Highly ethylene permeable film: development and application in packaging

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Abstract
In postharvest and distribution chain management, ethylene gas is the most problematic chemical. Ethylene gas is plant growth hormone that is effective in minute level (ppb to ppm). In spite of its benefit in plant growth and fruit ripening, ethylene causes major problems in handling of the perishable products like fresh fruit and vegetable. Thus, development of highly ethylene permeable film for retarding ripening and senescence of fresh produces was carried out. The film was developed according to the concept of 'Mixed Matrix (Composite) Membrane', where highly permeable zeolite particles distributed in polymer matrix enhances the film's permselectivity to ethylene gas to the higher level than the intrinsic property of polymer matrix without sacrificing the permeation performance. Here, the ethylene gas selectively permeated through the film with an assistance of the hydrophobic zeolite distributed throughout the film. Ethylene permeability ranging of 1,900 – 2,200 $cm^3.mm/m^2.day.atm$ was obtained where oxygen permeability was still in an acceptable range, i.e., 220 to 600 $cm^3.mm/m^2.day.atm$ (or oxygen transmission rate of 5,500 to 15,000 $cm^3/m^2.day.atm$). The application of such packaging film to tropical produces, i.e., initially, Thai coriander and 'Nam Dok Mai' mango, was promising. Ethylene level in the package was reduced to less than 3 ppm, which is less than half of that detected in the other modified atmosphere packages used. Modified atmosphere was obtained in the packages of both produces; 12%Oxygen and 2%Carbon dioxide in coriander packages stored at 7°C, and 2%Oxygen and 8%Carbon dioxide in mango package stored at 13 °C. Moreover, shelf life extension of the produces was achieved in both commercial EMA package and the film developed: 6 to 8 day vs. 4 day (control) for coriander packages and 18 days vs. less than 15 days (control) for mango packages.
Keywords: ethylene permeation, hydrophobic zeolite, packaging for fresh produces, modified atmosphere, and packaging film.

1. INTRODUCTION

Preserving freshness and quality of fresh produces can be efficiently carried out via proper postharvest management practices. Removal of ethylene gas from storage and handling environment is one of the effective ways to slow down ripening process and retard deterioration. Ethylene gas is a plant hormone that is effective in minute level (ppb-ppm)[1] and frequently causes major problems in fresh produce handlings. The gas can cause over-ripening in fruits; and it is responsible for physiological disorders in plants and plant parts, e.g., flower and leaf abscission, loss of chlorophyll, development of russet spot, sprouting and toughening. Due to detrimental effect of ethylene gas to produce quality, there, recently, have been extensive efforts to harness the ethylene problem.

Cold storage and modified atmosphere is found to effectively suppress ethylene production and activity of the fresh produces.[2] However, temperature fluctuation in only 3 – 5°C can trigger ethylene production and activity, and thus accelerate deterioration.[3] Ethylene scrubbing systems and ethylene scavengers/absorbers are frequently used in commercial scales. Potassium permanganate-based ethylene scavenger is the common one, however, the chemical is not allowed to contact with food. Ethylene receptor block substance, e.g., 1-MCP (1-Methylcyclopropene) has been recently attracted a great deal of interest. Its commercial use is still limited. Molecular sieve, mainly, zeolite, used in scrubbing system has been currently applied to individual package by inserting inside the package or incorporating into the plastic film. However, ethylene absorption capability of zeolites in the individual package is still questionable.[4 - 5] Therefore, the application of zeolites in this area is limited,

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despite of non-toxic nature of zeolitic material. Zeolite-filled bag currently commercial available evidently were able to keep the freshness of fresh fruits and vegetables effectively.[5]

