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**Directeurs de
recherche:** Abdellah Ajji
Advisors:

Programme: Génie chimique
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**Development of Ethylene Scavenging Systems Based on Pumice and Potassium
Permanganate for Food Packaging Applications**

CHUNYU WANG

Département de génie chimique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiae Doctor*

Génie chimique

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POLYTECHNIQUE MONTRÉAL

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Cette thèse intitulée :

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présentée par **Chunyu WANG**

en vue de l'obtention du diplôme de *Philosophiae Doctor*

a été dûment acceptée par le jury d'examen constitué de :

Marie-Claude HEUZEY, présidente

Abdellah AJJI, membre et directeur de recherche

Amir SAFFAR, membre

Saïd ELKOUN, membre externe

DEDICATION

To my beloved parents and sister.

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RÉSUMÉ

Dans les emballages alimentaires actifs, les absorbeurs d'éthylène jouent un rôle essentiel dans la prolongation de la durée de conservation des fruits et légumes en éliminant l'éthylène produit dans l'espace de tête de l'emballage. Le permanganate de potassium (KMnO_4) est largement utilisé pour préparer des absorbeurs d'éthylène, et il est généralement soutenu par des matériaux poreux inertes pour augmenter la surface en contact avec l'éthylène. La pierre ponce est un adsorbant de gaz potentiel avec une structure poreuse et une propriété d'adsorption de gaz, mais sa combinaison avec KMnO_4 en tant que absorbeurs d'éthylène n'a pas été développée. Les sachets et les films sont deux formes de absorbeurs d'éthylène, mais aucune étude complète sur l'application de KMnO_4 et de pierre ponce dans les emballages alimentaires actifs n'a été réalisée. Par conséquent, le projet vise à développer un système de récupération d'éthylène contenant du KMnO_4 et de la pierre ponce, sous forme de sachets et de films, pour conserver les fruits et légumes.

La première partie du projet consistait à développer un piègeur d'éthylène composé de pierre ponce et de KMnO_4 . La pierre ponce a été choisie comme matériau de support principalement en raison de son faible coût, de sa bonne propriété d'adsorption et de sa grande disponibilité. Tout d'abord, la taille des particules de pierre ponce a été étudiée pour déterminer que la plus petite taille était favorable à l'adsorption de l'éthylène. Ensuite, la pierre ponce et le KMnO_4 ont été broyés jusqu'à l'uniformité pour étudier l'influence de leur rapport pondéral sur l'adsorption d'éthylène, et un rapport pondéral de 10 à 1 (pierre ponce sur KMnO_4) s'est avéré être le choix optimal. De plus, une humidité relative (HR) élevée n'était pas bénéfique pour l'adsorption d'éthylène car l'humidité entrerait en compétition avec l'éthylène pour les sites d'adsorption sur la surface de la pierre ponce. Plus important encore, il a été découvert que la combinaison de pierre ponce et de KMnO_4 améliorerait considérablement la capacité de piégeage de l'éthylène par rapport à la pierre ponce seule ou au KMnO_4 seul. Cela est dû à l'effet synergique de la pierre ponce adsorbant physiquement l'éthylène et du KMnO_4 oxydant chimiquement l'éthylène. De plus, le mélange de pierre ponce et de KMnO_4 a été appliqué comme piègeur d'éthylène pour conserver des avocats. Les résultats ont révélé que le piègeur d'éthylène éliminait efficacement l'éthylène produit par les avocats et inhibait la production de dioxyde de carbone (CO_2). Enfin, la durée de conservation des avocats a été prolongée d'environ une semaine à 25 °C par rapport au groupe témoin sans absorbeurs d'éthylène.

La deuxième partie du projet consistait à préparer un film de piégeage d'éthylène (épaisseur: environ 60 μm) à travers une extrudeuse bivis, constitué de polyéthylène basse densité (PEBD) comme matrice, du mélange de pierre ponce et de KMnO_4 (rapport pondéral: 10 à 1) comme agents actifs, et polyéthylène greffé anhydride maléique (PE-g-MA) comme compatibilisant. La dispersion des agents actifs a un effet essentiel sur les propriétés thermiques, mécaniques et de barrière aux gaz des films, et la fonction du PE-g-MA est de favoriser la dispersion. Les images microscope électronique à balayage (SEM) ont montré qu'une faible charge d'agents actifs (1 % en poids et 3 % en poids) étaient uniformément dispersés dans un film PEBD, mais qu'ils s'agglomèrent à charge plus élevée (5 % en poids et 10 % en poids). La transparence des films diminue avec l'augmentation de la teneur en agents actifs en détectant la couleur de surface. Le film de piégeage d'éthylène incorporant 3% en poids d'agents actifs a présenté les meilleures performances de barrière aux gaz et la capacité de piégeage d'éthylène la plus élevée, et a en outre prolongé la durée de conservation des avocats à 20 jours à 25 °C, contre seulement 10 jours pour les avocats emballés avec un film pur de PEBD. De plus, les concentrations d'éthylène et de CO_2 dans l'espace de tête de l'emballage ont été bien contrôlées et la perte de fermeté des avocats a été réduite.

Dans la dernière partie, un film multicouche (épaisseur: 60-80 μm) a été produit via la ligne d'extrusion soufflée multicouche en prenant en sandwich une couche centrale contenant des agents actifs entre deux couches extérieures contenant du chlorure de sodium (NaCl). La structure morphologique du film multicouche a été observée par SEM, et la couleur de surface, les propriétés thermiques, mécaniques et de barrière aux gaz ont également été étudiées. L'ajout d'agents actifs et de NaCl a entraîné une légère réduction de la transparence et des propriétés mécaniques mais a augmenté la perméabilité aux gaz du film multicouche. La couche centrale a doté le film multicouche d'une capacité de piégeage d'éthylène et les couches extérieures ont conféré une capacité d'absorption d'eau. Le film multicouche a prolongé la durée de conservation des avocats de moins de 10 jours à 16 jours à 25 °C, contrôlé les concentrations d'éthylène et de CO_2 dans l'espace de tête de l'emballage, inhibé la fermeté et la perte de poids des avocats. Plus important encore, les couches extérieures évitent non seulement le contact direct entre les agents actifs et les avocats, mais empêchent également la migration des agents actifs vers les avocats, ce qui protégeait les avocats de la contamination et offrait une garantie de sécurité.

ABSTRACT

In active food packaging, ethylene scavengers play an essential role in extending the shelf life of fruits and vegetables by removing the ethylene produced in the packaging headspace. Potassium permanganate (KMnO_4) is widely applied to prepare ethylene scavengers, and it is usually supported by inert porous materials to increase the surface area in contact with ethylene. Pumice is a potential gas sorbent with a porous structure and gas adsorption property, however its combination with KMnO_4 as ethylene scavengers has not been developed. Sachets and films are two forms of ethylene scavengers, but no complete studies on the application of KMnO_4 and pumice in active food packaging have been performed. Therefore, this thesis aims to develop an ethylene scavenging system containing KMnO_4 and pumice, including sachets and films, to preserve fruits and vegetables.

The first part of this thesis was to develop an ethylene scavenger made up of pumice and KMnO_4 . Pumice was chosen as supporting material mainly owing to its low cost, good adsorption property, and easy availability. First of all, the size of pumice particles was studied to determine that the smaller size was favorable to ethylene adsorption. Then, pumice and KMnO_4 were ground to uniformity to investigate the influence of their weight ratio on ethylene adsorption. A weight ratio of 10 to 1 (pumice to KMnO_4) was confirmed to be the optimal choice. In addition, a high relative humidity was not beneficial to ethylene adsorption because moisture would compete with ethylene for the adsorption sites on the pumice surface. More importantly, it was discovered that the combination of pumice and KMnO_4 significantly improved the ethylene scavenging capacity compared to pumice or KMnO_4 alone. This is due to the synergistic effect combining pumice physically adsorbing ethylene and KMnO_4 chemically oxidizing ethylene. Further, the mixture of pumice and KMnO_4 was applied as an ethylene scavenger to preserve avocados. The results revealed that the ethylene scavenger efficiently removed the ethylene produced by avocados and inhibited the production of carbon dioxide (CO_2). Finally, the shelf life of avocados was extended by approximately one week at 25 °C compared to the control group without ethylene scavengers.

The second part of the thesis was dedicated to the preparation of an ethylene scavenging film (thickness: around 60 μm) using a twin-screw extruder, consisting of low-density polyethylene (LDPE) as the matrix, the mixture of pumice and KMnO_4 (weight ratio: 10 to 1) as active agents,

and maleic anhydride grafted polyethylene (PE-g-MA) as the compatibilizer. The dispersion of active agents had a vital effect on the thermal, mechanical and gas barrier properties of films, and the function of PE-g-MA was to promote the dispersion. Scanning electron microscopy (SEM) images showed that a low loading of active agents (1 wt.% and 3 wt.%) evenly dispersed in LDPE film, but active agents agglomerated at a high loading (5 wt.% and 10 wt.%). The transparency and lightness of films decreased with the increase of the content of active agents by detecting the surface color. The ethylene scavenging film incorporating 3 wt.% active agents exhibited the best gas barrier performance and the highest ethylene scavenging capacity, and furthermore extended the shelf life of avocados to 20 days at 25 °C, compared to only 10 days for avocados packaged with pure LDPE film. Moreover, the ethylene and CO₂ concentrations in the packaging headspace were controlled well, and the firmness loss of avocados was reduced.

In the last part of the thesis, a multilayer film (thickness: 60-80 μm) was produced via the Multilayer Blown Extrusion Line by sandwiching one core layer containing active agents between two skin layers with sodium chloride (NaCl). The morphological structure of the multilayer film was observed by SEM images, and the surface color, thermal, mechanical and gas barrier properties were also studied. The addition of active agents and NaCl caused a slight reduction in the transparency and mechanical properties but increased the gas permeability of the multilayer film, which was favorable to ethylene removal. The core layer endowed the multilayer film with ethylene scavenging ability and the skin layers imparted water absorbing ability. The multilayer film prolonged the shelf life of avocados from less than 10 days to 16 days at 25 °C, controlled the ethylene and CO₂ concentrations in the packaging headspace, and inhibited the firmness and weight losses of avocados. More importantly, the skin layers not only avoided the direct contact between active agents and avocados, but also prevented the migration of active agents to avocados, which protected avocados from contamination and provided a safety guarantee.

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LIST OF ABBREVIATIONS

ΔH_m	Melting enthalpy
AA	Active agents
BET	Brunauer-Emmett-Teller
C_2H_4	Ethylene
CG	Control group
CO_2	Carbon dioxide
DSC	Differential scanning calorimetry
EG	Experimental group
EVA	Ethylene vinyl acetate
EVOH	Ethylene vinyl alcohol
FTIR	Fourier transform infrared
HDPE	High-density polyethylene
H_2O	Water
HNO_3	Nitric acid
ICP-MS	Inductively coupled plasma mass spectrometry
$KMnO_4$	Potassium permanganate
KOH	Potassium hydroxide
LDPE	Low-density polyethylene
$MgCl_2$	Magnesium chloride
MnO_2	Manganese dioxide
NaCl	Sodium chloride
OP	Oxygen permeability
OTR	Oxygen transmission rate

O ₂	Oxygen
PE	Polyethylene
PE-g-MA	Maleic anhydride grafted polyethylene
PET	Polyethylene terephthalate
PKM	Pumice and potassium permanganate
PP	Polypropylene
PP-g-MA	Maleic anhydride grafted polypropylene
RH	Relative humidity
SEM	Scanning electron microscopy
TiO ₂	Titanium dioxide
T _m	Melting temperature
WVP	Water vapor permeability
WVTR	Water vapor transmission rate
X _c	Crystallinity

CHAPTER 1 INTRODUCTION

The preservation of fresh fruits and vegetables has always been a concern because improper preservation can cause significant food and economic losses. It is well known that ethylene plays a very important role in accelerating the maturation of fruits and vegetables by increasing their respiration rate. Ethylene can be produced by fruits and vegetables through metabolism, so if ethylene in the packaging headspace is not removed in time, its accumulation can speed up the ripening and senescence of fruits and vegetables resulting in a short shelf life. Ethylene scavengers have been studied for a long time to remove ethylene from the storage environment to extend the shelf life and maintain the postharvest quality. Generally, there are two forms of ethylene scavengers. One is using sachets containing active agents, and another by the application of active packaging films incorporating active agents [1]. However, there has been only limited research about the application of ethylene scavengers in terms of polymer-based active packaging films [2].

