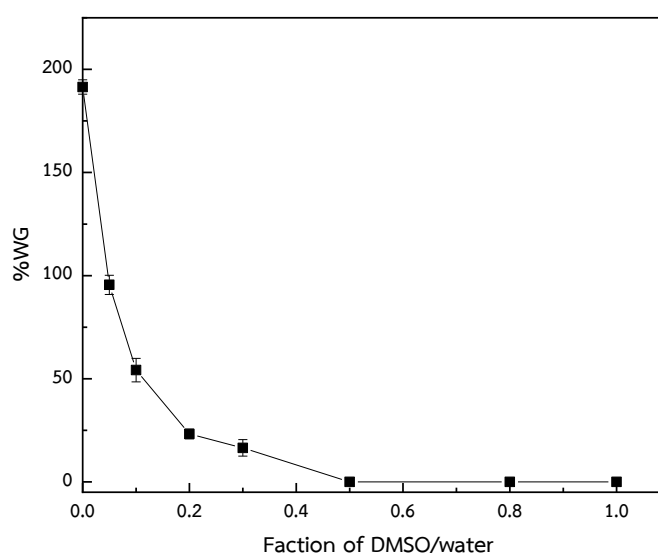


Figure 4.2 The effect of DMSO/water cosolvent system on WG of composite membrane

This decline in %WG with increasing DMSO content can be attributed to the dielectric properties of solvent. This decline in %WG with increasing DMSO content can be attributed to the dielectric properties shown as table 4.2. Water, with a high dielectric constant (80.4), efficiently absorbs microwave energy, leading to rapid and uniform heating during microwave-assisted polymerization. This efficient heating promotes effective polymerization and results in a more hydrophilic membrane capable of higher water uptake.

Conversely, DMSO has a significantly lower dielectric constant of 47, which reduces the overall dielectric constant of the cosolvent mixture as its concentration increases. A lower dielectric constant diminishes the solvent's ability to absorb microwave energy, leading to less efficient heating (Corporation, n.d.). This inefficiency in heating can cause incomplete polymerization and a denser polymer network with reduced porosity, thereby decreasing %WG.

Additionally, the loss tangent ($\tan \delta$), defined as the ratio of dielectric loss (ϵ'') to dielectric constant (ϵ'), quantifies the efficiency of microwave energy conversion into heat. Solvents with higher $\tan \delta$ values, such as DMSO (0.825), indicate greater energy dissipation, leading to faster heating. However, excessive energy dissipation can lead to localized overheating, adversely affecting polymerization and membrane integrity (Kappe et al., 2012).

Furthermore, dielectric loss (ϵ'') represents the energy lost as heat per cycle of the applied electric field. Solvents with higher dielectric loss values are more effective at converting microwave energy into heat (Corporation, n.d.). However, if the heat generation exceeds the system's capacity to dissipate it, it can lead to thermal degradation of the membrane, further reducing %WG.

Therefore, the observed decrease in %WG with increasing DMSO content is a complex interplay of reduced microwave energy absorption due to lower dielectric constant and increased risk of thermal degradation due to higher $\tan \delta$ and dielectric loss.

Table 4.2 Dielectric constant (ϵ), $\tan \delta$, and dielectric loss (ϵ'') of water and DMSO (CEM Corporation,n.d.)

Solvent	Dielectric constant (ϵ)	Tan δ	Dielectric loss (ϵ'')
Water	80.4	0.123	9.889
DMSO	45.0	0.825	37.125

4.2.3 Monomer concentration and crosslinker addition

Figure 4.3 displays the significant impact of NIPAm concentrations and crosslinker addition on the weight gain (%WG) of PNIPAm-PET composite membranes. At a fixed microwave output power of 600 W (P600) and an irradiation time of 15 min(T15), the %WG initially happened at 2 % w/t of NIPAm concentration and gradually increased with higher NIPAm concentrations to of 191.25% at 10% w/t of NIPAm concentration. This increase is attributed to the enhanced polymerization and swelling behavior facilitated by the higher availability of NIPAm monomers (Katesripongsa & Trongsatitkul, 2019). However, at 15% w/t NIPAm, the %WG did not increase linearly, indicating a plateau effect.

This plateau in %WG at higher NIPAm concentrations can be explained by the saturation of active sites for polymerization. As the concentration of NIPAm increases, the viscosity of the solution rises, leading to a decrease in the mobility of monomers and radicals. This reduced mobility limits the propagation of polymer chains, resulting in a less efficient polymerization process (Rana & De la Hoz Siegler, 2021).

The addition of crosslinkers, such as *N,N'*-methylenebisacrylamide (BIS), further influenced the %WG. At optimal concentrations (P600T15), The %WG increased with every concentration of NIPAm. For instance, at a concentration of 5 %w/t, the

%WG increased from 121.56 to 456.42, representing approximately a fourfold increase when a crosslinker was added. Crosslinkers facilitated the formation of a three-dimensional polymer network, enhancing the structural integrity and swelling capacity of the composite membrane. Incorporating crosslinkers increased the %WG by approximately fourfold compared to membranes without crosslinkers. This significant enhancement is attributed to the formation of a denser network structure (Bashir et al., 2020). However, the PNIPAm layer (%WG > 200) became too thick for PET membrane to maintain its shape.