Zeolite is, in fact, a huge class of aluminosilicate material with well-defined channels and cavities in the 3-D framework structure.[6] There are hundreds of zeolites with different framework structures that allow the selective adsorption possibilities. Hydrophobic zeolites with pore size larger than kinetic diameter of ethylene gas, i.e. 0.39 nm, were found to preferentially adsorb ethylene gas. The hydrophobic zeolites with MFI, MOR, FAU, OFF, and ERI structure have been reported to selectively adsorb volatile hydrocarbons like ethylene gas.[7] The development of the ethylene-removing film in this study was then utilizing selective adsorption of zeolite to facilitate ethylene gas transport across the packaging film according to the concept of mixed matrix (composite) membrane.[8 - 9] Selective permeation of ethylene gas of the film was optimized via a well balance of absorbing performance of incorporated particles and structure of polymer matrix. Therefore, the present study was explored material characteristics and structure of the film that gave rise to high ethylene permeability for the application of fresh produce packaging. Furthermore, an application in Thai fresh produce packaging was evaluated. The article presented here was intended to demonstrate the essential elements of the film development, thus technical details were included only if necessary.

2. MATERIALS AND METHOD

Materials and Material Characterization

Low density polyethylene (LDPE, MFI = 5.5 from TPI, Thailand) was used as major component in matrix; and Kraton G1657 (styrene-ethylene-butylene-styrene block copolymer with 13% styrene from Kraton Polymer) as a highly ethylene permeable component. Hydrophobic zeolites, i.e., two type of ZSM-5 with Si/Al (XRF) of 26 and 107, respectively, from Zeolyst International, and silicalite synthesized in this study were used as the adsorbent particles incorporated into polymer matrix. The studied zeolites have average particle sizes (D_{50}) in the range of 0.5 – 2 μm and specific surface areas > 350 m^2/g of adsorbent (BET, N_2)

Film Preparation

The compounds were prepared in an internal mixer (Rheomix 3000P, Haake) with roller rotor at 190℃ and 60 rpm rotor speed. 0.2% anti-blocking agent was added if required. The compounds was then fabricated by blow film extrusion process using single screw extruder, Rheotex 252P, Haake, with standard screw (3:1) and screw speed of 40 - 60 rpm. A temperature profile in the single screw extruder was maintained in the range of 160 - 200℃ and 200℃ in a die zone. The films obtained have a thickness of 30 - 35 µm.

Film Characterization

Thermal property and transition temperatures of polymeric films were determined using a differential scanning calorimeter (Metter Teledo DSC 822e.) with temperature range of 0 to 130℃ and heating/cooling rate at 10℃/min. The microscopic morphology and distribution of particles in the polymeric matrix was investigated on the gold coated cryo-fracture surface using scanning electron microscope (SEM - JSM 5410). Tensile property of the film were determined using Universal Testing Machine (Instron model 55R45) with crosshead speed of 500 mm/min and load cell of 100 N. The specimens are 1.5 x 15 mm film strips cut in both machine and transverse directions. A thickness of the specimens was 35 ± 5 µm.

Gas Permeability Measurement

Oxygen, carbon dioxide, ethylene transmission rate and permeability measurement of the films were performed using a Mocon Oxtran (OTR; Model 2/21) , Mocon Permatran (CO_2TR; Model 4/41) and GC-FID with permeation cell, respectively. Flat films of similar thickness (30 ± 5 µm) were tested at 1 atm and temperature of: 23℃ for OTR, CO_2TR and room temperature for Ethylene-TR. The value reported in the unit of cm^3/m^2.day.atm for gas transmission rate and cm^3.mm/m^2.day.atm for permeability.

Packing Test

The produces, 'Nam Dok Mai' mango and Thai coriander, were prepared according to export standards (HACCP and RSI) by local companies. Briefly, the produces were hand-harvested from the orchard/field. They were then transported to temperature controlled packing house for pre-cooling, cleaning, sizing, trimming and packing in the whole-sale size bags before delivery to the lab in foam boxes within 12 hours. Mango fruits (~ 300 g) were then packed in an individual pack, the 5 x 10 inch bag, and stored at 13 °C. Bunches of 75 g coriander was packed in the 6 x 14 inch bag and stored at 7 °C. The produces were also packed in commercially available films, for comparison. At least three packs of each sample set were investigated by weight loss measurement, head space gas analysis using Pac Check O_2/CO_2 gas analyzer(Mocon), and visual quality assessments: color, withering and diseases.