Over the last two decades, natural porous materials such as zeolite, halloysite, and montmorillonite, have drawn much attention as ethylene scavengers [2-4], because they have porous structures and high specific surface areas with a capacity of adsorbing ethylene. On the one hand, the relevant research has been performed to explore the ethylene adsorption performance of porous materials; on the other, some porous materials have been incorporated into polymer films to make ethylene scavenging films [5-7]. However, to further improve the ethylene scavenging capacity, the porous materials were normally not utilized alone as ethylene scavengers; instead, they were always combined with potassium permanganate (KMnO_4) which is very effective to oxidize ethylene. By doing so, the adsorption-oxidation system would generate the synergistic effect, consisting of physical adsorption and chemical oxidation, and then much more ethylene would be removed. Nevertheless, the synergistic effect has not been systematically investigated.

Of note, pumice also has the same properties as the porous materials mentioned above, simultaneously cost-efficient and eco-friendly. According to literature records [2, 8, 9], pumice is a potentially promising material with respect to preserving fruits and vegetables by adsorbing ethylene, but very few studies have been performed. In addition, although the ethylene scavenging films containing KMnO_4 have been studied in recent years [10-12], their development is limited because one of the main drawbacks is the safety hazard that may be caused by the migration of KMnO_4 to the food surface. Therefore, how to avoid the migration of KMnO_4 is a challenge.

The goal of this project is to develop an active packaging film incorporating pumice and KMnO_4 with the function of scavenging ethylene to extend the shelf life of fruits and vegetables. Simultaneously, solving the problem of KMnO_4 migration is also one of the goals of this work.

This thesis consists of the following sections:

Chapter 2 provides a literature review about the introduction of active agents and ethylene, the research progress of ethylene scavengers, the application of KMnO_4 and pumice, and the development of compatibilizers and multilayer extrusion in the field of melt blending. Chapter 3 lists the main objective and specific objectives of the project as well as the organization of articles. The three contributions of this work are presented in Chapters 4, 5 and 6 in the form of scientific articles: Chapter 4 is about the ethylene scavenger made up of pumice and KMnO_4 in the form of sachet; Chapter 5 is to make the ethylene scavenging film by incorporating pumice and KMnO_4 into LDPE film using twin-screw extruder; Chapter 6 is about the LDPE-based multilayer film with three layers to avoid the migration of KMnO_4 and pumice. A general discussion regarding the articles is given in Chapter 7. At the end, Chapter 8 concludes the thesis and shares recommendations for future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Active food packaging and active agents

At present, food packaging is the most common way to protect food from physical damage and environmental impact in the transport, preservation, and sale processes. However, the traditional packaging pattern is a kind of passive protective barrier because it can only separate food from the ambient environment but cannot prevent inherent impact caused by oxygen, moisture, carbon dioxide, ethylene, or microorganism, which cannot be simply insulated by traditional packaging [13]. Consequently, foods are still spoiled or only kept a short shelf life even though they are avoided being destroyed out of physical damage. Over the last two decades, there is an increasing tendency to protect food with active food packaging [14-16], and simultaneously, it has been researched, developed, applied, and is getting more and more highlighted attention in recent years. In fact, active food packaging is familiar to us because it exists in our daily life and is a quite useful approach to preserving food. For example, oxygen scavengers, antioxidants, and water absorbers can always be found in some packaged snacks and nuts or dried fruits in bags. In short, active food packaging maintains the quality of food and extends the shelf life by scavenging or releasing specific objects, such as releasing antimicrobial agents or carbon dioxide, scavenging moisture, oxygen, ethylene, or odor. What's more, the key to active food packaging systems is to discover various appropriate active agents (Figure 2.1), because it is active agents that impart the releasing or scavenging function. Up to now, a variety of active food packaging systems have been studied and developed, mainly including oxygen absorbers, moisture scavengers, ethylene scavengers, antioxidant releasers, carbon dioxide emitters and antimicrobial packaging systems [1, 13]. The goal of this work is to develop ethylene scavengers in order to protect fresh fruits and vegetables. Therefore, in the next sections, the influence of ethylene on fruits and vegetables and the research progress of ethylene scavengers are discussed.



Figure 2.1 Active agents for active good packaging [17]

2.2 Role of ethylene on fruits and vegetables

How to avoid excessive food loss around the globe is becoming a great challenge that each country, company, family, and person should emphasize. Among the food loss, nearly 50% is associated with fruits and vegetables [18]. Thus, figuring out how to control and reduce fruits and vegetables loss appears to be of great importance. Ethylene plays a quite significant role in the shelf life of fruits and vegetables because it acts as a growth-stimulating hormone initiating and accelerating the ripening and senescence, then leading to decay [19]. In general, the presence and accumulation of ethylene would negatively affect the quality and shelf life of fruits and vegetables by increasing the respiration rate. Therefore, fruits and vegetables would obtain a longer shelf life by lowering the ethylene level, which could reduce the food loss, as illustrated in Figure 2.2.



Figure 2.2 Process of extension of shelf life of postharvest produce using ethylene scavenger [20]

According to ethylene production rate and respiration rate during the maturation process, fruits and vegetables can be classified into climacteric and non-climacteric produces [21]. The climacteric produces are those performing a peak stage in both respiration rate and ethylene production rate during ripening, while the non-climacteric ones would not show the peak stage [21-23]. According to what is introduced in some references, climacteric produces (for example apple, tomato, banana, kiwifruit, avocado, mango, broccoli, pear, and apricot) are more easily influenced and controlled by ethylene after harvest, compared with non-climacteric ones (such as cucumber, grape, strawberry, pineapple, and citrus) [21, 23]. However, this does not mean that ethylene would make no effect on non-climacteric produces. Ethylene production rate was found approximately $1-10 \mu\text{L kg}^{-1} \text{h}^{-1}$ prior to the maturity of climacteric produces, and then the value could increase at least 10-fold during the ripening process, whereas non-climacteric produces usually generate no more than $1 \mu\text{L kg}^{-1} \text{h}^{-1}$ of ethylene at $20 \text{ }^\circ\text{C}$ [24-26]. The ethylene production rate and sensitivity levels for various fruits and vegetables are shown in Table 2.1. Ethylene is physiologically active even at low concentrations, so a small amount of ethylene can make a big difference. Research shows that even $0.1 \mu\text{L L}^{-1}$ of ethylene concentration would have a great impact on the shelf life and quality of fruits and vegetables [25, 26].

Table 2.1 Ethylene production rates and sensitivity levels of several fruits and vegetables [18, 25]

Commodity	Classification	Ethylene production rate	Ethylene sensitivity level
Avocado	Climacteric	high	H
Apple	Climacteric	very high	H
Banana	Climacteric	moderate	H
Carrot	Non-climacteric	very low	H
Citrus	Non-climacteric	very low	M
Fig	Climacteric	moderate	L
Kiwifruit	Climacteric	low	H
Passionfruit	Climacteric	very high	H
Pear	Climacteric	high	H
Strawberry	Non-climacteric	low	M
Tomato	Climacteric	moderate	H

Ethylene production rate ($\mu\text{L kg}^{-1} \text{h}^{-1}$): very high > 100 , high $10 - 100$, moderate $1.0 - 10$, low $0.1 - 1.0$, very low < 0.1 ; Ethylene sensitivity level (ppm): H = high ($0.01 - 0.5$), M = moderate ($0.5 - 3$), L = low ($3 - 5$).

The accumulation of ethylene can speed up the ripening of fruits and vegetables regardless of climacteric or non-climacteric. Normally, the quality and nutrition values are reduced under the influence of ethylene, exhibiting color changes, softening, sugar and taste alteration, weight reduction, and texture changes [26]. In the meantime, the ripening and senescence are always involved with the acceleration of chlorophyll degradation rates, especially in leafy produces, as well as wilting [27]. In addition, the accumulation of ethylene might lead to an increasing possibility of pathogen susceptibility and physiological disorders [26]. As a result, the shelf life of fruits and vegetables after harvest is greatly shortened owing to the ethylene accumulation, which will cause great food and economic losses.

When transported from source areas to other regions, stored in warehouses, or sold in markets, fruits and vegetables continue their maturing process accelerated by ethylene because the ethylene

can be produced by fruits and vegetables themselves [20]. Hence, it is of great significance to remove and control ethylene by means of some effective methodologies. In the last two decades, scientists have always been trying to extend the shelf life of fruits and vegetables by scavenging ethylene from the storage environment [28-31]. The application of ethylene scavengers is a useful way to preserve fruits and vegetables by removing ethylene in order to maintain the quality and prolong the shelf life.

Avocados

Among numerous climacteric fruits and vegetables, avocados are very special to experimental investigation. This is because avocados not only have a high ethylene production rate, but also are very sensitive to ethylene, which is conducive to the study on the influence of ethylene. Besides, avocados have a short shelf life, which is beneficial to the observation period of packaging tests. Moreover, the avocado quality is associated with the level of ripeness (firmness) and inner defects (browning or bruising) [32, 33], so one can make a judgement of the quality by means of flesh appearance and firmness. As mentioned above, avocados are definitely an appropriate fruit applied in ethylene scavenging systems.

As is well-known, avocados are a very popular fruit all over the world owing to their delicious taste and rich nutrition. On the one hand, avocados are full of lipidic compositions including monounsaturated fatty acids, saturated fatty acids, and polyunsaturated fatty acids [34], among which monounsaturated fatty acids are able to help prevent some diseases, such as cardiovascular diseases, high cholesterol, diabetes, and obesity [34, 35]. On the other, many essential nutrients for human body can be obtained from avocados, such as folic acid, protein, vitamins, and minerals [36]. In addition, avocados possess great economic value. As a commercial fruit, avocado-producing countries such as Mexico and Peru produce and export millions of tons of avocados every year [35, 36]. In the year of 2018, approximately 6.4 million tons and 2.4 million tons of avocados were produced and exported worldwide respectively, which created nearly USD \$5.6 billion in economic value [36].

However, their perishable feature with a short shelf life is the most challenging problem to tackle. Nowadays, cold storage is the most widely adopted method to preserve avocados during the transportation process after harvest [35]. Nevertheless, cold storage may lead to chilling injury of

avocados and the risk increases with the extension of cold storage time [37, 38]. In addition, it is not realistic to always preserve avocados through cold storage, especially when they are sold at grocery stores and fruit markets or brought to home kitchens. Hence, the investigation on the preservation of avocados at room temperature is of great significance. As a climacteric tropic fruit, the ripeness and senescence of avocados are closely affected by ethylene and respiration rate [35, 39]. Thus, active food packaging is a possible method that can be used to extend the shelf life of avocados by removing ethylene and adjusting gas composition in the packaging headspace [40].

2.3 Ethylene scavengers

2.3.1 Basic information

The technology of active food packaging used to remove ethylene is associated with ethylene scavengers. Figure 2.3 presents two types of ethylene scavengers to remove ethylene, ethylene-absorbing sachets and active packaging films [14]. The main difference is that sachets are normally placed in the same packaging bags with food, so people sometimes worry it may lead to safety risks if the sachets are broken resulting in the leakage of active agents [41], while active packaging films can remove ethylene using a safer way because active agents are incorporated and immobilized in the films. In practice, although active agents are immobilized in the film, the worry about the migration of active agents to food surfaces remains.