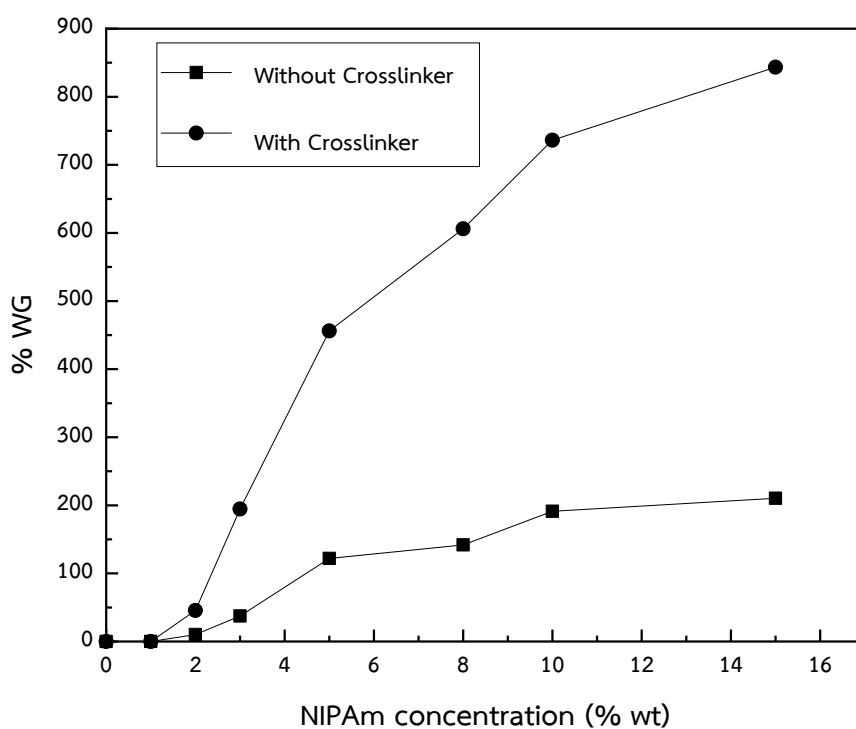


Figure 4.3 The effect of NIPAm concentration and crosslinker addition on WG of composite membrane under microwave output power 600 W and irradiation time 15 min

4.2.4 Aero-pressure assisted and vacuum-assisted technique

The P600T15 sample (microwave power: 600 W, irradiation time: 15 min) was used to compare the performance of aeropressure-assisted and vacuum-assisted techniques under identical microwave-assisted polymerization conditions. The baseline weight gain (WG) of the PNIPAm–PET composite membrane was 191.45 %. When aeropressure assistance was applied, WG increased to 210.25 %, and a similar enhancement was observed for the vacuum-assisted method, which also raised WG to 210.25 %.

These results indicate that both pressure-assisted methods significantly improve the penetration of NIPAm monomers and initiators into the PET membrane structure prior to microwave-induced polymerization. The applied pressure—either positive (aeropressure) or negative (vacuum)—enhances mass transfer by forcing the reaction medium into the membrane surface and pore network, resulting in more uniform polymer distribution.

From a mechanistic perspective, pressure-assisted impregnation reduces boundary layer resistance, promotes infiltration into pores of membrane, and ensures more effective polymer chain anchoring during subsequent microwave irradiation. Microwaves then accelerate polymerization by providing rapid volumetric heating, which promotes chain propagation. Consequently, the improved WG can be attributed to the combined effect of enhanced monomer/initiator transport and increased polymerization efficiency.

These findings align with previous reports showing that vacuum-assisted impregnation improves polymer loading in porous substrates by reducing air entrapment and enhancing liquid penetration into pores (Siti et al., 2017). Similarly, aeropressure has been reported to facilitate impregnation and improve coating uniformity in polymer–membrane systems (Katesripongsa & Trongsatitkul, 2019).

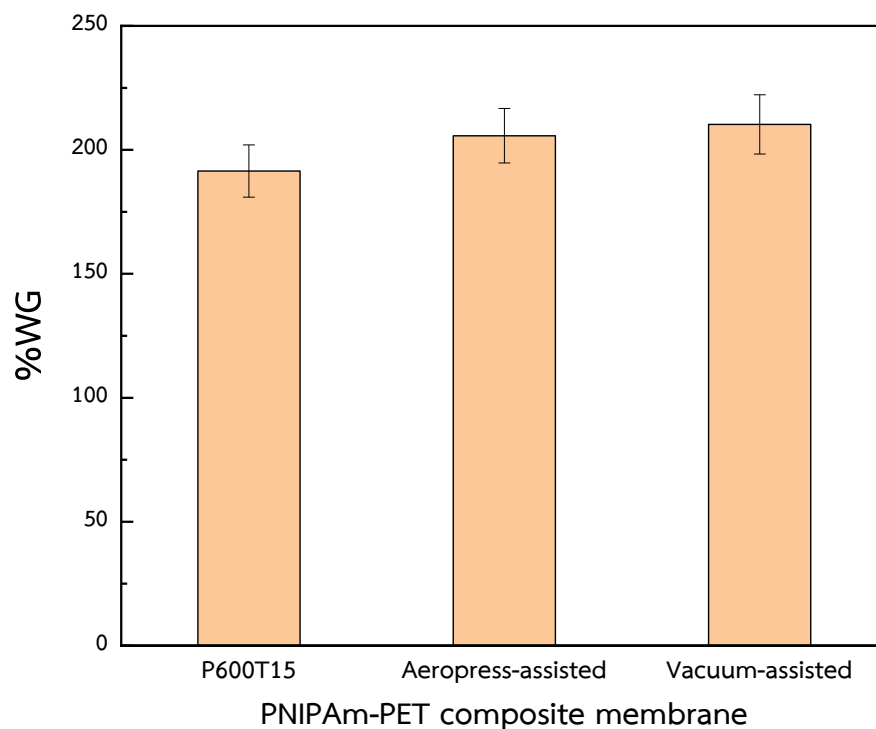


Figure 4.4 The WG of the PNIPAm-PET composite membrane with the pressure techniques

Summarized, the study examined the effect of microwave output power, irradiation time, NIPAm concentrations, crosslinker addition and vacuum-assist technique, on the weight gain of the PNIPAm-PET membrane. The weight gain increased with the output power because of the reaction in the system along with the increased irradiation time. The vacuum-assisted technique introduced the NIPAm monomer and initiator into the pore, improving the weight gain. Furthermore, the addition of the crosslinker enhanced the weight gain due to the formation of covalent bonds between the polymer chains.

4.3 FT-IR Analysis

Figure 4.5 shows the FT-IR spectra of PNIPAm film and PNIPAm-PET composite membranes. The absorption bands at 3285 cm^{-1} (N-H stretching), 3080 cm^{-1} (N-H stretching resonant with Amide II overtone), 1638 cm^{-1} (Amide I), and 1540 cm^{-1} (Amide II) belonged to the characteristic absorption peaks of PNIPAm film (Gong et al., 2020). The PET membrane displayed the characteristic bands at 1408 cm^{-1} (phenyl ring stretching), 1240 cm^{-1} , and 1118 cm^{-1} (C-O-C stretching) (Park et al., 2021). The PNIPAm-PET composite membrane presented the characteristic absorption bands of both PNIPAm and PET membrane on the FT-IR spectra, suggesting that the PNIPAm-PET composite membrane was composed of both PNIPAm and PET components. The similar FT-IR spectra of PNIPAm-PET composite membrane with and without BIS crosslinker addition were similar due to the NIPAm peak and the caused H-bond between isopropyl groups that relate with the literature report.(Kurecic et al., 2012) Besides, the FT-IR analysis of the PNIPAm-PET composite membrane did not detect any shift in the PET peak, indicating that the microwave irradiation did not chemically change the PNIPAm and PET structures.