3. RESULTS AND DISCUSSION

Gas Adsorption Behavior of Zeolite

The zeolites used, i.e., ZSM-5 and silicalite had Si/Al > 25 which is thus a characteristic of hydrophobic. They have a large specific surface area which is an indicative of good adsorbent. Adsorption ability of such porous materials is generally determined by pore size, surface area and chemistry of internal surface. This study aims to develop the packaging film for fresh produce. Thus, adsorption isotherms of the zeolites to O_2, CO_2 and ethylene, the three gases involving in the biological activity of fresh produces, were investigated.

Adsorption isotherms of all gases show Type I adsorption behavior. Adsorption capability, characterized by volume of gas adsorbed at $P/P_o = 1$, is shown in Table 1. Weak adsorption of O_2 on the zeolites were found as limited amount of non-polar O_2 adsorbed, whereas CO_2 and ethylene strongly adsorbed on internal surface of the zeolites. Moreover, the hydrophobic zeolites used were found to preferentially adsorb considerable amount of ethylene gas. It is pertinent to note that ethylene adsorption of the hydrophobic zeolites is typically insensitive to %RH. Utilization of such zeolites in developing fresh produce packaging which involves with high moisture should be thus appropriate. The parameter primarily determining adsorbed gas is the ratio of kinetic diameter of a target molecule to a pore size of adsorbent. Generally, adsorption of the zeolite occurs if the pore size is 1.3 times larger than kinetic diameter of target molecule. In this study, the zeolites selected have pore sizes around 1.4 times larger than kinetic diameter of ethylene gas. In this case, the chemistry of internal/pore surface thus determines adsorption capacity.

Table 1 O_2, CO_2 and ethylene adsorption capacity at P/P_o of the zeolites.

Zeolite	Si/Al (XRF)	Gas adsorption at P/P_o=1 cm^3/g ofadsorbent		
		O_2	CO_2	Ethylene
ZSM-5[1]	26	8.5	75	90
ZSM-5[2]	107	7.5	55	80
Silicalite	∞	7.5	55	75

Development of Highly Ethylene Permeable Film: Hydrophobic Zeolite filled PE-based Film

Enhanced selective permeation can be obtained by the concept of mixed matrix (composite) membrane where target molecule selectively transports across the membrane through highly permeable (inorganic) zeolite particles distributed in the (organic) polymeric matrix.[8-9] Permselectivity to the specific gas was assisted by the selective adsorption of the zeolite particles; therefore, such property was enhanced to the higher level than the intrinsic properties of polymer matrix without losing the permeation performance. This study thus developed high ethylene permeable film, accordingly. Here, the ethylene gas selectively permeated through the film with an assistance of the hydrophobic zeolites distributed throughout the film.

Low density polyethylene (LDPE) was used as a major polymeric component since it has been widely used in packaging applications. LDPE as well as other olefins has been reported to have ethylene permeability approximately 1.5 – 2 times to oxygen permeability.[10] The ethylene permeation of such polymers may restrict the transportation of ethylene molecule to reach adsorbent particles. Therefore, that might be the reason for most of commercial-available zeolite filled PE films to contain the zeolite particles with diameter larger than the thickness of the film. Our objective was to develop the packaging film for fresh produce such that clarity and acceptable mechanical property was crucial. In order to retain clarity and mechanical integrity upon incorporation of adsorbent particle, thin gauge of film is required; and particle size of the adsorbent should be in sub-micron range.

The fine zeolite particle used in this study was distributed uniformly in PE matrix (see Figure 1), Nevertheless, the composite films obtained had ethylene permeability just comparable to that of pure LDPE as illustrated in the permeation kinetics of ethylene gas through the films (see Figure 2). An enhanced permeability of ethylene gas was not observed in this system may be due to an inadequate ethylene permeability of LDPE. However, increase of rate of permeation kinetics was observed when zeolite was presented in the film. Highly ethylene permeable polymer was then applied.