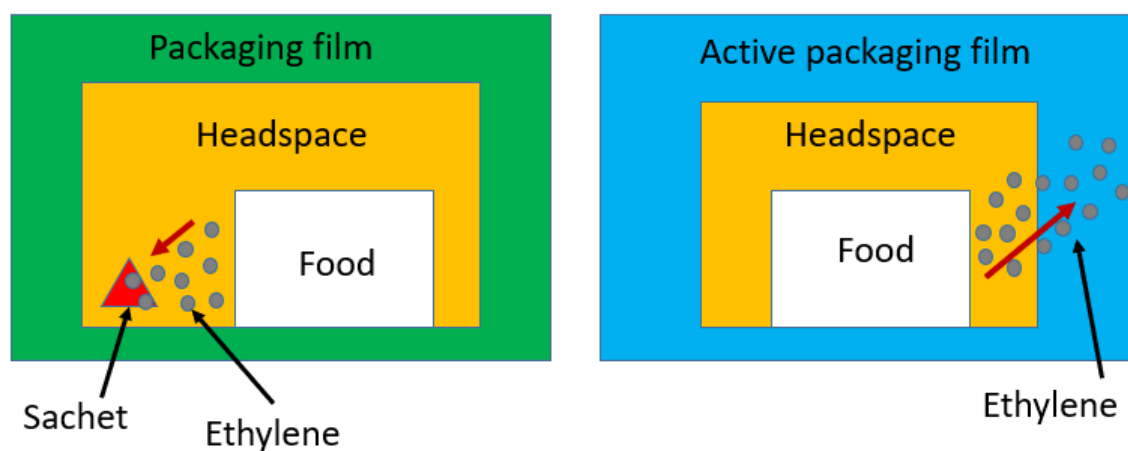


Figure 2.3 The illustration of ethylene-absorbing sachet and active packaging film [14]

On the one hand, active agents such as potassium permanganate (KMnO_4), nano-titanium dioxide (nano- TiO_2), and palladium, as high-efficiency ethylene absorbers, are often packaged in the sachets to make an impact. These active agents generally have a strong ability to remove ethylene [42, 43]. On the other, inert porous materials such as zeolite, activated carbon, montmorillonite, and vermiculite, can also serve as active agents due to their ethylene adsorption ability. In order to be better utilized to preserve fresh fruits and vegetables, KMnO_4 , nano- TiO_2 and palladium are always supported in the inert porous materials to constitute sachets [43, 44]. This is because the porous materials possess porous structures and high specific surface areas, which can increase the contact areas of KMnO_4 , nano- TiO_2 and palladium with ethylene.

Using polymer-based ethylene-scavenging active packaging film is also an efficient way to preserve postharvest produces. It is well understood that some polymers like polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) are often applied as traditional packaging films to package food [16]. To qualify these traditional polymer films with the function of removing ethylene, some active agents such as KMnO_4 , nano- TiO_2 , zeolite, kaolin, halloysite, and montmorillonite, are incorporated into polymer substrates to prepare active packaging films. Moreover, the incorporated active agents can not only absorb ethylene, but also adjust the permeability of the films, so that ethylene and carbon dioxide will diffuse more rapidly, and oxygen will enter more readily than through pure polymer films [45]. Whether the active packaging films are opaque is also a limited element to influence the application of the films, which is a challenging task for researchers to confront because the transparency of films is normally reduced with the addition of active agents. Now in the market, commercial ethylene scavenging films are mostly zeolite-based, for instance, Evert-Fresh, PEAKfresh, Profresh, and Bio-Fresh [2].

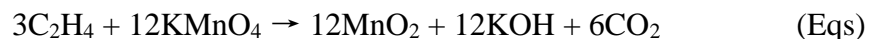
2.3.2 Mechanisms of scavenging ethylene

To date, a wide range of active agents has been applied in controlling ethylene levels or removing ethylene as ethylene scavengers in active food packaging. They make effects by means of different mechanisms summarized into three categories as follows [46]:

Strong oxidants. The potassium permanganate (KMnO_4) is the most representative oxidizing agent and one of the most efficient active agents. It can oxidize ethylene (C_2H_4) to water and carbon dioxide in almost any condition. The stoichiometric oxidation reaction is shown in the following

Eqs [25]. For active packaging, KMnO_4 is often put into sachets, but in recent studies, it was designed to be embedded into packaging films, which is going to be explained in detail later. The main advantage of KMnO_4 used to remove ethylene is the high efficiency and low cost, while the shortcoming is its safe hazard in case KMnO_4 contacts food or is eaten by accident.

Stoichiometric oxidation reaction:



Catalysts. Palladium and TiO_2 nanoparticles are the most common catalysts in active packaging, oxidizing ethylene to water and carbon dioxide under specific conditions such as ultraviolet (UV) irradiation and high temperature. When irradiated by UV light, TiO_2 can generate hydroxyl radicals and superoxide ions on the surface to oxidize ethylene [47, 48]. Except for palladium and TiO_2 , nano-Ag is also found to act as an ethylene-removing agent. These active agents can play a crucial role in both sachets and packaging films. Although catalysts are efficient to remove ethylene, the biggest disadvantage is the specific working conditions such as high temperature and UV irradiation, and the high cost is also the reason to limit their use. In addition, they may cause safety problems if touching food.

Sorbents. The popular ethylene adsorbents are usually based on porous materials, such as zeolite, activated carbon, montmorillonite, and halloysite, which can adsorb ethylene on account of their porous structure and high surface area. In general, these adsorbents physically adsorb ethylene without chemical reaction. It is found that polymer films can incorporate sorbents to perform the function of removing ethylene in active packaging. Compared with strong oxidants and catalysts, the biggest advantage of sorbents is safe and green, as well as cost-efficient, but the low ethylene efficiency is the disadvantage.

Of note, all these active agents normally cannot be used alone to remove ethylene in active packaging because of the existing shortcomings. As a rule, two or more active agents mentioned above are combined as ethylene scavengers, and the relevant applications on active food packaging will be introduced later. To study active food packaging, the prerequisite is to determine the proper active agents.

2.3.3 Application of KMnO_4 and porous materials

As mentioned earlier, nano- TiO_2 and palladium work under certain conditions and are extremely expensive, so these are the chief reasons why their research and applications are less than KMnO_4 in terms of ethylene scavengers. The color of KMnO_4 changes from deep purple to light brown, indicating the ethylene has been removed. In most cases, KMnO_4 was applied in the form of sachets normally in combination with porous materials, and besides, KMnO_4 was also incorporated into polymer films to make ethylene scavenging films.

As mentioned in the mechanism section, KMnO_4 has an extremely strong oxidizing property. For the sake of facilitating and enhancing the oxidation process, KMnO_4 would have better efficacy when supported onto porous materials (Table 2.2), such as alumina, silica gel, zeolite, vermiculite, and montmorillonite. Then an adsorption-oxidation system is created, where a synergetic effect of physically adsorbing and chemically oxidizing ethylene would perform [49]. The ethylene absorption capacity of the adsorption-oxidation systems relies on the surface area of the supports and the content of KMnO_4 . Although various KMnO_4 -based ethylene scavengers have been commercial [26], such as Purafil Select, Ethysorb[®], Sofnofil[™] and Ryan[®], they are not applied in food packaging. In addition, consumers cannot well accept the sachet-based ethylene scavengers applied in food packaging in Europe. As is known to us all, excess KMnO_4 is toxic and harmful to bodies if eaten by mistake, so the food is not edible when sachets containing KMnO_4 are broken.

Table 2.2 Overview of the use of support materials in KMnO_4 -based ethylene-scavenging sachets

Produce	Support	Effects on produce quality	Reference
Sapodilla fruit	Vermiculite	Retard the loss of firmness and vitamin C degradation.	Freitas et al. (2017) [29]
Maxixe fruit	Vermiculite	Maintain chlorophyll content, green coloration, and less loss of vitamin C.	Silva et al. (2015) [50]
Papaya	Vermiculite	Delay fruit ripening and peel color index change, reduce fruit matter loss.	Silva et al. (2009) [51]
Blueberry	Montmorillonite	Inhibit fungal decay incidence, preserve weight, firmness for longer.	Álvarez-Hernández et al. (2019) [52]

Tomato	Zeolite and bentonite	Delay softening, slow vitamin C content decrease and lycopene content increase.	Mansourbahrmani et al (2014) [42]
Tomato	Zeolite	Delay weight loss, slow firmness loss and total soluble solid (TSS) increase.	Salamanca et al. (2014) [53]
Apple	Zeolite	Delay firmness loss and de-greening process. Minimize TSS accumulation.	Sardabi et al. (2013) [54]
Guava	Silica gel	Delay ripening rate and greenness loss of peel, reduce mould growth severity.	Murmu and Mishra (2018) [55]
Pear	Alumina	Delay yellowing, reduce core browning and flesh spot decay.	Giraldo et al. (2015) [56]
Apricot	Sepiolite	A significant decrease in weight loss, and less fungal incidence.	Álvarez-Hernández et al. (2020) [57]

KMnO₄-LDPE nanocomposite film was ever prepared by directly melt blending KMnO₄ with LDPE pellets via a twin-screw extruder [10]. The addition of KMnO₄ increased the oxygen permeability of LDPE film and decreased the crystallinity. According to the peel color indices, the shelf life of bananas was prolonged up to twice when the film contained 5 wt.% KMnO₄. Recently, the ethylene scavenging nanocomposite film was developed by incorporating KMnO₄-impregnated halloysite nanotubes (P-HNTs) into LDPE film [12]. The presence of 1 wt.% P-HNTs did not generate a significant change regarding the mechanical and gas barrier properties of films, but endowed the film with an ethylene scavenging capacity of 31.22 $\mu\text{l}/(100 \text{ cm}^2)$ within 72 h. Further, the ethylene production rate and respiration rate of cherry tomatoes were lowered, and the shelf life was extended to 21 days at 20 °C.

Except for the use of melt blending, KMnO₄ could also be loaded on the film by solvent-drying method. Tirgar and others [58] prepared a novel ethylene scavenging membrane containing KMnO₄, alumina nanoparticles, and alumina nanofibers, where KMnO₄ was attached by means of the solution vacuum drying process. The study revealed that this membrane had higher absorption efficiency to ethylene in comparison with the commercial ethylene absorber, Blueapple Freshness Ball. Beyond that, chitosan and KMnO₄ were blended to make active packaging film by solvent-casting method [59]. The study found that the fragility of the active packaging film increased with

more KMnO_4 added, suggesting that the compatibility between the two materials was not good. By comparing the color change of tomatoes' skins, a conclusion was made that the active packaging film could slightly inhibit the ripening of tomatoes.

Although KMnO_4 has got many applications as ethylene scavengers, consumers' acceptance must be considered comprehensively. Almost everyone concerns about possible health problems that may be caused by KMnO_4 , because people worry about accidentally eating food contaminated by KMnO_4 . In fact, KMnO_4 has been regarded as an eco-friendly and "green" oxidizing agent in many redox reactions and has been widely used in environmental protection to neutralize some pollutants [26], but that still cannot dispel safety concerns. Although some polymer films incorporating KMnO_4 have been studied to preserve fruits and vegetables by scavenging ethylene [10-12], the safety hazard was not evaluated that KMnO_4 might migrate from films to food surfaces during packaging applications. Therefore, the evaluation of the KMnO_4 migration will be one of the goals of this work.

Except as the support, porous materials, such as zeolite, activated carbon, halloysite, kaolin and montmorillonite, were directly incorporated into polymers to prepare ethylene-absorbing packaging films to preserve fresh fruits and vegetables, as shown in Table 2.3. Compared with pure polymer, those composite films not only can absorb ethylene, but also are able to alter the permeability of the films [45].

Table 2.3 Overview of different porous materials in ethylene-absorbing packaging films

Minerals and clays	Base materials	Produces	Effects on produce quality	Reference
Halloysite	LDPE	Banana, tomato, strawberry	Free of brown spots and remaining green color for bananas, better firmness of tomatoes, less weight loss of strawberries.	Tas et al. (2017) [5]
Zeolite	LDPE	Broccoli florets	Improvement of overall quality and increase in shelf-life up to 20 days at 4°C.	Esturk et al. (2014) [6]

		Mango	Extension of shelf life up to 40 days at 12°C, reduction in weight loss, maintaining firmness.	Boonruang et al. (2012) [7]
Kaolin (combined with Nano-Ag, Nano-TiO ₂)	PE	Strawberry	Decay rate, anthocyanin, and malondialdehyde contents were decreased.	Yang et al. (2010) [60]
		Chinese bayberry	Controlling green mold decay, reduced respiration rate and ethylene production.	Wang et al. (2010) [61]
		Chinese jujube	Prevention of fruit softening, weight loss, browning and ethylene control.	Li et al. (2009) [62]
Montmorillonite (combined with Nano-Ag, Nano-TiO ₂)	PE	Kiwifruit	Inhibition of ethylene production and physiological changes.	Hu et al. (2011) [63]
Activated carbon	Cellulose	NS	Ethylene gas adsorption was increased.	Ummartyotin et al. (2016) [64]
Alkaline halloysite nanotubes	LDPE	Cherry tomatoes	The shelf life was increased to 21 days at 8 °C, reduction in firmness and weight loss	Boonsiriwit et al. (2020) [65]

2.4 Pumice

2.4.1 Basic information

The same as most porous materials, pumice also has a porous structure with adsorption sites and gas adsorption properties [66]. Pumice is a lightweight and very porous volcanic rock with a spongy structure forming during explosive volcanic eruptions [67]. As for chemical composition, it mainly consists of silicon dioxide (more than 70%) and aluminum oxide (around 15%), with traces of other metallic oxides [68, 69]. The pumice surface consists of silanol groups which are active groups easily reacting with polar organic compounds and functional groups [70], as shown in Figure 2.4.