Figure 4.5(b) illustrates the FT-IR spectra of the PNIPAm-PET composite membrane prepared under different conditions. The comparison of microwave power output in P300T15, P600T15, and P850T15 (300, 600, and 850 W with constant irradiation time of 15 min) reveals different intensities of characteristics, peaking at 1638 cm^{-1} for Amide I, 1540 cm^{-1} for Amide II, and 3285 cm^{-1} for N-H stretching, depending on the specific conditions. The intensity of the peaks aforementioned above increased with microwave power output up to 600 W and decreased when power output rose to 800 W.

It was noticeable that the intensity of the characteristic absorption peak of PET at 1715 , 1250 , and 1110 cm^{-1} showed a decreasing trend with the WG obtained from different synthesis conditions. Along with the effect of irradiation time (P600T5, P600T10, and P600T15), it also improved the intensity of peaks, which could have

happened in the same way as the effect of the vacuum-assisted technique and crosslinker addition. This phenomenon was associated with improved weight gain, which created more PNIPAm over the PET surface. Therefore, the microwave-assisted technique did not chemically change the substrate, and the increase in the intensity of the characteristic peak of the composite depended on the microwave synthesis condition, which related to weight gain on a substrate. In the case of the effect of crosslinker addition, the spectra seemed to show the PNIPAm-PET composite membrane, and few detected the PET characteristic peak due to the increased PNIPAm layer.

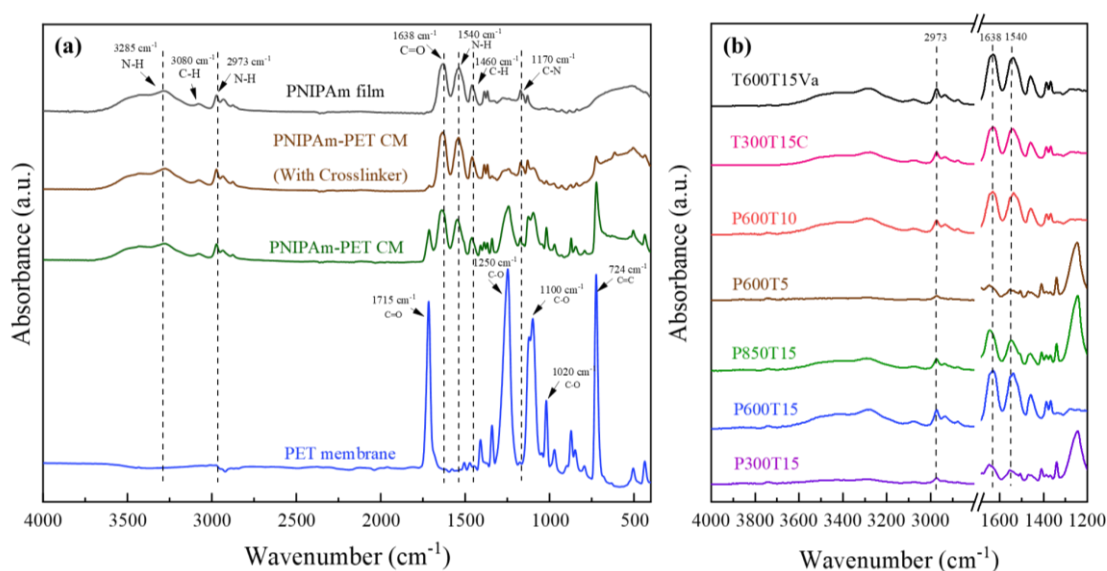


Figure 4.5 (a) The FT-IR spectra of PNIPAm film, PET membrane, and PNIPAm-PET composite membranes (without and with crosslinker), (b) The FT-IR spectra of the PNIPAm-PET composite membranes fabricated using various conditions.

4.4 The morphology of the PNIPAm-PET composite membranes

Figure 4.6 shows the morphology of the PNIPAm-PET composite membranes on the top surface (left hand) and the cross-sectional area (right hand), as observed by SEM. The PET membrane displayed the random distribution of similar-sized pores and vertical cylinder structures. The increased WG from the influence of microwave output and irradiation time was displayed in Figure 4.6b (P300T15) and 4.6c (P600T15). These results explored that the PNIPAm cluster was randomly distributed covering the surface and partially in pores. At the high output power of P850T15 shown as figure 4.6d, 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 effect of vacuum-assisted and aeropress-assisted (figure 4.7a and 4.7b) helped the PNIPAm cluster disperse and flatten the layer on the PET surface. In the cross-sectional area, the pressure enhanced the PNIPAm cluster, resulting in more coverage inside the pore than it would have been without the vacuum technique. However, the pressure resulted in damage and a gathering of pores. The addition of a crosslinker in Figure 4.7c formed the PNIPAm layer into a large cluster, encircling the cover surface and pores.