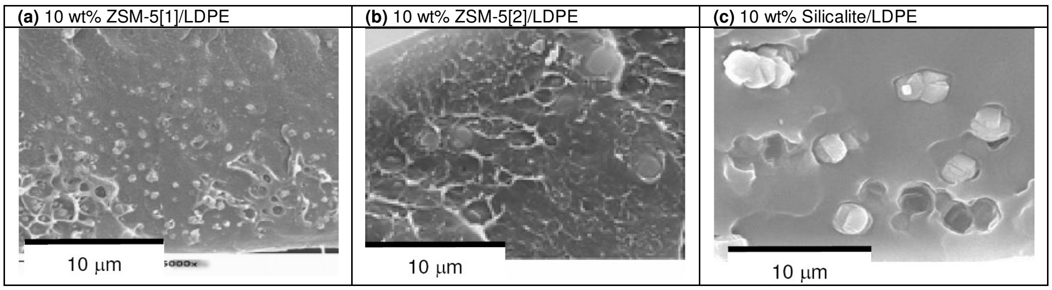

Figure 1 Scanning electron micrograph of cryo-fracture surface of LDPE film containing 10 wt% of (a) ZSM-5[1], (b) ZSM-5[2] and (c) silicalite with magnification of x5,000.

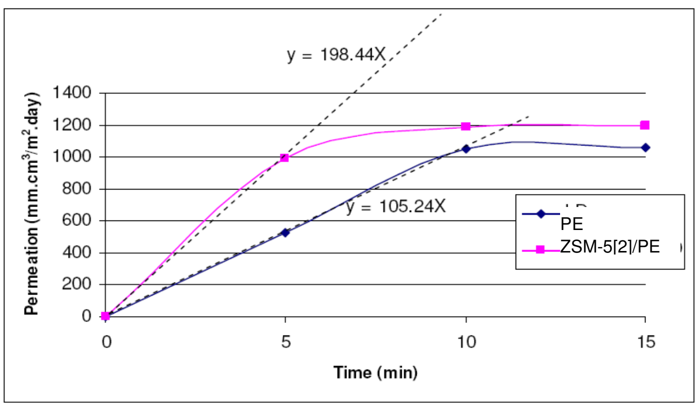

Figure 2 Permeation kinetics of the 10 wt% ZSM-5[2] filled/unfilled LDPE films.

Styrene-ethylene-butylene-styrene block copolymer (SEBS), a styrenic block copolymer which had high ethylene permeability and thermal stability in the presence of zeoites, was chosen as the second polymeric constituent. Kraton G1657, an elastomeric SEBS with 13% styrene content, was used in this study. Gas permeability of LDPE/SEBS blend system was found to follow Maxwell model. However, only the blends with LDPE/SEBS ratio of 90/10 – 70/30 can be fabricated by blown film extrusion. The study was thus focused on the blend with the highest content of SEBS, i.e., **70**LDPE/**30**SEBS.

5 – 10% zeolite filled **70**LDPE/**30**SEBS films were prepared. Structure of the films was investigated using scanning electron microscopy (see Figure 3). Zeolite particles were uniformly distributed in the polymer matrix. In addition, the presence of small voids and cracks at the interface was observed in the blend containing ZSM-5[2] and silicalite. Ethylene permeability, however, was enhanced significantly. The following section will illustrate that selective permeation of ethylene gas was exhibited despite of the presence of the cracks and voids. Figure 4 showed ethylene permeability of 10 wt.% zeolite-filled **70**LDPE/**30**SEBS films.

Ethylene permeability was significantly enhanced when zeolites was incorporated in the polymer matrix.