According to reference, hydroxyl groups and oxygen bridges are filled with the pumice surface, performing as adsorption spots [71].

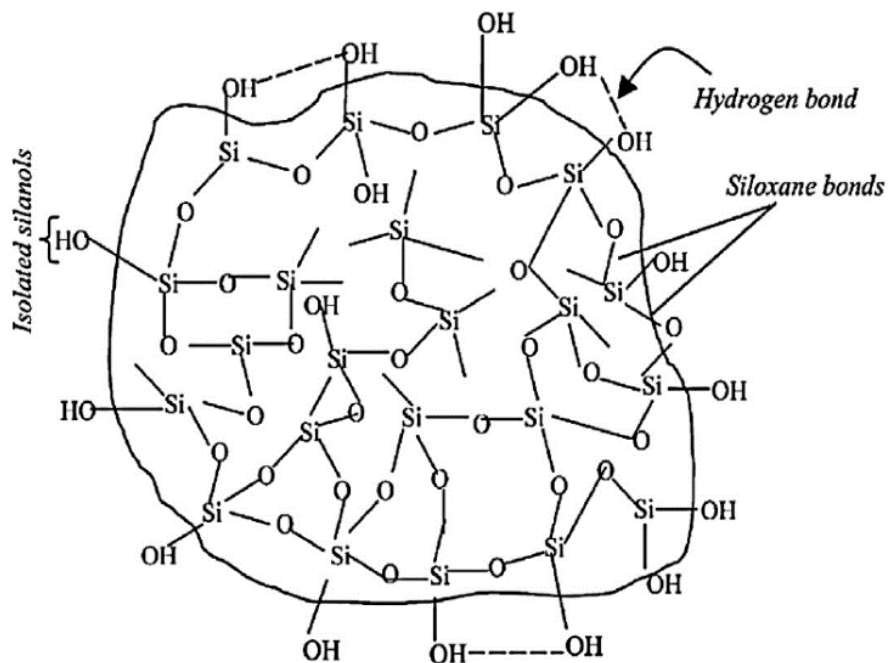


Figure 2.4 Structure of silica surface [70]

Because of the porous structure and high porosity, pumice is very lightweight, with a density of around 0.25 g/cm^3 . If put into water, they can float until slowly become waterlogged and then sink [72]. Pumice is an inert material and has a neutral pH-7.2, so pumice will not react with other compounds easily. Additionally, the friable nature of pumice is one of its most significant characteristics, meaning pumice is easily crushed and refined without losing its utility. Furthermore, it is inexpensive, green, non-toxic, and non-hazardous. Owing to these excellent properties, pumice has been put into many applications. For instance, pumice is an ideal additive for a variety of health and beauty products, and it has been used to produce some cleaning, polishing and exfoliating products, such as Lava Soap and Foot Scrub Cream. In addition, pumice can be used to remove impurities in liquids as filtration media with a long lifespan. Another common use is in landscaping and horticulture. Not only can plant roots easily obtain moisture and oxygen through pumice-combined soils, but the carbon dioxide respired by the roots is able to easily escape the root zone. Besides, pumice has some other properties such as being temperature-resistant, heat-

insulating, refractory, and sound-absorbent [73, 74], which make pumice widely applied in the construction and building fields.

2.4.2 Research progress of pumice

The porous structure and amorphous properties qualify pumice with relatively high specific surface area and skeleton structure, which grant pumice excellent performance in many fields. A large range of applications of pumice has been reported between 1995 and 2015 as shown in Figure 2.5 [75]. It is revealed that pumice gradually became popular and drew attention since 2000. Besides, an increasing trend of studying pumice has occurred in terms of building materials and water and wastewater treatment. Nevertheless, the research about air treatment using pumice was limited all the time.

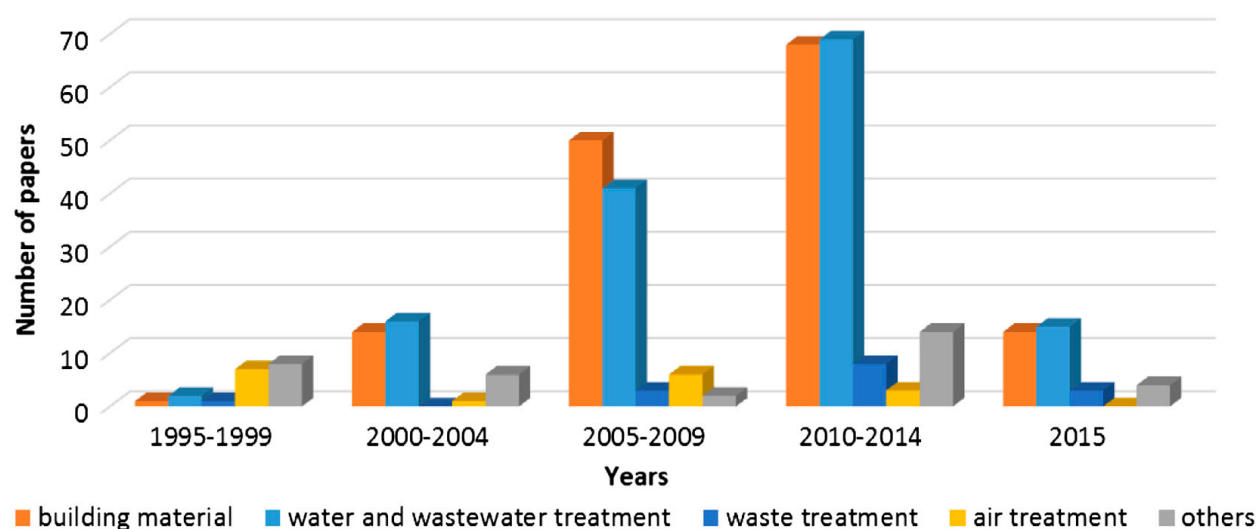


Figure 2.5 Summarization of pumice application in different fields between 1995 and 2015 [75]

In recent years, pumice has been studied through modification with acid or alkali to enhance the adsorption capacity [76, 77]. For example, the natural pumice was pretreated with hydrochloric acid or sulfuric acid solution for removing impurities or enhancing porosity [78-80], and sometimes alkali was also used to modify pumice [81]. As for catalyst, pumice is a wonderful support material to improve catalytic efficiency for the advanced oxidation process. Research about metal-coated pumice, such as iron, copper, zinc, and magnesium, was exploited to deal with different environmental pollutants [82-85]. Also, pumice was even incorporated into polymers like poly(vinyl alcohol) and chitosan to improve their properties [86, 87], but there are not many studies

about composite materials of pumice and polymers. Although some studies have made some gains, exploration of pumice requires to be continued and developed, because the scientific achievement and application of pumice are still limited compared with other clay minerals, such as zeolite, halloysite and montmorillonite. We believe pumice will inevitably become a research hotspot in near future.

2.4.3 Application of Pumice in active food packaging

Nevertheless, in the field of ethylene scavenger or active food packaging, relevant reports and papers about pumice application are extremely rare. There are only several papers and books mentioning that pumice can adsorb ethylene to protect fruits and vegetables because of its porous structure [2, 8]. But no detailed explanation or introduction about pumice scavenging ethylene can be found. A patent published in 1989 [88], took an example of pumice absorbing ethylene. Pumice was incorporated into PE to prepare the composite film. This film was applied to store spinach at room temperature. The graph (Figure 2.6) is the change of ethylene concentration during three days of preservation, and the composite film of PE and pumice resulted in lower ethylene concentration. As for color change, in packages with composite PE film containing pumice, only two leaves were discolored to yellowish brown, whereas in packages of pure PE film, seven leaves were discolored, and four leaves were discolored for that spinach not wrapped. This patent indicated that pumice could protect spinach by absorbing ethylene.

Up to now, this patent is the only report setting an example about pumice absorbing ethylene. The feature of pumice applying to scavenge ethylene seems to have been forgotten by researchers. Although pumice has got many applications in other fields, it did not gain enough attention in the field of ethylene scavengers and active food packaging. Anyway, pumice is a kind of promising material that needs us to study and develop.

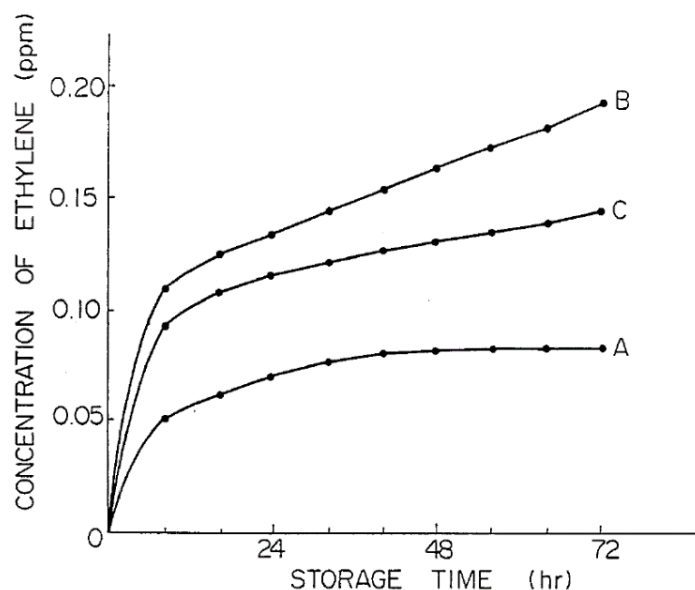


Figure 2.6 The change trend of ethylene concentration along with storage time (A: composite film of PE and pumice, B: pure PE film, C: not wrapped) [88]

2.5 Compatibilizer, multilayer extrusion, and migration of active agents

2.5.1 Selection of polymer matrix

To make active packaging films, it is important to select an appropriate polymer matrix because the matrix can influence the properties of films. Nowadays, some polymers have been used to produce packaging films, including but not limited to polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), polyamide (PA), high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polyvinyl alcohol (PVA). They are selected on the basis of various needs, such as cost, recyclability, safety performance, production conditions, and the nature of packaged products. In active packaging filed, LDPE is the most prevalent polymer with some advantages, clarity, high flexibility, chemical resistance, heat sealability, impact resistance and good water vapor barrier properties [10, 89, 90]. Compared with other polymers, LDPE is cost-efficient, which can greatly reduce the production cost. In addition, in consideration of decomposition temperature of KMnO_4 (240 °C), the melting temperature of polymer must be lower than 240 °C. Moreover, it needs to be noted that the temperature zone of single- or twin-

screw extruder is normally set to 40-60 degree above the melting temperature of polymer. The melting temperature of LDPE is around 110 °C, and a temperature zone of 150-170 °C is usually proper for single- or twin-screw extruder, which would not cause decomposition of KMnO_4 . Moreover, LDPE is a safe material, so there is no need to worry that it would contaminate fruits and vegetables. According to section 2.3.3, a number of active packaging films based on LDPE have prepared. Thus, LDPE is a good choice for active packaging film.

2.5.2 Application of compatibilizers in melt blending

The preparation of active packaging films is correlated to the incorporation of porous materials into polymer films, so three approaches are available, namely melt blending, solution blending and in-situ polymerization [91, 92]. Compared with the other two methods, melt blending is more economic, more flexible, and more compatible with industrial processes like extrusion, and it can provide better dispersion of porous materials in polymer films with the aid of appropriate compatibilizers or surface modifiers. The melt blending of composite films is usually achieved above the polymer's softening point by ordinary compounding devices such as the twin-screw extruder. In practice, it is difficult to achieve completely homogeneous dispersion of porous materials in a polymer matrix because the agglomeration of particles always happens. This problem can be mitigated or overcome by using a compatibilizer to strengthen the compatibility between particles and matrix.