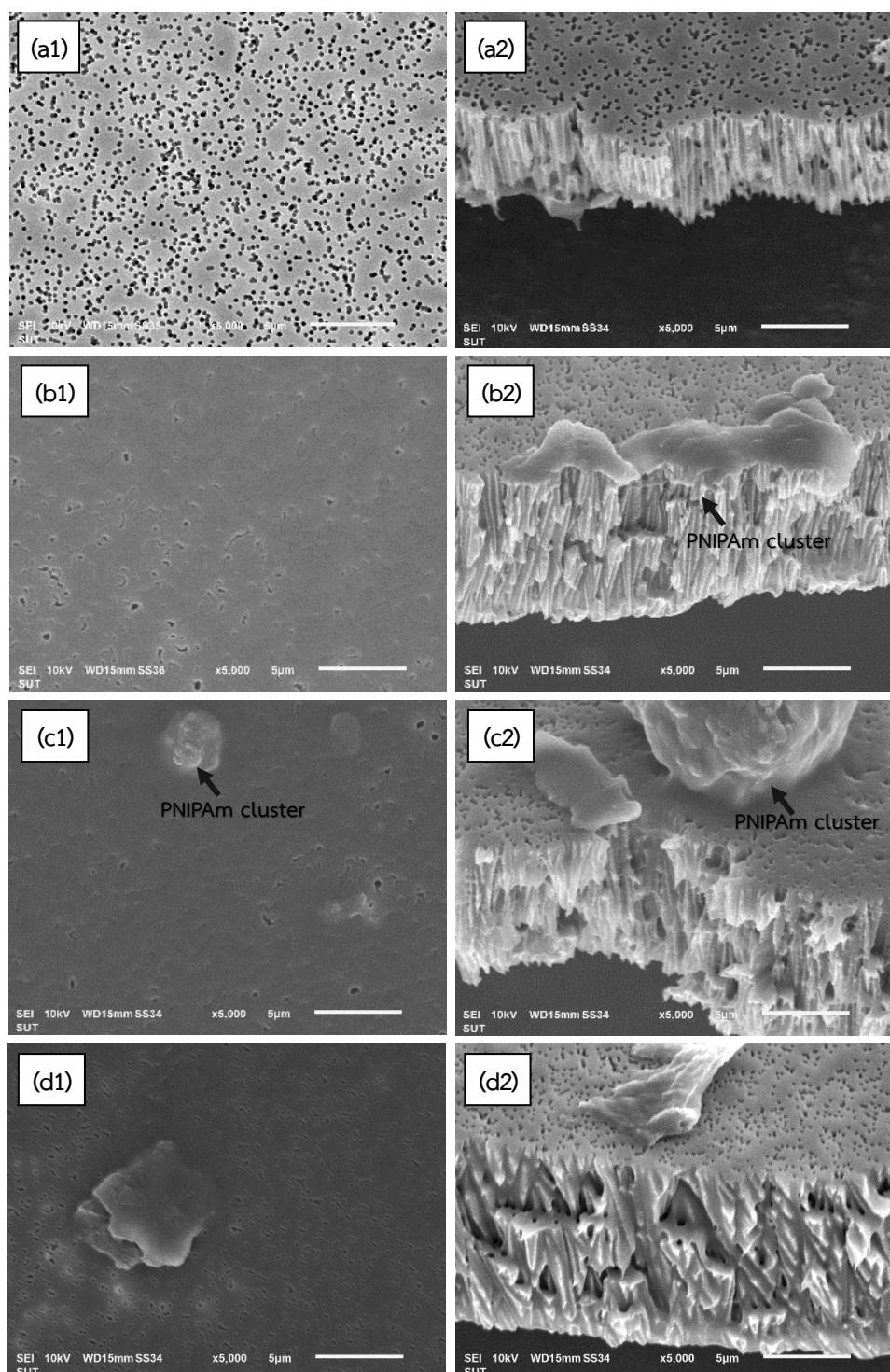


Figure 4.6 SEM photographs of the surface on top (left hand) and cross-section area (right hand) on the bottom of (a) PET membrane and PNIPAm-PET composite membranes with different conditions: (b) P300T15, (c) P600T15 (d) P850T15

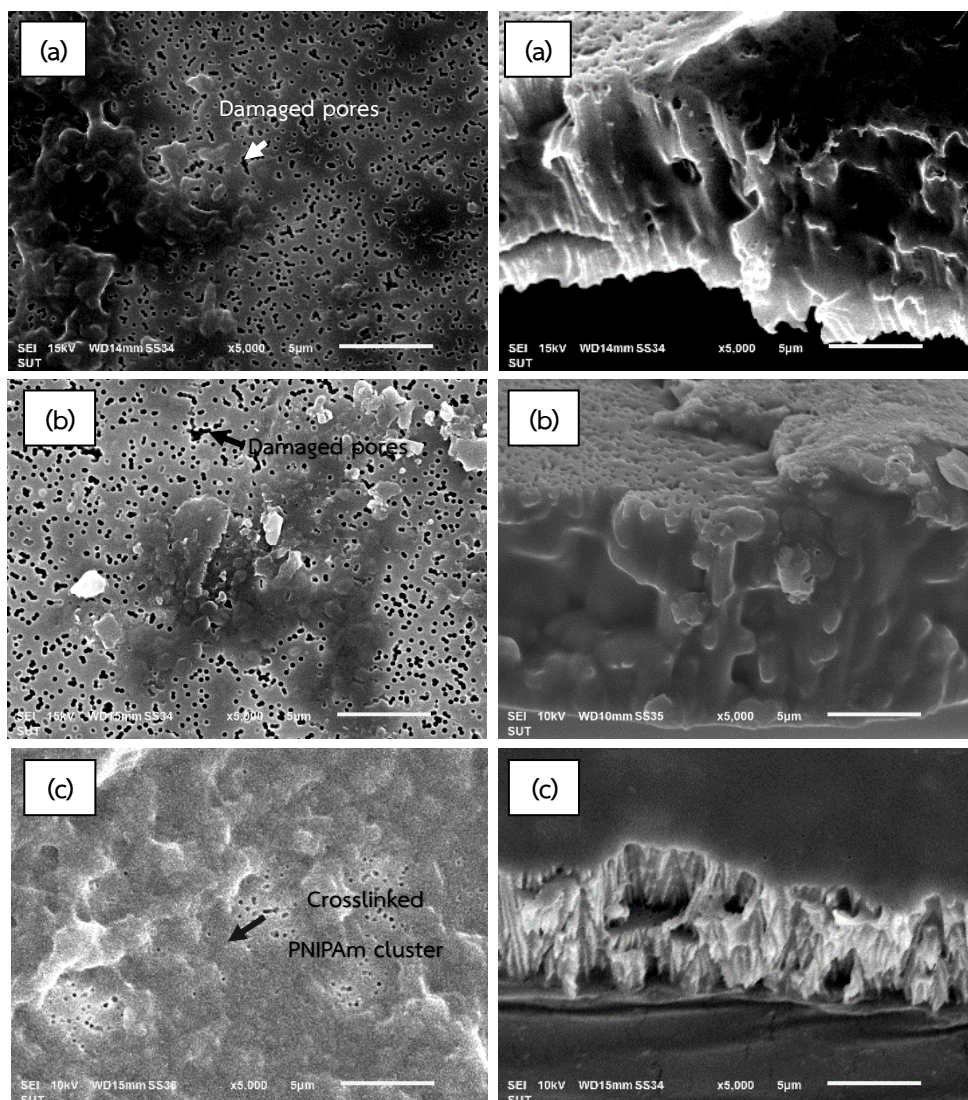


Figure 4.7 SEM photographs of the surface on top (left hand) and cross-section area (right hand) on the bottom of PNIPAm-PET composite membranes with different parameters: (a) P600T15Va, (b) P600T15Ae and (c) P300T15C

4.5 Determination of the lower critical solution temperature (LCST) *via* DSC analysis

The DSC thermogram in Figure 4.8 revealed distinct thermal behaviors of the PET membrane, PNIPAm film, and PNIPAm–PET composite membranes. The neat PET membrane exhibited no discernible thermal transition within the investigated range, and displayed only a gradual baseline shift, which was consistent with its high thermal stability and the absence of thermoresponsive moieties.