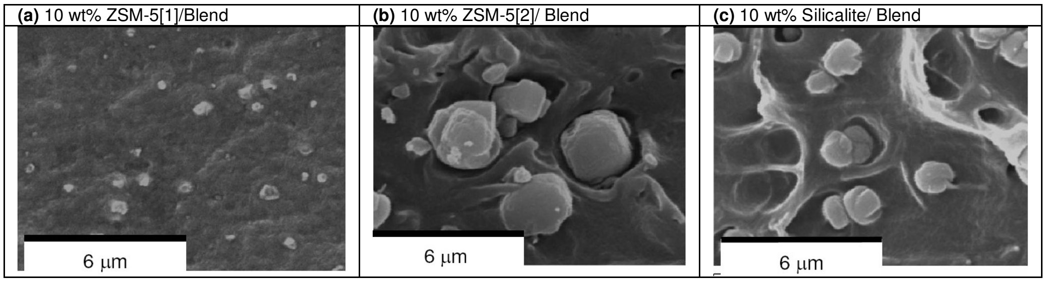

Figure 3 Scanning electron micrograph of cryo-fracture surface of **70**LDPE/**30**SEBS film containing 10 wt% of (a) ZSM-5[1], (b) ZSM-5[2] and (c) silicalite with magnification of x8,000.

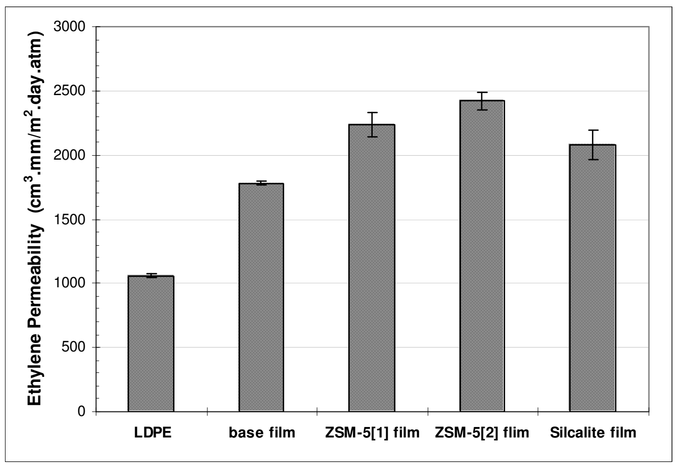

Figure 4 Ethylene permeability of the films of 70LDPE/30SEBS (base film) and **70**LDPE/**30**SEBS containing 10wt% zeolites comparing to that of LDPE film.

Gas Permeation of the Zeolite Filled 70LDPE/30SEBS Films

Gas permeation of hydrophobic zeolite-filled **70**LDPE/**30**SEBS films was analyzed. The permeation behavior according to the concept of mixed matrix membrane will be demonstrated. High ethylene permeability was attained (see Table 2) when using the blend with high ethylene permeability as a matrix. Generally, gas permeability of semi-crystalline polymer was principally determined by percentage of crystallinity. Here for the films with the blend matrix, melting temperature and crystallization temperature (at 10℃/min) of LDPE, a major constituent of the blend, in the filled and unfilled polymer films was identical (see Table 2). However, percentage of crystallinity of LDPE in zeolite-filled systems was somewhat lower than that of the unfilled (17 – 23 for filled and 28 for unfilled, see Table 2). According to relationship of gas permeability and amorphous phase volume fraction of PE reported by Michaels and Parker (1959),[11] gas permeability of PE will increase roughly 50% when percentage of crystallinity decreases from 28 to 17. Gas permeability of the blend system, calculated using Maxwell permeation model,[12] should increase approximately 20%, accordingly. Ethylene permeability of zeolite-filled **70**LDPE/**30**SEBS films, however, was found to be much higher than the mentioned values.

Table 2 Transition temperatures, percentage of crystallinity and gas permeation properties of zeolite filled **70**LDPE/**30**SEBS films.