In the field of nanocomposite films, it can be noted that the compatibilizers are always applied to improve the dispersion of nanoparticles in polymer films during the melt blending process, because hydrophobic polymer and hydrophilic nanoparticles are not compatible well. The mechanism is that compatibilizers can increase interfacial interaction between hydrophilic nanoparticles and hydrophobic polymer matrix, as displayed in Figure 2.7, so that nanoparticles can disperse uniformly in polymer films [93]. Hence, nanoparticles are often incorporated into the polymer matrix by means of a compatibilizer to reduce the affinity difference between nanoparticles and matrix [94, 95].

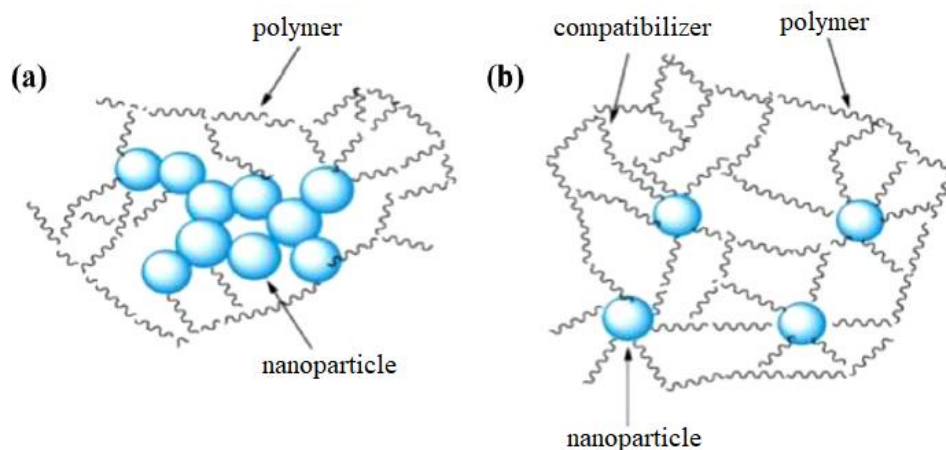


Figure 2.7 Schematics of: (a) agglomerated nanoparticles in polymer and (b) homogeneous dispersion of nanoparticles due to compatibilizer [96]

Maleic anhydride-based compatibilizers are very common and they are often applied to prepare composite films by means of melt blending [97, 98]. For example, the composite film was prepared by melt blending PP with montmorillonite (MMT) in the presence of a compatibilizer, maleic anhydride grafted polypropylene (PP-g-MA) [93]. It was found that the orientation of MMT (9 wt.%) increased on account of homogeneous dispersion with the aid of PP-g-MA (9 wt.%), and the corresponding composite film showed higher tensile modulus at 361 MPa than the film without compatibilizer at 318 MPa. In addition, PE-MMT composite film was obtained easily by melt blending via a twin-screw extruder, when maleic anhydride grafted polyethylene (PE-g-MA) was used as compatibilizer [94]. It was found that MMT dispersed homogeneously in the PE matrix, so that PE-MMT composite film exhibited superior mechanical properties compared to the neat PE film. Besides maleic anhydride-based compatibilizers, some other agents can also act as compatibilizers during the melt blending process. Poly(lactic acid) (PLA)/polybutylene adipate co-terephthalate (PBAT) blends incorporating graphene nanoplatelets (GNP) were prepared by melt blending with the aid of glycidyl methacrylate (GMA) as the compatibilizer [95]. The application of GMA increases the impact strength of nanocomposite compared with uncompatibilized blending, because GNP evenly dispersed in the compatibilized nanocomposite. TiO₂/Ag nanoparticles were dispersed in PE through melt blending, where paraffin acted as compatibilizer [99]. The improved mechanical properties of PE-nanocomposite were obtained when using

paraffin as compatibilizer in comparison with the neat PE. The results showed that paraffin as the compatibilizer improved the degree of dispersion of TiO₂/Ag nanoparticles in the PE matrix.

As mentioned in section 2.5.1, LDPE is a good choice to be used as polymer matrix of active packaging films. Then, PE-g-MA is a proper compatibilizer. The main chain of PE-g-MA can be compatible with LDPE, and the maleic anhydride of PE-g-MA can bind with hydroxyl groups on the surface of pumice. Besides, the density and melting flow index of LDPE and PE-g-MA are close, which is beneficial to melt blending using sing- or twin-screw extruder. For example, the density (23 °C) and melt flow index (190 °C/2.16 kg) of LDPE (NOVAPOL® LF-0219-A) are 0.918 g/cm³ and 2.3 g/10 min, and the density (23 °C) and melt flow index (190 °C/2.16 kg) of PE-g-MA (BYNELTM 4206) are 0.92 g/cm³ and 2.5 g/10 min.

2.5.3 Multilayer extrusion

The same as monolayer films, multilayer films have been developed for many years to make an effect on active food packaging [100, 101]. Compared with monolayer films, the gas barrier properties of multilayer films can be significantly enhanced [102], which is one of the main features. In addition, multilayer films can also be equipped with special functions when combined with active agents. There are several process production techniques to prepare multilayer films, including multilayer extrusion (or coextrusion), casting, electrospinning, compressing mold, layer-by-layer deposition [103, 104]. Casting, electrospinning, and layer-by-layer deposition are time-consuming and normally involved with solvent evaporation. So, polymers should first dissolve in solvents, however, the solvents used are generally toxic, which will cause environmental pollution and safety hazard. Compressing molding (or thermoforming) is also one common method but needs to prepare monolayer film in advance. A humidity-regulating tray was prepared by thermoforming with a three-layer structure: outside barrier layer (PP), inside sealing layer (PP/EVOH/PE), and in-between active layer (PP incorporating 18 wt.% NaCl) [105]. The tray could absorb excess moisture released by mushrooms because NaCl is hygroscopic. By comparison, multilayer extrusion can directly produce multilayer film with strong interfacial adhesion and achieve high-volume production, so it is easy to scale up in terms of industrial application. The high cost of equipment is a shortcoming of multilayer extrusion. For polymers that are not easy to dissolve in solution such as PE and PP, multilayer extrusion is a proper way to make multilayer films. In

general, multilayer extrusion contains several extruder streams, and one extruder can form one layer, as shown in Figure 2.8.

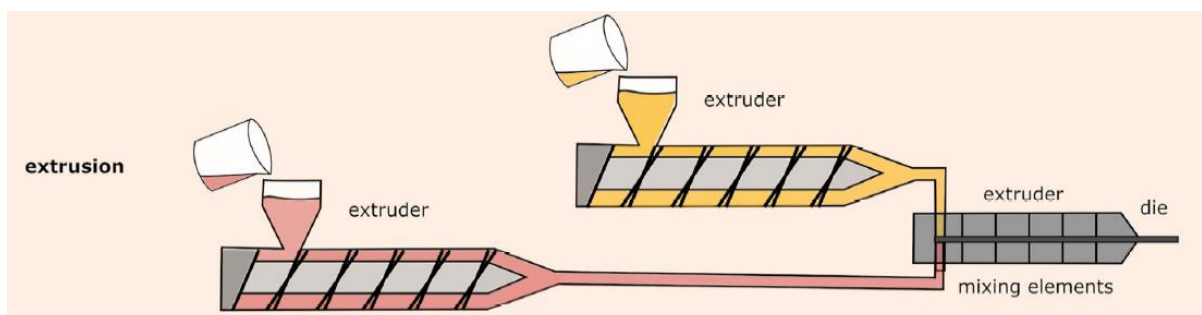


Figure 2.8 Schematic representation of multi-extrusion [103]

In active food packaging, one prevalent application of multilayer films is to preserve food in combination with antioxidants or O₂ scavengers. The PET-based multilayer film was developed through multilayer extrusion with three layers [106]; an active layer (PET and 10 wt.% copolyester-based polymeric O₂ scavenger) was located between two skin layers (pure PET). This multilayer film maintained the quality of mango cuts during the storage of 7 days at 4 °C by limiting the color change and hardness decrease. Lu et al. prepared a bilayer film via multilayer extrusion [107]; one layer was HDPE, and the other layer was LDPE containing quercetin (antioxidant), EVA and diatomite. The study showed that the addition of diatomite facilitated the diffusion of quercetin, and the antioxidative property of the bilayer film was improved with the increasing content of EVA. In addition, the multilayer films with the functions of antibacterial and enhanced gas barrier were also studied using multilayer extrusion [108-110].

2.5.4 Multilayer films prevent migration of active agents

As mentioned in section 2.3.1, although active agents are immobilized in the active packaging films, the migration of active agents from films to food is still a potential safety hazard. When applied to preserve food, active packaging films are usually in direct contact with food. Then, it is possible for active agents to migrate from monolayer film to food surface, causing food contamination [1, 111]. After this, health issues may happen if the contaminated food is ingested and digested. To solve this problem, multilayer films are prepared to prevent the migration of active agents. To this end, active agents are incorporated into active layers, which are located between

layers (barrier layer or control layer) without active agents, as can be seen in Figure 2.9. By doing so, active layers with active agents are isolated from food, avoiding food contamination. For example, Leneveu-Jenvrin et al. [112] prepared the PET-based multilayer film by multilayer extrusion with three layers, in which the skin layers avoided the contact between active layer and mango cuts and prevented the migration of O_2 scavenger. The method that multilayer films prevent the migration of active agents has been declared to be feasible in Regulation 450/2009/EC published by the Official Journal of the European Union [41].

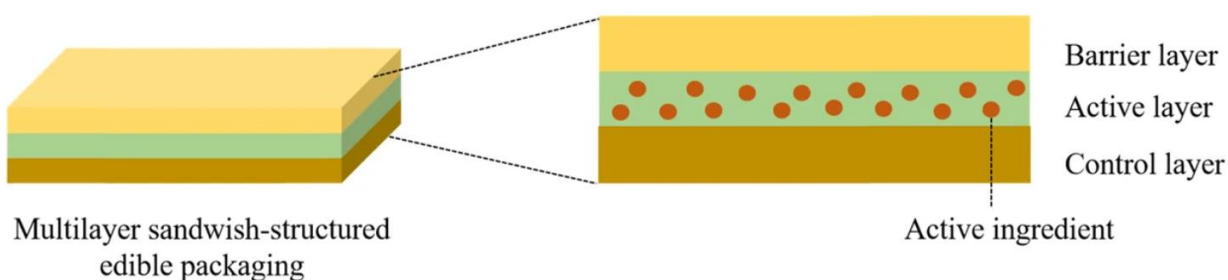


Figure 2.9 Layer structure of multilayer films [113]

According to COMMISSION REGULATION (EU) 2016/1416 of 24 August 2016, plastic materials and articles shall not release aluminium (Al) and manganese (Mn) in quantities exceeding 1 mg/kg food and 0.6 mg/kg food, respectively. This rule can be regarded as the migration limits of porous materials and $KMnO_4$.

2.6 Summary

Ethylene can accelerate the ripening process and even lead to rapid senescence by boosting the respiration rate of fruits and vegetables. In consequence, the influence caused by ethylene is the shortened shelf life and reduced quality. Therefore, it is meaningful to remove ethylene from the storage environment using ethylene scavengers. On the one hand, there are two forms to preserve fruits and vegetables, one using sachets and the other applying active packaging films. On the other, there are three mechanisms; in brief, the first uses a strong oxidant to oxidize ethylene, the second uses an active catalyst to catalyze ethylene, and the third applies sorbents with porous structure and high surface area to adsorb ethylene. In this project, the two forms will be involved, and the mechanisms of oxidant ($KMnO_4$) and sorbent (pumice) will be combined.

Figure 2.10 exhibits the schematic diagram of two forms regarding the combination of pumice and KMnO_4 . Pumice is a very cheap, user-friendly, and potential silicate with a porous structure, meaning that it is hopeful to produce pumice-based ethylene scavenger at a low cost. One branch is to prepare a sachet by the combination of pumice and KMnO_4 . Another is to prepare composite film by incorporating pumice and KMnO_4 into the polymer with the aid of proper compatibilizer through melt blending. Then both the sachet and film will serve as ethylene scavengers to be used in the food application. Overall, this work is to study ethylene scavengers containing pumice and KMnO_4 to preserve fruits and vegetables and extend their shelf life.