In contrast, the PNIPAm film displayed a sharp endothermic peak at approximately 35–37 °C, corresponding to the well-documented lower critical solution temperature (LCST) of PNIPAm. This peak reflected the coil-to-globule transition of PNIPAm chains, during which the polymer underwent dehydration and phase separation upon heating. The pronounced endothermic response indicated a highly cooperative transition, as typically observed in bulk PNIPAm systems.

The PNIPAm–PET composite membrane without crosslinker also exhibited a transition at approximately 35 °C, similar to the PNIPAm film. The transition occurred within the same temperature range, although with reduced peak intensity compared with the PNIPAm film. This attenuation suggested restricted chain mobility when PNIPAm was immobilized on the PET substrate, thereby suppressing the enthalpic contribution of the LCST transition. The PET support likely constrained the swelling and collapse of PNIPAm domains, which led to a broader and less cooperative transition.

By contrast, the PNIPAm–PET composite membrane with crosslinker showed no distinct endothermic peak in the 20–50 °C region. Instead, the thermogram remained relatively flat, which indicated that crosslinking significantly suppressed or eliminated the cooperative LCST transition. This behavior was attributed to the restricted conformational flexibility of the PNIPAm chains within the crosslinked network, which hindered large-scale dehydration–rehydration events that were detectable by DSC.

Although thermoresponsive properties might still have been present at the molecular level, the enthalpic signature was effectively masked due to structural rigidity.

Overall, these results confirmed that PNIPAm retained an LCST-type phase transition near physiological temperature ($\sim 37^\circ\text{C}$), but the magnitude and sharpness of the transition depended strongly on its physical state and its interaction with the PET substrate. Crosslinking further diminished the detectable thermal response, underscoring the inherent trade-off between mechanical stability and thermoresponsive functionality in composite membranes. These findings were consistent with previous reports describing the suppression of sharp LCST transitions in crosslinked or surface-grafted PNIPAm systems.

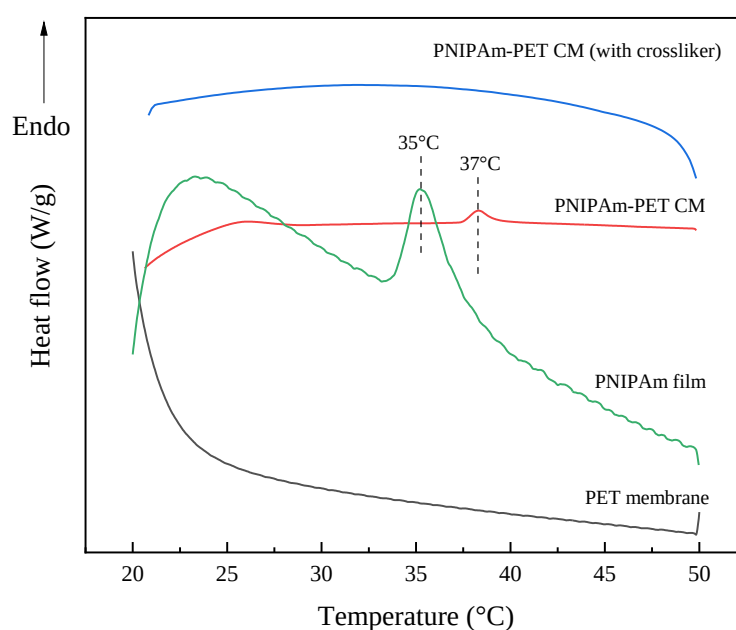


Figure 4.8 DSC thermograph of PET membrane, PNIPAm film, and PNIPAm-PET composite membrane

4.6 The hydrophilicity-hydrophobicity analysis

The thermoresponsive hydrophilic-hydrophobic properties of PNIPAm were determined by the water contact angle measurement. The PET sheet was replaced with the PET support membrane because of the pore-connecting channels that caused the water droplets to migrate toward it. Figure 4.9 depicts the water contact angle of the PNIPAm-PET composite sheets prepared by various conditions. The water contact angles of the PET sheet slightly changed from 77° to 75° when the temperature changed from 25 to 40 °C, indicating that there were no thermoresponsive “hydrophilic-hydrophobic” switching properties. Conversely, the microwave-assisted polymerization-prepared PNIPAm sheet demonstrated a significantly different water contact angle of 40° and 80° at 25 °C and 40 °C, respectively. At a temperature of 25 °C, the effects of microwave output power were compared for P300T15, P600T15, and P850T15, which gave a water contact angle of 58°, 40°, and 61°, respectively. We compared the irradiation times of P600T5, P600T10, and P600T15, resulting in contact angles of 67°, 53°, and 40°, respectively. The increased effects enhanced the weight gain of the composite sheets, resulting in a decrease in the water contact angle. These phenomena were hydrophilic because the hydrophilic groups ($\text{NH}_2\text{-C=O}$) interact with water by H-bonding, which could happen in the effect of crosslinker addition. In the case of a temperature of 40 °C, the contact angle of the composite sheets is almost higher than at 25 °C. For example, in Figure 4.7 (b), the contact angle of P600T15 could be 55.9° and 72.8° at 25°C and 40°C, respectively. The change of contact angle with temperature was well accepted for both hydrophilic groups ($-\text{CH}(\text{CH}_3)_2$) and hydrophobic groups ($\text{NH}_2\text{-C=O}$) in PNIPAm (Yang et al., 2019). The weight gain plays a role in the water contact angle change because of the increased PNIPAm content on the PET surface, which improved its unique characteristics. In addition, the effect of crosslinker addition was compared between the P300T15C and the P600T15Va, which were closely weighted. This result found that the difference in water contact angle at 40°C and 25°C of