Zeolite	Tm ℃	Tc @ 10℃/min ℃	$\%\chi_c$	Average gas permeability $cm^3.mm/m^2.day.atm$			α[ethylene/O_2]
				O_2	CO_2	Ethylene	
-	106	97	28	248	1,042	1,780	7.1
ZSM-5[1]	106	96	19	359	1,240	2,174	6.2
ZSM-5[2]	106	96	17	307	1,403	2,423	7.9
Silicalite	106	96	23	356	1,126	2,079	5.8

Maxwell permeation model has also been applied in the prediction of gas permeability of zeolite-filled membrane.[8] Both zeolite particle and polymeric matrix were considered to be permeable entities. Here, ethylene permeability of inorganic membrane of silicalite with the value of 154,100 $cm^3.mm/m^2.day.atm$ was used as a representative value for the zeolites used in this study. With assumptions that 70PE/30SEBS blend was a homogeneous mixture; and zeolite particles were uniformly distributed in the polymeric matrix, calculated value of ethylene permeability of 5 – 10 wt% zeolite-filled 70LDPE/30SEBS films was approximately 1,960 $cm^3.mm/m^2.day.atm$. Again, the measured values of ethylene permeability of the composite films were significantly higher than the calculated ones. Therefore, the enhanced ethylene permeation of the films should be arisen from the effect of low crystallinity together with activated permeation by zeolite particle according to mixed matrix membrane concept. In addition, permselectivity to ethylene gas, here represented by α[ethylene/O_2], the ratio of ethylene permeability to oxygen permeability, of the films was significantly improved (see Table 2). This is an evidence of selective adsorption-mediated permeation of mixed matrix membrane. It is pertinent to note that, unlike this system, gas permeability of the film incorporated with impermeable particles was found to be non-selective to ethylene gas.

Properties of the Prototyping Film

The prototyping film (patent pending) was developed according to the findings mentioned in the earlier sections. The film was fabricated by blow film extrusion process. Gas transmission rate of the film was shown in Table 3. Ethylene transmission rate of the film was significantly higher than the commercially available films,[10,13] where O_2 and CO_2 transmission rate was still in the suitable range for packaging of fresh produce.

Table 3 O_2, CO_2 and ethylene permeability of the prototyping films

Thickness μm	Average gas Transmission Rate $cm^3/m^2.day.atm$		
	O_2	CO_2	Ethylene
32 ± 3	9,400	44,300	77,500

Figure 5 showed the distribution of zeolite particles investigated by optical and scanning electron microscopy. The zeolite particles were found to be uniformly distributed in polymer matrix. A high magnification image revealed a strong adhesion at the particle/polymer interface as no void and crack around the particle surface observed.

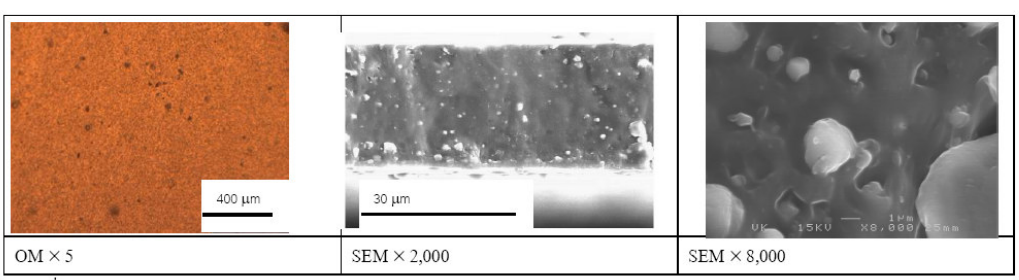

Figure 5 Optical micrograph and scanning electron micrograph of cryo-fracture surface of the prototyping film with magnification of x2,000 and x8,000.

Tensile properties of the prototype film were illustrated in the Table 4. The tensile properties of the film were comparable to those of commercial LDPE film.

Table 4 Tensile properties of the prototyping films and commercial films

Film Type	Direction	Tensile Modulus MPa	Tensile Strength MPa	Elongation at Break %	Toughness MPa
Commercial Film (LDPE)[14]	-	-	7 – 24	220 – 600	-
Prototyping Film	MD	61.5 ± 6.0	9.6 ± 0.6	235 ± 37	17.4 ± 3.4
	TD	80.8 ± 6.7	8.8 ± 0.7	303 ± 28	20.2 ± 2.5

Ethylene removing ability of the prototyping film was investigated by monitoring the ethylene gas inside the bag at room temperature. The initial concentration of ethylene was 4 ppm. The prototyping film exhibited the higher rate of ethylene reduction (K (Film) = 0.17 vs. K (LDPE) = 0.057) and less ethylene remained as shown in Figure 6.