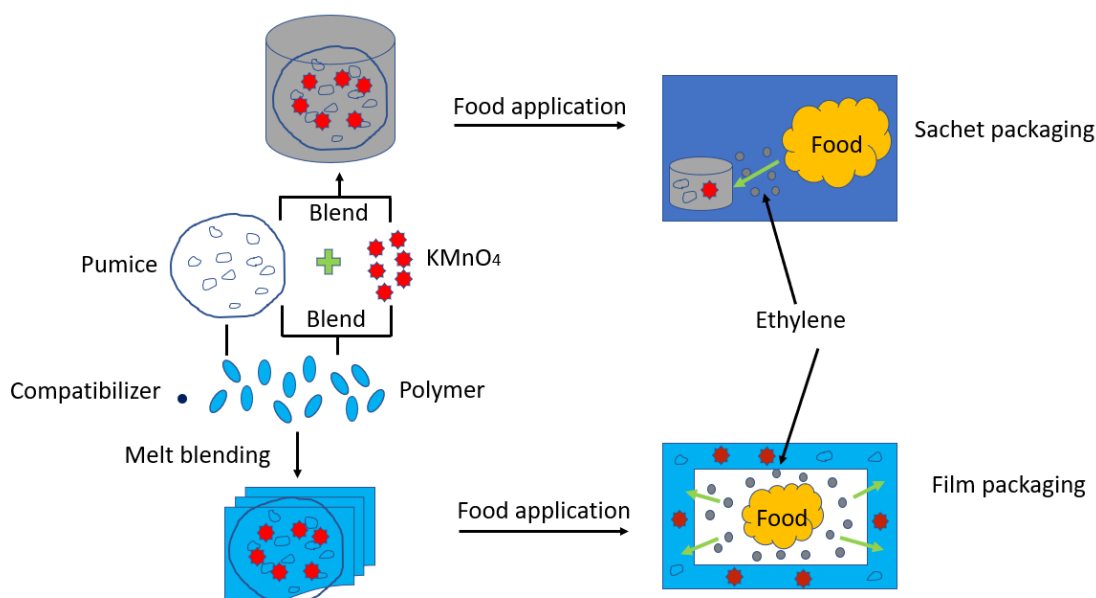


Figure 2.10 Schematic diagram of the combination of pumice and KMnO_4

2.7 Problem identification

The loss of fruits and vegetables is a serious challenge all over the world. The key to solving this challenge is to prolong the shelf life and maintain the quality by means of efficient methods of scavenging ethylene in the storage environment, because ethylene is a growth hormone accelerating the ripening and senescence. Therefore, it makes sense to discover and explore novel and efficient ethylene scavengers. Although some methods of scavenging ethylene have been commercial, there are still some existing limitations. For example, ozone preservation, vacuum preservation, and 1-methylcyclopropene as the inhibitor, all of them need to adopt specific

equipment and complex process conditions, which result in high production costs. Thus, it is meaningful and important to develop an efficient, user-friendly, and cost-effective technology to achieve the goal of preserving fruits and vegetables.

Pumice is a practical material in the fields of construction and catalysis due to its porous structure and relatively high specific surface area. Nevertheless, its function of scavenging ethylene in terms of active food packaging seems to have been forgotten in the last three decades. Several papers and books mentioned that pumice could be applied as the ethylene scavenger, but no detailed explanation was ever revealed. The only example was demonstrated in one patent around 30 years ago. According to various investigations and studies [66-69], pumice is a kind of porous silicate, which is potential to remove ethylene as supports in sachets or fillers in packaging films. Meanwhile, pumice is very economical and eco-friendly, making it possible to reduce the cost and act as a safe ethylene scavenger in the field of active food packaging.

As for KMnO_4 , its research is mainly focused on sachets supported with inert porous materials. However, the development of active packaging film incorporating KMnO_4 was rare over the past few years. Only from the year 2020, the relevant studies about melt blending KMnO_4 and inert materials with polymer films obtained attention [11, 12]. However, how to avoid KMnO_4 migrating from films to food surfaces is also a considerable problem to solve, but no research ever evaluated it. In addition, the combination of KMnO_4 and inert materials can make full use of the synergistic effect of chemical oxidation and physical adsorption to scavenge ethylene. Nevertheless, such research and discussion have not been investigated systematically.

This work aims to solve the existing problems mentioned above in the following aspects:

- Develop pumice in the application of active food packaging.
- Combine pumice and KMnO_4 to make a novel ethylene scavenger and study the synergistic effect of physically adsorbing and chemically oxidizing ethylene.
- Prepare an ethylene scavenging film incorporating pumice and KMnO_4 .
- Prevent the migration of KMnO_4 from film to food surface by developing a multilayer film.

CHAPTER 3 OBJECTIVES AND ORGANIZATION OF ARTICLES

3.1 General objective

The main objective of this thesis is:

To develop ethylene scavenging systems based on pumice and KMnO_4 to extend the shelf life of avocados in the form of sachets and active packaging LDPE-films.

3.2 Specific objectives

- To develop a novel ethylene scavenger comprising pumice and KMnO_4 and study its effect on avocados preservation.
- To prepare an ethylene scavenging LDPE-film containing pumice and KMnO_4 as active agents to extend the shelf life of avocados.
- To develop a multilayer LDPE-film that can prevent the migration of active agents from the core layer onto the avocado surface.

3.3 Organization of articles

The scientific contributions of this thesis are displayed in the form of three research articles, corresponding to three Chapters 4, 5, and 6.

The primary purpose of Chapter 4 was to optimize the weight ratio of pumice to KMnO_4 and investigate their synergistic effect of physically adsorbing ethylene (pumice) and chemically oxidizing ethylene (KMnO_4). The investigation of this section was necessary and important to the whole work because the optimal weight ratio of pumice to KMnO_4 was the prerequisite to the preparation of ethylene scavenging films in Chapters 5 and 6. The ethylene scavenging capacity of the mixture of pumice and KMnO_4 was tested according to different weight ratios. The synergistic effect was studied by comparing the ethylene scavenging capacity between the mixture of pumice and KMnO_4 and the pumice or KMnO_4 alone. In addition, the influence of RH on ethylene absorption was also analyzed to figure out the competitive relationship between water and ethylene. Furthermore, the mixture of pumice and KMnO_4 was applied as the ethylene scavenger to preserve avocados. The resulting paper entitled “Development of a novel ethylene scavenger made up of

pumice and potassium permanganate and its effect on preservation quality of avocados” has been published in “*Journal of Food Engineering*” (<https://doi.org/10.1016/j.jfoodeng.2022.111101>).

Based on the optimal weight ratio obtained in Chapter 4, the ethylene scavenging films were prepared by melt blending LDPE with active agents (the mixture of pumice and KMnO_4) with the aid of compatibilizer (PE-g-MA), as presented in Chapter 5. To produce ethylene scavenging films, different content of active agents was incorporated into LDPE films via a twin-screw extruder. The optimal content of active agents was determined by characterizing and analyzing the properties of the films, including the dispersion, surface color, thermal property, mechanical property, gas permeability, and ethylene scavenging capacity. Further, the ethylene scavenging films were applied to extend the shelf life of avocados. The paper entitled “Ethylene scavenging film based on low-density polyethylene incorporating pumice and potassium permanganate and its application to preserve avocados” was submitted to the journal “*Polymer Testing*”.

Chapter 6 is about the development of the multilayer film based on the aforementioned research. The multilayer film has three layers; the core layer is LDPE film containing optimal content of active agents (pumice and KMnO_4), and the skin layers are LDPE film containing NaCl. The primary purpose of developing the multilayer film was to avoid the safety hazard by preventing the migration of KMnO_4 from the core layer to the food surface. Moreover, except the ethylene scavenging property, the addition of NaCl endowed the film with water absorbing property. SEM images, film transparency, thermal and mechanical properties, gas permeability, ethylene and water absorption of the film were characterized. Furthermore, the avocados preservations and the migrating test were carried out. This paper entitled “Development and application of LDPE-based multilayer film incorporating KMnO_4 and pumice for avocado preservation” was submitted to the journal “*Food Chemistry*”.

CHAPTER 4 ARTICLE 1 : DEVELOPMENT OF A NOVEL ETHYLENE SCAVENGER MADE UP OF PUMICE AND POTASSIUM PERMANGANATE AND ITS EFFECT ON PRESERVATION QUALITY OF AVOCADOS

Chunyu Wang, Abdellah Ajjj*

3SPack, Research Center for High Performance Polymer and Composite Systems (CREPEC),
Chemical Engineering Department, Polytechnique Montréal, Montréal, Québec, H3C 3A7, Canada

* Corresponding author.

E-mail addresses: chunyu.wang@polymtl.ca (C. Wang), abdellah.ajji@polymtl.ca (A. Ajjj).

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4.1 Abstract

The purpose of this research was to develop a novel ethylene scavenger by combining pumice and potassium permanganate (KMnO₄) to preserve fruit and vegetables. The study showed that pumice with smaller particle sizes and lower relative humidity (RH) were favorable to ethylene adsorption. The optimal ratio was 1 g of pumice (< 5 µm) to 100 mg of KMnO₄ with approximately 620 µL/g of ethylene adsorption capacity within 24 h at lab room RH (30 %). Further, this novel ethylene scavenger restricted the ethylene production rate of avocados to 0 µL/kg/h for nine days, and simultaneously, the carbon dioxide (CO₂) production rate remained below 25 mL/kg/h. In addition, the firmness of avocados preserved by the novel ethylene scavenger was 4.04×10^5 N/m² on the 9th d. The results confirmed that the shelf life of avocados was extended by one week at 25 °C under the preservation of the novel ethylene scavenger.

Keywords: ethylene scavenger, pumice, KMnO₄, ethylene adsorption capacity, avocado, shelf life

4.2 Introduction

It is well known that fruit and vegetables are perishable products, and they accounted for nearly 50 % of food loss in the world [1], which would cause a significant loss, ranging from households and restaurants to wholesale markets and industries. Furthermore, fruit and vegetables are delicious, healthy, full of vitamins and essential nutrients. Therefore, the way to preserve fresh fruit and vegetables has obtained more and more attention in recent years. Ethylene, a plant hormone, is closely related to the ripening and senescence of fruit and vegetables by accelerating their respiration and metabolism [2-4]. Numerous fruit and vegetables are sensitive to ethylene so that a tiny amount of ethylene (higher than 0.1 $\mu\text{L/L}$) can make unripe products mature or even spoiled, showing black spots on peel, mushy flesh, off-flavor or green leaves turning yellow during a short period [5, 6]. Ethylene can be generated by the metabolism of fresh products, which is the leading cause of ripening and senescence [7, 8]. In addition, ethylene as a light gas (density: 1.178 g/L at 15 °C) can diffuse freely from one food shelf to another, which intensifies the ripening process when varieties of fresh products are displayed concurrently [1, 7]. Hence, removing ethylene is necessary to prolong the shelf life of fruit and vegetables.

During the past decades, the combination of KMnO_4 and porous materials such as montmorillonite, sepiolite and zeolite has gained widespread application and served as ethylene scavengers [9-11]. Porous materials are capable of physically adsorbing ethylene under the surface adsorption effect [12, 13]. In addition, KMnO_4 is considered the most efficient agent that can oxidize ethylene to water and CO_2 under almost any condition [14]. The overall stoichiometric oxidation reaction is: $3\text{C}_2\text{H}_4 + 12\text{KMnO}_4 \rightarrow 12\text{MnO}_2 + 12\text{KOH} + 6\text{CO}_2$ [8], and its working mechanism is explained in detail in the supplemental information. Many ethylene scavengers containing KMnO_4 have been developed to protect fruit and vegetables due to their high efficiency and low cost [15-17]. The main reason that KMnO_4 needs to be combined with porous materials is to expose KMnO_4 to the air as much as possible by reaching a higher surface area, which can improve its oxidation efficacy [18]. Furthermore, the synergistic effect can be carried out by forming an adsorption-oxidation system, consisting of physical adsorption from porous materials and chemical oxidation through KMnO_4 [19, 20]. Thus, ethylene is adsorbed on the surface of porous materials and then oxidized through the chemical reaction by KMnO_4 .