P300T15C was lower than P600T15Va. This phenomenon indicates that the BIS crosslinker restrained the free chain of PNIPAm, leading to the limitation of the swelling ability, which is similar to the previous report.(T. Kajornprai et al., 2023)

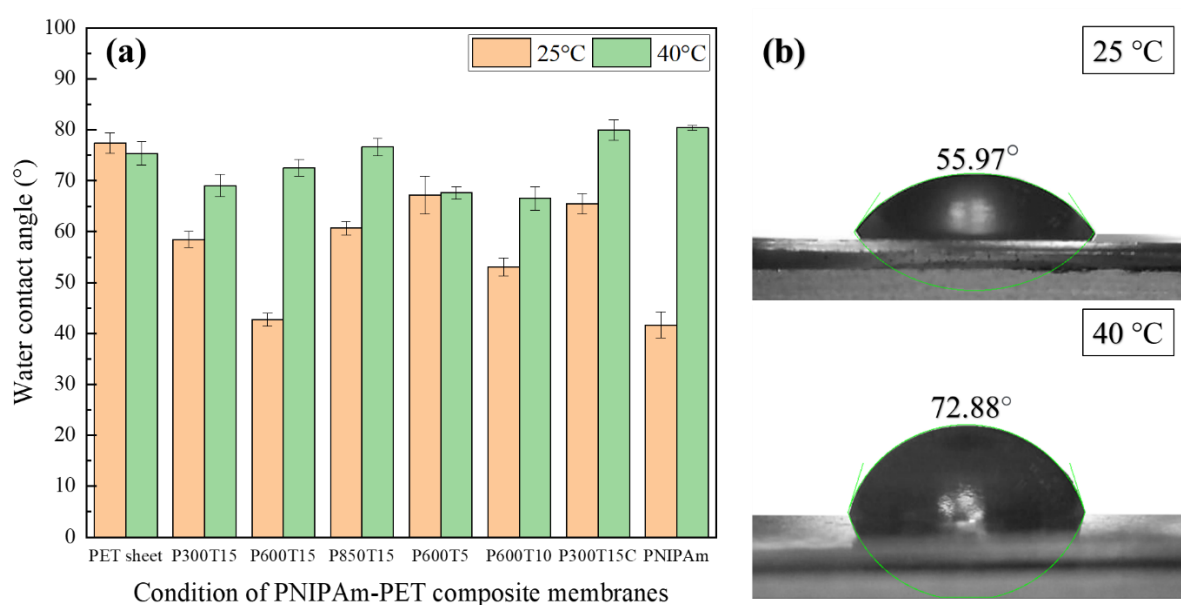


Figure 4.9 Water contact angle at 25 and 40°C of the PNIPAm composite membrane the various conditions and (b) water contact angle measurement of PNIPAm composite membrane (P600T15) of 55.9° and 72.8° at temperatures 25 and 40°C, respectively.

4.7 Water vapor permeability of PNIPAm-PET composite membrane

Fresh produce packaging relies heavily on water vapor permeability due to its connection to transpiration. Moreover, water vapor permeability was one factor in humidity optimization to restrict bacterial growth and prolong shelf life.(Mahajan et al., 2021) Table 4.3 shows the relationship between the WVTR of various PNIPAm-PET composite membranes at 25 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 at 25 °C and 168 at 40 °C— respectively—suggesting that temperature impacted the WVTR,

as higher temperatures allowed more water vapor molecules to permeate through the material.(Macedo et al., 2013) P300T15, P600T10, and P600T15 demonstrated the output power and irradiation time affect their WVTR. The P300T15 displays a low WG, indicating a WVTR comparable to that of a PET membrane at 25 °C. The pores of the composite membrane could not reveal the characteristics of PNIPAm due to the low coverage of PNIPAm. The increased WG of P600T10 and P600T15 led to a decrease in the WVTR at 25 °C. This was due to the expansion of the PET pore covered with PNIPAm, which in turn limited water transmission through the composite membrane. In this case, the effect of the vacuum-assisted technique gave a WVTR of 83 g/(h·m⁻²) at 25 °C, which is more permeable than P600T10 due to the morphology section. For the effect of crosslinker addition, P300T15C gave a WVTR of 82 g/(h·m⁻²) at 25 °C. The composite membranes P300T15, P600T10, P600T15, and P600T15Va exhibited a WVTR similar to the PET membrane at 40 °C. The aforementioned effects boosted the WG, a crucial factor in water vapor permeability, suggesting that an increase in PNIPAm content can improve the "on-off" gate for water vapor. Effect crosslinker addition gave the WTVR of 88 g/(h·m⁻²) at 40 °C, which was close at 25 °C. These phenomena revealed a significant change as a result of the crosslinker chain movement being obstructed.

R_{WVTR} is exhibited to reveal the ability to have thermoresponsive characteristics. In theoretical terms, the ratio of the volumetric flow rate of the water vapor transmission through a membrane at 25 °C, 90% RH, and at 40 °C, 90% RH, is 2.32 based on Darcy's law.(Phromphen, 2015) The R_{WVTR} of the PET membrane and P300T15 is lower than 2.32 because of their pores and holes. The composite membrane with high WG exhibited an R_{WVTR} greater than 2.32, indicating that some other additional mechanisms occur beyond Darcy's law. Additional diffusion actions through PNIPAm polymers and changes in pores during water vapor transmission at 40°C are examples of these additional mechanisms. In the case of crosslinker addition, the R_{WVTR} is lower than 2.32 because neither might act at 40 °C to form pores in the membrane.

Table 4.3 Water vapor transmission rate at 25 and 40°C of the PNIPAm-PET composite membrane under various conditions.