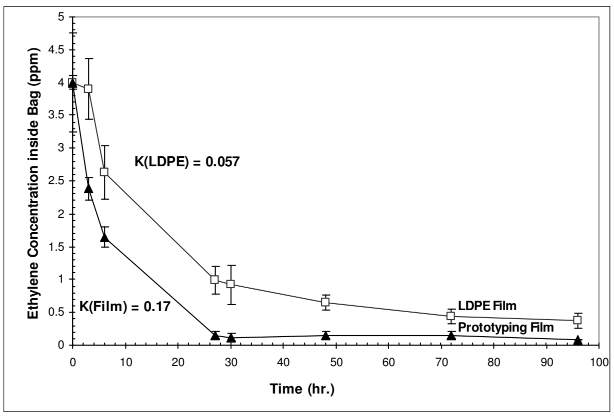

Figure 6 Ethylene concentration inside the bags of prototyping film and commercial LDPE film as a function of time. The initial ethylene concentration was 4 ppm.

Packing Tests: 'Nam Dok Mai' mango and Thai coriander

Packing tests on 'Nam Dok Mai' mango and Thai coriander have been carried out by using package size and storage temperature according to commercial uses. O_2 and CO_2 compositions were monitored periodically during storing period. A comparison study of film type was carried out using prototyping film, LDPE bag and commercial available EMA film. Oxygen transmission rate of LDPE was 5,420 cm^3/m^2.day.atm. EMA film chosen has a value of oxygen transmission rate comparable to that of the prototyping film i.e., 10,570 cm^3/m^2.day.atm. Results of packing test were shown in Table 5. Packing format and flesh color of mango at the end of shelf life were shown in Figure 7.

Table 5 Results of packing test on 'Nam Dok Mai' mango and Thai coriander.

Commodities	Packaging Format/ Postharvest Loss	Shelf Life* in day/Ethylene Accumulated in ppm (%O_2 and %CO_2 inside the package at steady state)			
		Control**	Prototyping film***	LDPE bag***	Commercial EMA film***
'Nam Dok Mai' mango	One fruit in 5 x 10 inch bag/ rapid ripening	<15 day/-	18 day/0.3 – 1.2 ppm (2%O_2 and 8%CO_2)	4 day/0.2 ppm (1.5%O_2 and 12%CO_2)	18 day/0.4 – 1.5 ppm (2%O_2 and 7%CO_2)
Thai coriander	75 g in 6 x 14 inch bag/ Yellow leaf	4 day/-	7 - 8 day/2 – 3 ppm (12%O_2 and 2%CO_2)	6 day/3 – 7 ppm (5%O_2 and 3%CO_2)	-

* the end of shelf life was identified by >2% weight loss for both commodities. In addition, off-flavor and visual quality for mango, and yellowing > 20% for coriander.

** wrapped by foam net for mango and packed in PP bag with 18 punched holes with diameter of ¼ inch for Thai coriander.

*** ethylene transmission rate of the prototyping film, LDPE and commercial EMA film is 77,500; 31,900 and 47,600 cm^3/m^2.day.atm, respectively.