Over thirty years ago, pumice and zeolite were applied as ethylene scavengers to preserve spinach and strawberry respectively for longer shelf life [21]. Although zeolite has been widely developed, pumice never appeared again as an ethylene scavenger. Pumice is a lightweight and very porous volcanic rock with a spongy structure formed during explosive volcanic eruptions [22]. As for chemical composition, it mainly consists of silicon dioxide (more than 70 %) and aluminum oxide (around 15 %). Pumice is a cost-efficient and eco-friendly material and has good adsorption capacity due to its highly porous structure and -OH groups on the surface, providing many possible adsorption sites [23]. During the past few years, pumice has been applied successfully to remove organic pollutants such as cyanide and phenol [24, 25].

The main aim of the research was to study ethylene adsorption of the ethylene scavenger consisting of pumice and KMnO_4 . First, different sizes of pumice were prepared, and their ethylene adsorption was studied. Then, the optimal ratio of pumice to KMnO_4 and the optimal RH were investigated. Furthermore, the inner appearance, flesh firmness, ethylene and CO_2 production rates of avocados were evaluated under the preservation of ethylene scavengers. To the best of our knowledge, there was no research performed on ethylene scavengers based on pumice and KMnO_4 .

4.3 Experimental

4.3.1 Materials

Pumice (size: $2 \mu\text{m} \sim 45 \mu\text{m}$) was purchased from Hess Pumice Company (Idaho, USA). KMnO_4 was supplied by Thermo Fisher Scientific, Canada. Ethylene was from Air Liquide, Canada. Fresh avocados (Delicia avocado, Mexico) without visual defects were collected from a local Walmart supermarket and selected to ensure uniformity in terms of weight ($220 \pm 10 \text{ g}$) and shape.

4.3.2 Sample preparation

First of all, mesh sieves (Thermo Fisher Scientific, Canada) were used to sieve pumice particles and four sizes of pumice were obtained with “ $< 5 \mu\text{m}$ ”, “ $5 - 25 \mu\text{m}$ ”, “ $25 - 38 \mu\text{m}$ ” and “ $> 38 \mu\text{m}$ ”. These pumice particles were dried at $70 \text{ }^\circ\text{C}$ for 24 h in a vacuum oven before performing the following experiments. Section 1 was designed to study ethylene adsorption

influenced by particle size, RH, and the ratio of pumice to KMnO_4 , while section 2 was for avocado preservation via the novel ethylene scavenger.

Section 1:

Sealed glass jars (volume: 1 L) were prepared for ethylene adsorption detection. Pumice particles (1 g) of different sizes were put on aluminum weighing dishes then placed in the glass jars, followed by sealing the opening. Subsequently, 200 μL of ethylene was injected into the sealed jar through rubber sleeve stoppers on the lids with a syringe. The ethylene concentration at a fixed time interval (2 h) was measured using F-950 Three Gas Analyzer (Felix Instruments, Camas, WA, USA), whose operating principle will be introduced in section 4.3.3.4. Finally, the ethylene adsorption capacity was obtained by the following equation.

$$\text{Ethylene adsorption capacity } (\mu\text{L/g}) = \frac{(\text{initial concentration}(\mu\text{L/L}) - \text{remaining concentration}(\mu\text{L/L})) \times \text{volume of jar (L)}}{\text{weight of pumice (g)}}$$

According to three ratios of pumice to KMnO_4 (1 g:50 mg, 1 g:100 mg, and 1 g:150 mg), three mixtures of 1 g of pumice and 50 mg, 100 mg, and 150 mg of KMnO_4 were ground uniformly via mortar and pestle to obtain 1.05 g, 1.10g, and 1.15 g of mixtures, respectively. Then, the ethylene adsorption capacity of the mixtures was measured using the same procedure and equation mentioned above. Herein, experiments involving the mixture of pumice and KMnO_4 were carried out with pumice smaller than 5 μm .

The lab room RH was around 30 %, and RH of 33 %, 75 %, and 99 % was controlled by saturated salt solutions of MgCl_2 , NaCl , and H_2O , respectively [12]. The lab room RH (30 %) was involved in section 4.4.2.1 and section 4.4.2.3 to study the influence of particle size and the ratio of pumice to KMnO_4 , while RH of 33 %, 75 %, and 99 % was considered in section 4.4.2.2 and section 4.4.2.4 to investigate the effect of relative humidity. All experiments were performed at room temperature (25 °C).

Section 2:

As for the shelf-life experiment, three experimental groups (EG) and one control group (CG) were designed. EG 1 was that 1 g of pumice (< 5 μm) and one avocado were placed inside a sealed glass jar (volume: 1L), while EG 2 and 3 had the same design as follows, 1 g of pumice (< 5 μm) and

100 mg of KMnO_4 were uniformly mixed and ground, and then placed inside a sealed glass jar together with one avocado. Ethylene and CO_2 production rates were tested every 24 h until the avocado was spoiled. The jars were opened and reconnected to the air for a short while (10 - 15min) every 24 h to ensure that the imbalance of gas composition did not influence the respiration of avocado because oxygen had been consumed and the jar was filled with CO_2 during 24 h of respiration. Among the three experimental groups, avocados of EG 1 and 2 were cut open to observe the inner appearance on the 9th d, while that of EG 3 was observed on the 17th d. As for CG, an avocado was placed in a sealed glass jar without ethylene scavenger, and the inner appearance was observed on the 9th d. All experiments were performed at room temperature (25 °C).

4.3.3 Characterization

4.3.3.1 Brunauer-Emmett-Teller (BET) analysis

According to nitrogen adsorption-desorption isotherm data, the BET technique was applied to determine the specific surface area of pumice with different particle sizes using AUTOSORB-1 (Quantachrome Instruments).

4.3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrophotometer (PerkinElmer) was applied to monitor the difference between mixtures before and after absorbing ethylene. Samples were scanned from 4000 to 600 cm^{-1} , and the spectra between 600 and 3000 cm^{-1} were analyzed.

4.3.3.3 Scanning Electron Microscopy (SEM)

SEM (Hitachi TM3030Plus equipment) was carried out to determine particle size and particle agglomeration at a voltage of 15 kV.

4.3.3.4 Ethylene adsorption analysis

The F-950 Three Gas Analyzer was used to determine ethylene concentration ($\mu\text{L/L}$) in the glass jars. This analyzer applies an electrochemical sensor to detect ethylene. During detection, the gas in the headspace is pumped into the analyzer at a sampling flow rate of 70 mL/min and a sampling

volume of 35 mL. After detection, the gas is pumped back to the headspace to prevent the vacuum from occurring.

4.3.3.5 Ethylene and CO₂ production rates, and firmness measurement

When ethylene concentration was measured via F-950 Three Gas Analyzer, CO₂ content (%) in the glass jars was simultaneously provided. Then ethylene and CO₂ production rates could be calculated using the known weight of avocados (220 ± 10 g) and volume of glass jars (1 L), expressed as μL/kg/h and mL/kg/h, respectively.

Avocado flesh firmness was measured using GY series fruit penetrometer (Shanghai Jingsheng Scientific Instruments Corporation, China) with a probe of 3.5 mm in diameter. Five testing points for each avocado were randomly measured after avocados were cut open, and firmness results were expressed as N/m².

4.3.3.6 Color change of ethylene scavenger

Color measurements of the ethylene scavenger were performed by a CR20 Colorimeter (Hangzhou CHNSpec Technology co. Ltd, China) with a testing aperture of 4 mm in diameter. Thus, the values of L*, a* and b* of each color would be obtained with the color change of the ethylene scavenger. When comparing the color difference (ΔE*), one must choose a reference color. Herein, the purple color of ethylene scavenger before preserving avocados was employed as a reference color. The ΔE* index represents the distance between two color points in CIE L*a*b* space coordinates, and it can be calculated according to the equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

4.3.3.7 Statistical analysis

All experiments were carried out in three replicates, and the statistical analysis of experimental data was performed using Minitab software (Minitab® 19 for windows, Minitab LLC, USA) according to one-way ANOVA with Tukey's test to ensure a significance level of $p \leq 0.05$.

4.4 Results and discussion

4.4.1 Characterization of pumice

4.4.1.1 BET

According to BET results, the specific surface area and pore volume of samples were 11.701 m²/g and 0.045 cc/g (“< 5 μm”), 7.624 m²/g and 0.037 cc/g (“5 - 25 μm”), 5.996 m²/g and 0.024 cc/g (“25 - 38 μm”), and 5.740 m²/g and 0.023 cc/g (“> 38 μm”), respectively. The specific surface area and pore volume increased with the decrease of particle size, which was beneficial for ethylene adsorption since ethylene can be in larger contact with the surface adsorption sites. Moreover, the pore radius was approximately 19 Å, larger than the kinetic diameter of ethylene (3.9 Å), which favors the diffusion of ethylene through the pores and ethylene adsorption on the surface [26]. The nitrogen adsorption-desorption isotherm and pore size distribution are shown in Figure S4.2 and S4.3 in the supplemental information.

4.4.1.2 SEM

The particle size difference of the studied samples is shown in the SEM images in Figure 4.1. Overall, the particles sizes in Figure 4.1 (a) (b) and (c) are larger than that in Figure 4.1 (d). Compared with particle sizes of “5 - 25 μm”, “25 - 38 μm” and “> 38 μm”, agglomeration marked with red arrows in Figure 4.1 (d) was apparent for that of “< 5 μm”, because smaller particles had a larger specific surface area, resulting in more interactions and unstable interface energy so that they needed agglomerate to maintain stability [27].

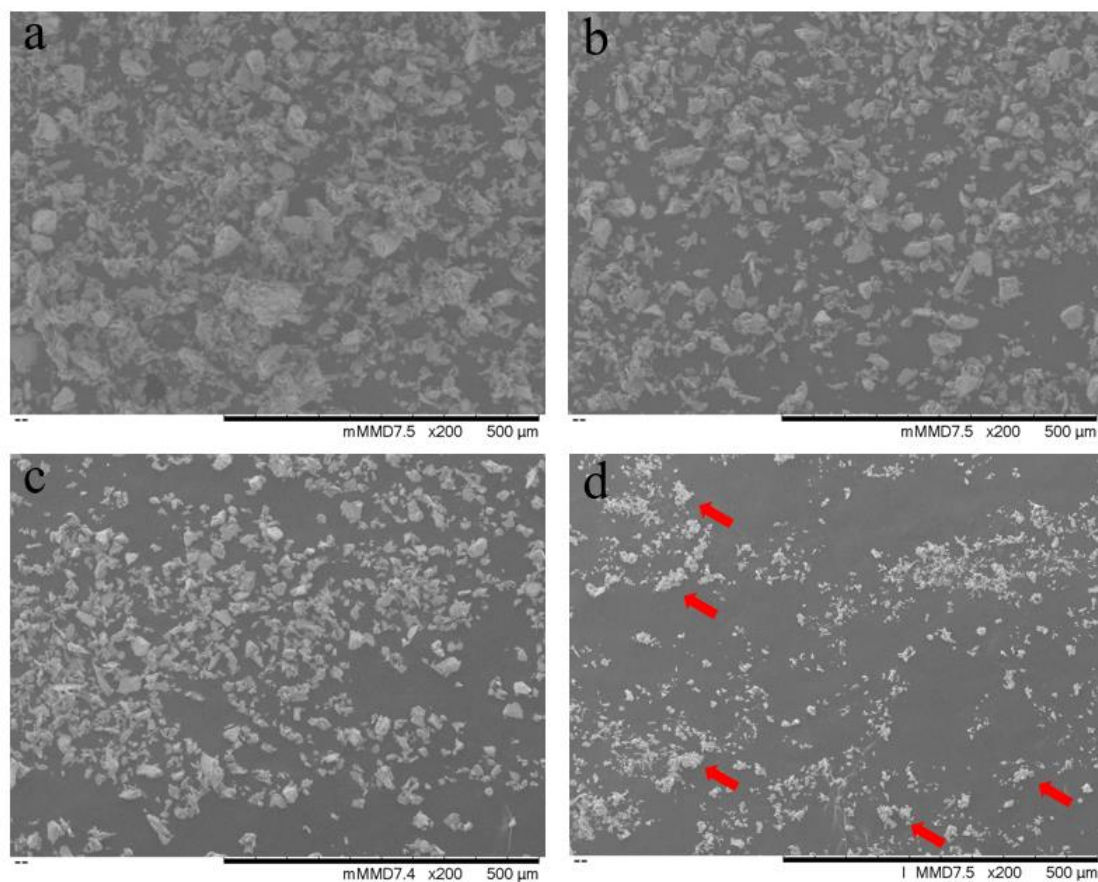


Figure 4.1 SEM images of pumice with different particle sizes: (a) “> 38 μm ”, (b) “25 - 38 μm ”, (c) “5 - 25 μm ” and (d) “< 5 μm ”

4.4.2 Ethylene adsorption results

4.4.2.1 The influence of particle size on ethylene adsorption for pumice

As shown in Figure 4.2, the ethylene adsorption capacity increased when the sizes of pumice particles became smaller. From 6 h to 24 h, the increase of ethylene adsorption capacity for pumice smaller than 5 μm was 61.58 %, while that for pumice larger than 38 μm was 42.15 %. This is interpreted as due to the larger specific surface area for smaller particles, such that pumice smaller than 5 μm could adsorb more ethylene than the others. Overall, 1 g of pumice smaller than 5 μm could adsorb 87.91 μL of ethylene within 24 h at lab room RH (30 %), followed by 59.05 μL (5 < size < 25 μm), 36.87 μL (25 < size < 38 μm) and 31.74 μL (size > 38 μm). Therefore, pumice with the size of “< 5 μm ” would be chosen in the following experiments.