Effect	Codename	%WG	WVTR (g/(h·m ²))		R _{WVTR}
			25 °C	40 °C	
PET membrane	-	-	134 ± 34	268 ± 6	2.0
Output power and irradiation time	P300T15	44	104 ± 30	219 ± 36	2.1
	P600T10	121	80 ± 20	229 ± 18	2.8
	P600T15	191	46 ± 16	214 ± 3	4.7
Vacuum-assisted technique	P600T15Va	210	83 ± 17	247 ± 15	3.0
Crosslinker addition	P300T15C	184	82 ± 24	88 ± 12	1.1

4.8 Gas permeability performance of composite membrane

Gas permeability is a required property to apply to implement self-regulating gas permeability in atmospheric packaging (MAP). Therefore, oxygen (O₂) and carbon dioxide (CO₂) gases, along with focus gases, could play a significant role in controlling gas concentrations in the MAP system and extending the shelf life of fresh produce. Table 4.4 displays the O₂TR and CO₂TR and β of PET membrane and PNIPAm-PET composite membranes under conditions with different weight gains at 25 and 40 °C. The PET membrane showed CO₂TR, O₂TR, and β at 25 °C of 60.65 cm³/h, 74.57 cm³/h, and 0.81, respectively. Generally, the O₂TR was higher than the CO₂TR because of the differences in the molecular sizes and diffusivities of oxygen and carbon dioxide. (Abdul Khalil et al., 2019; Siracusa, 2012) The raised temperature up to 40 °C increased both CO₂TR and O₂TR, which resulted in β because the higher temperatures enhanced the motion of molecules from increased kinetic energy, helping the gas molecules overcome barriers and pass through the pore more easily. (Nur Hanani et al., 2023) The

condition P300T15 with a weight gain of 44 examined O₂TR and CO₂TR at 25 °C and 40 °C were similar to the PET membrane because of the slight partial coverage of PNIPAm on the PET surface. The coverage of PNIPAm was influenced by switching gas transmission when increased microwave output power and irradiation time improved weight gain. The conditions P600T10 and P600T15 have WG of 121 and 191 enhanced PNIPAm coverage on the PET surface decreased O₂TR and CO₂TR at 25 °C, indicating that the swelling of the PNIPAm chain below the LCST restricted gas transmission. When the temperature reached 40 °C, above LCST, the PNIPAm chain switched to deswelling. The collapsed PNIPAm resulted in more PET membrane being exposed. Consequently, O₂TR and CO₂TR decreased near PET membrane.

Table 4.4 Gas transmission rate (O₂, CO₂) of PET membrane and PNIPAm -PET composite membranes with different 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	74.57	0.81	74.93	91.02	0.82
Output power and irradiation time	P300T15	44	55.29	73.68	0.75	78.72	92.32	0.85
	P600T10	122	51.88	43.05	1.21	61.43	84.42	0.73
	P600T15	191	19.80	14.50	1.36	56.59	77.46	0.73
Vacuum-assisted technique	P600T15Va	210	44.09	54.82	0.80	66.61	84.18	0.79
Crosslinker addition	P300T15C	184	31.95	41.50	0.76	48.10	78.40	0.61

The vacuum-assisted technique in P600T15Va was used to enhance the PNIPAm is deposition uniform onto the PET membrane and increase the WG. As a consequence, its O₂TR, CO₂TR, and β at 25 °C were 44.09, 54.82, and 0.89, respectively,

indicating that the O_2TR and CO_2TR were higher and β was lower than those of P600T15. The pressure in the vacuum-assisted technique was an important factor that affected the gas transmission rates because it damaged the pores, causing them to connect into larger pores, which allowed gas to enter through the membrane. From the previous study (T. Kajornprai et al., 2023), the grafted PNIPAm on a Nylon porous membrane with high grafting yields show β at 25 °C close to 1.1, whereas the PNIPAm-PET composite membrane with high %WG could show higher β than 1.1. The increased β caused this composite membrane to be selected as an alternative with a simple process and fewer chemical ingredients. Moreover, the suitable gas per selectivity selection depends on the species of fresh produce due to their different respirations, which is important in the atmosphere-controlling packaging field to prolong the shelf life of fresh produce.

4.9 Fresh produce storage and transportation simulation analysis

4.9.1 The gas composition analysis of fresh produces

The preservation of fruits and vegetables for extended periods requires that the gas concentrations within the packaging headspace suit the characteristics of each produce type. A temperature change during transportation, from the storage environment to the conveyance, affects fresh produce respiration and transpiration rates. Elevated temperature directly accelerates plant metabolism, thereby increasing respiration and water loss (D. Ramasamy & Joyner, 2017). If the film does not allow appropriate gas exchange between the external environment and the headspace, the produce will rapidly wilt and perish. Consequently, the ratio between CO_2 transmission rate (CO_2TR) and oxygen transmission rate (OTR), denoted as β , is critical for regulating gas exchange between the external atmosphere and the packaging headspace

(Todsapol Kajornprai et al., 2023). In addition, β is essential to prevent condensation and microbial spoilage in fruits (Pramod & Dong Sun, 2023).

The composite membrane with P600T15 was chosen for this simulation and compared to the commercial LDPE film due to its high β . Figure 4.10 displays the gas composition (O_2 and CO_2) of the asparagus headspace during storage. The suitable concentrations of O_2 and CO_2 for asparagus storage at 5 °C were 15-20% and 5-10%, respectively (Kargwal et al., 2020). In terms of O_2 concentration monitoring, the open (control) showed a continuous concentration of 20%, while the CM and LDPE both reached 17%. Next, the asparagus chambers were heated to 35 °C for 2 hours (hours 49–50), which exhibited a dramatically decreasing O_2 concentration under three conditions due to the accelerating plant respiration. Finally, the chamber was returned to 5 °C for 9 days (hours 51–216), during which the respiration of fresh produce decreased compared to the previous condition. In hour 72, the open perforated material reached 20% and entered equilibrium, indicating that the O_2 was constant over storage time. While the CM and LDPE reached O_2 concentrations as low as 11–12% under the abused temperature condition, the reduction was attributed to elevated O_2 consumption resulting from increased respiration rates at high temperature (Plasquy et al., 2021). After return to the storage temperature, The O_2 slightly reach up, both conditions were at equilibrium concentration around hour 140, and the O_2 concentration of CM was in a concentration range suitable for storage for asparagus. The three conditions maintained the CO_2 concentration within the range of 0 to 3% for a duration of 2 days. After that, the CO_2 concentration experienced a sudden increase at 35 °C for two days, followed by a slight decrease until it reached the equilibrium concentration. Therefore, both the LDPE film and the PNIPAm-PET composite membrane regulated the CO_2 concentration and reached a range suitable for asparagus storage.