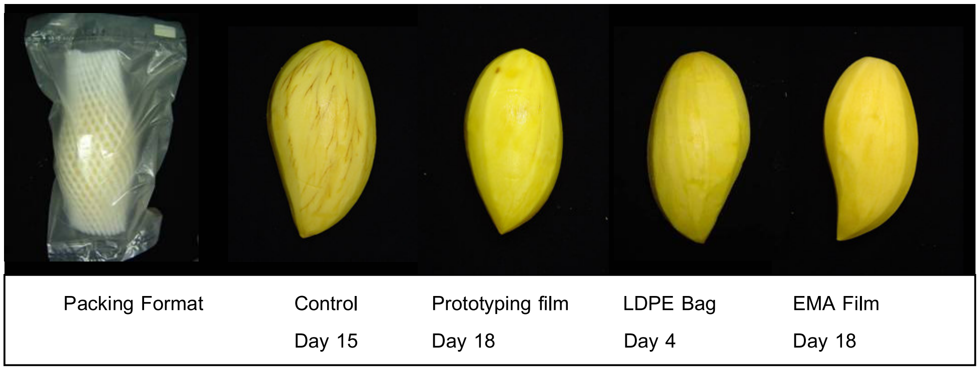

Figure 7 Packing format and flesh color of 'Nam Dok Mai' mango at the end of shelf life.

"Control", the produces stored in the atmospheric gas composition, has a limited shelf life. Physiological disorders determining shelf life of "control" are withering for coriander and brown veins in the flesh for mango. Modified atmosphere, reduced oxygen and elevated carbon dioxide, was obtained in the packages of all film types. Shelf life extension by modified atmosphere was observed in both mango and coriander. Shelf life of 'Nam Dok Mai' mango and Thai coriander was extended to 18 days and > 5 days, respectively. Shelf life of Thai coriander was determined by leaf yellowing; however, shelf life of 'Nam do Mai' mango was limited by diseases. In the case of mango in LDPE bag, the results were found differently. 1.5%O_2 and 12%CO_2 detected may exceed the tolerance limit of the mango,[15] thus off-flavor was detected on Day 4. In addition, LDPE bag containing mango on Day 4 have a rather low oxygen level and the mango may be still in pre-climacteric stage, thus very low in-pack ethylene concentration was detected. Ethylene concentration in the bag from the prototyping film was found to be relatively low when compared with that of the EMA film. Nevertheless, this study was found that the lower ethylene concentration inside the packages from the prototyping film marginally extended the shelf life of Thai coriander to 7 – 8 days where 6 days for EMA film. The results obtained in this study, however, was promising. Further investigation will be carried out to evaluate the commercial benefit of such film.

4. CONCLUSION

Packaging film with high ethylene permeability can be developed by utilizing activated permeation of the polymeric film containing hydrophobic zeolite particles distributed in the polymer matrix, according to the concept of mixed matrix (composite) membrane. A highly ethylene permeable matrix, here is 70LDPE/30SEBS with 13%Styrene, was found to facilitate the activated permeation of the film. The prototyping film can be developed by well control process and fabricated by blown film extrusion. Ethylene transmission rate of the prototyping film was 77,500 cm^3/m^2.day.atm, where oxygen transmission rate is in the order of 9,400 cm^3/m^2.day.atm. The prototyping film and commercial EMA film extended the shelf life of 'Nam Dok Mai' mango and Thai coriander, to 18 days and > 5 days, respectively, where "control" had a shelf life of < 15 days for mango and 4 days for coriander. Mango in LDPE bag, however, had a shorten shelf life due to off-favor. Ethylene level in the package from the prototyping film was less than half of that found in the other modified atmosphere packaging used. Modified atmosphere was obtained in the prototyping film containing both produces: 12%Oxygen and 2%Carbon dioxide in coriander packages stored at 7°C, and 2%Oxygen and 8%Carbon dioxide in mango package stored at 13 °C. From the observations in this study, low ethylene concentration inside the prototyping film gave rise to just marginal shelf life extension of Thai coriander (7 – 8 days vs. 6 days for EMA film). Nevertheless, further investigation will be carried out to evaluate the commercial benefit of such film.

ACKNOWLEDGEMENT

The present work is supported by MTEC funding. The authors are grateful for the packing tests on 'Nam Dok Mai' mango by Mr. Chanit Wanikanukul, a master student of Department of Packaging Technology, Kasetsart University under the supervision of Assoc. Professor

Vanee Chonhenchob. Technical information and assistance from staffs of MTEC testing labs are appreciated.

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