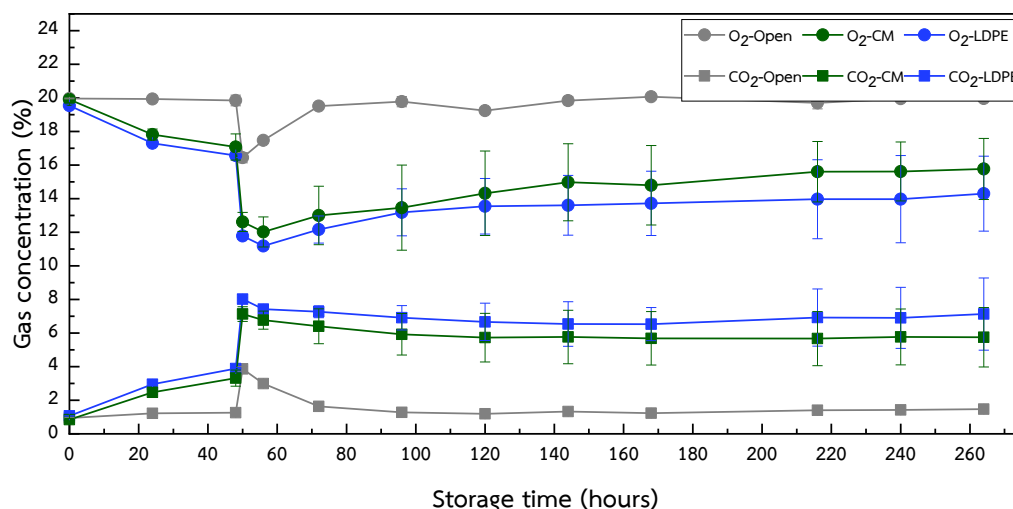


Figure 4.10 Gas composition of the asparagus during the storage time of the open (control), commercial LDPE film, and PNIPAm-PET composite membrane (P600T15)

4.9.2 The green asparagus quality analysis

The results presented in Table 4.5 demonstrate the effects of different storage conditions on the postharvest quality of green asparagus after 11 days of simulated storage. Visual inspection revealed clear differences in the extent of soft rot among the treatments. Asparagus stored under open control conditions exhibited the lowest incidence of soft rot (1.72%), suggesting that the absence of packaging might reduce moisture accumulation on the spear surface and thereby limit microbial proliferation.

In contrast, samples stored in LDPE packaging showed the highest level of deterioration, with 6.45% soft rot observed after 11 days. This outcome is likely attributed to the limited gas permeability of LDPE, which can create a microenvironment conducive to condensation, excess humidity, and subsequent microbial infection. The anaerobic conditions within LDPE may further accelerate soft rot development due to the activity of spoilage microorganisms.

Interestingly, the composite-membrane (CM) cover provided intermediate protection, with 3.12% soft rot recorded. The CM treatment appears to balance gas exchange and humidity control more effectively than LDPE, reducing microbial growth compared to conventional plastic packaging. However, its performance was not superior to the open system, suggesting that further optimization of film permeability and moisture management may be necessary.

Overall, the findings highlight that packaging type plays a critical role in maintaining the postharvest quality of asparagus during storage. While traditional LDPE packaging may inadvertently increase susceptibility to microbial decay, composite membranes offer a promising alternative with improved quality retention. These results align with previous studies reporting that modified or semi-permeable packaging films can extend the shelf life of fresh produce by regulating moisture and gaseous exchange

Table 4.5 Photographs of green asparagus before and after simulated storage under different packaging conditions.

Condition	Before storage	After storage (11 days)	% Soft rot
Open (control)			1.72
LDPE			6.45

Condition	Before storage	After storage (11 days)	% Soft rot
CM			3.12

Figure 4.11 (a) displayed the weight loss for each condition. The weight losses of open (control), LDPE film, and composite membrane were 3.13%, 2.73%, and 2.85%, respectively. The reduced weight loss indicates that the film and composite membrane restrict asparagus transpiration. However, weight loss for this study has not significantly changed. Figure 4.9 (b) shows the firmness of asparagus before and after storage in the open (control), commercial LDPE film, and PNIPAm-PET composite membrane. At 5 cm from tips, the firmness of asparagus after storage under all three conditions was greater than it was before. Increased fiber content and fiber lignification contributed to the increased firmness (Hernández-Rivera et al., 1992). Moreover, both the LDPE and CM conditions exhibit a firmness that surpasses that of the open condition by approximately 180 N, primarily due to moisture loss. Even though the firmness at cutting 10 cm from the tips of the 4 conditions was greater previously due to fiber content change with the position of asparagus spears, but examined the firmness trend like previously cutting.

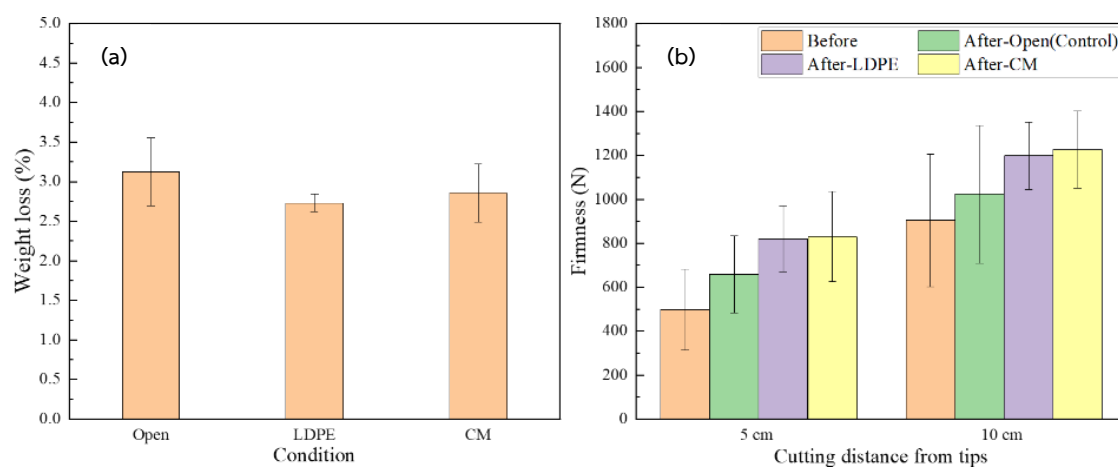


Figure 4.11 (a) weight loss and (b) the firmness of the asparagus during the storage time of the open (control), commercial LDPE film, and PNIPAm-PET composite membrane (P600T15)