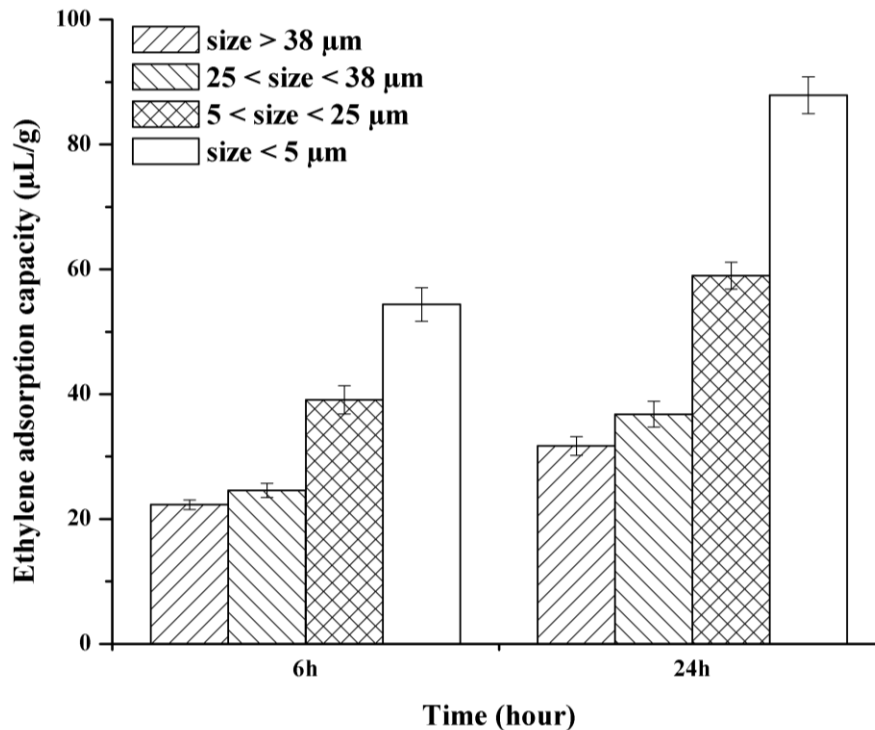


Figure 4.2 The ethylene adsorption capacity of pumice (1 g) with different particle sizes within 6 h and 24 h at lab room RH (30 %)

4.4.2.2 The influence of RH on ethylene adsorption for pumice

Figure 4.3 depicts the influence of RH on the ethylene adsorption capacity of pumice (1 g, “< 5 μm”). It can be observed that the ethylene adsorption capacity decreased with RH increasing. At 33 % RH, 48.44 μL and 77.63 μL of ethylene were adsorbed within 6 h and 24 h respectively, while the value was only 25.05 μL and 40.52 μL at 99 % RH because the water could compete with ethylene for the adsorption sites on the surface of pumice [28]. On the one hand, pumice is hydrophilic so that water is easily adsorbed to the surface of pumice, which could be proved by water adsorption by calculating the weight difference of pumice before and after the experiment. The water adsorption of pumice was approximately 4.66 mg at 33 % RH, 14.74 mg at 75 % RH, and 21.52 mg at 99 % RH. On the other, considering molecular weight, the water molecule is lighter than the ethylene, which favors water to diffuse quickly and get the priority to reaching the pumice surface [29, 30]. When water adhered to the surface, ethylene was prevented from

contacting the surface. Therefore, the presence of excess water had an adverse effect on ethylene adsorption, especially in a high RH atmosphere.

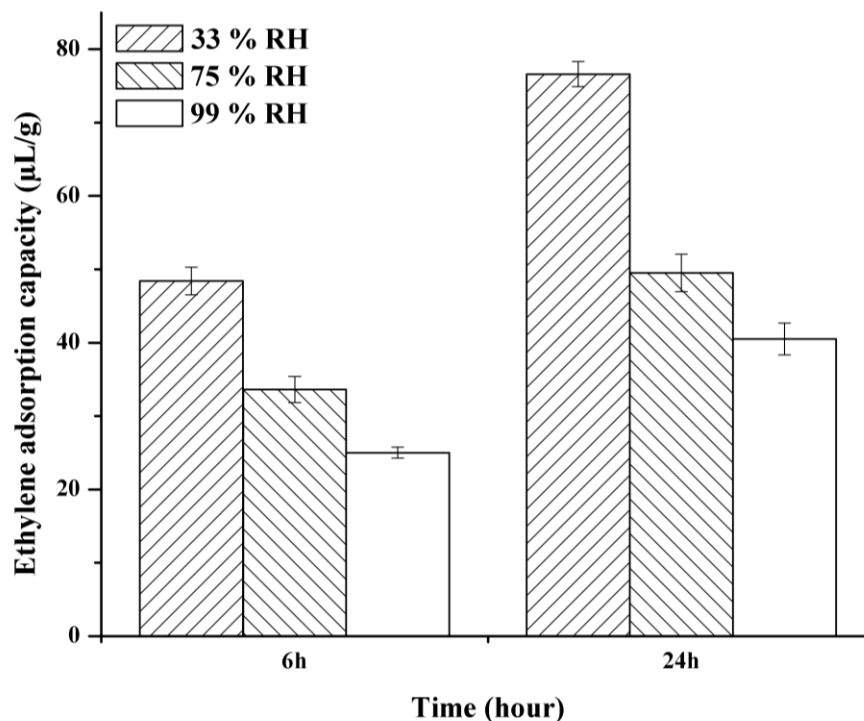


Figure 4.3 The ethylene adsorption capacity of pumice (1 g, “<math>< 5 \mu\text{m}</math>”) within 6 h and 24 h at different RH

4.4.2.3 The effect of KMnO_4 presence and its ratio to pumice

As mentioned in the introduction, the synergistic effect means the combined action of physical adsorption (Pumice adsorbs ethylene) and chemical oxidation (KMnO_4 oxidizes ethylene). Making full use of the synergistic effect, one can apply the mixture of pumice and KMnO_4 to remove more ethylene than either pumice or KMnO_4 alone. As shown in Figure 4.4, 100 mg of KMnO_4 was only able to scavenge 54.38 μL and 55.89 μL of ethylene within 6 h and 24 h respectively, illustrating the oxidation process of ethylene through KMnO_4 mainly took place in the first six hours. In addition, 54.43 μL and 87.91 μL of ethylene were adsorbed by 1 g of pumice within 6 h and 24 h respectively. However, when 1 g of pumice was combined with 100 mg of KMnO_4 , the ethylene adsorption capacity of the mixture increased significantly to 417.87 $\mu\text{L/g}$ within 6 h and 620.09 $\mu\text{L/g}$ within 24 h at lab room RH (30 %). For the mixture of 1 g pumice and 50 mg KMnO_4 and

the mixture of 1 g pumice and 150 mg KMnO_4 , their ethylene adsorption capacity was close and smaller than that of the mixture of 1 g pumice and 100 mg KMnO_4 (Figure 4.4). In the light of the above results, the mixture of 1 g pumice and 100 mg KMnO_4 was applied to protect avocados in the shelf-life experiment.

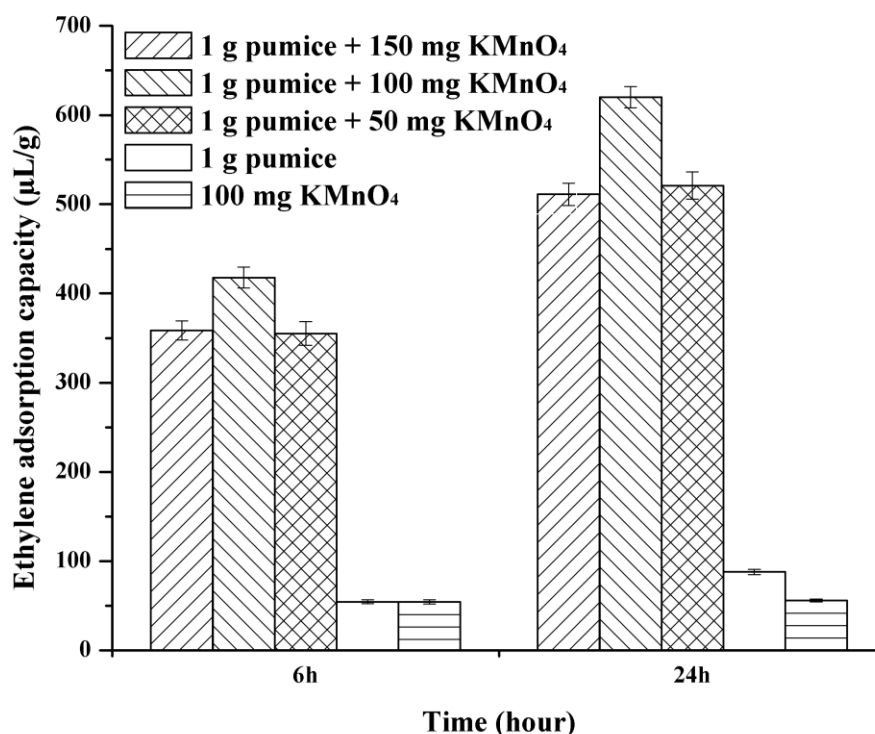


Figure 4.4 The ethylene adsorption capacity of the mixture of pumice (1 g, “< 5 μm ”) and KMnO_4 within 6 h and 24 h at lab room RH (30 %) (For 100 mg KMnO_4 , the unit of ethylene adsorption capacity is $\mu\text{L}/100\text{mg}$)

4.4.2.4 The influence of RH on ethylene adsorption for the mixture of pumice and KMnO_4

Since excess water reduced ethylene adsorption by pumice, it was of interest to investigate its effect when KMnO_4 was present. The mixture of 1 g pumice (“< 5 μm ”) and 100 mg KMnO_4 was applied in this trial. As shown in Figure 4.5, the ethylene adsorption capacity at 33 % RH, 75 % RH, and 99 % RH within 6 h was 401.90 $\mu\text{L}/\text{g}$, 319.72 $\mu\text{L}/\text{g}$, and 242.36 $\mu\text{L}/\text{g}$ respectively, and increased to 581.63 $\mu\text{L}/\text{g}$, 489.63 $\mu\text{L}/\text{g}$, and 431.72 $\mu\text{L}/\text{g}$ respectively after 24 h. As mentioned earlier in section 4.4.2.2, water competes with ethylene for adsorption sites, which could be validated by water adsorption of the mixture during the experiment, nearly 5.25 mg at 33 % RH, 28.44 mg at

75 % RH, and 49.21 mg at 99 % RH. At high RH, ethylene was in insufficient contact with the mixture due to the presence of water, resulting in lower adsorption capacity.

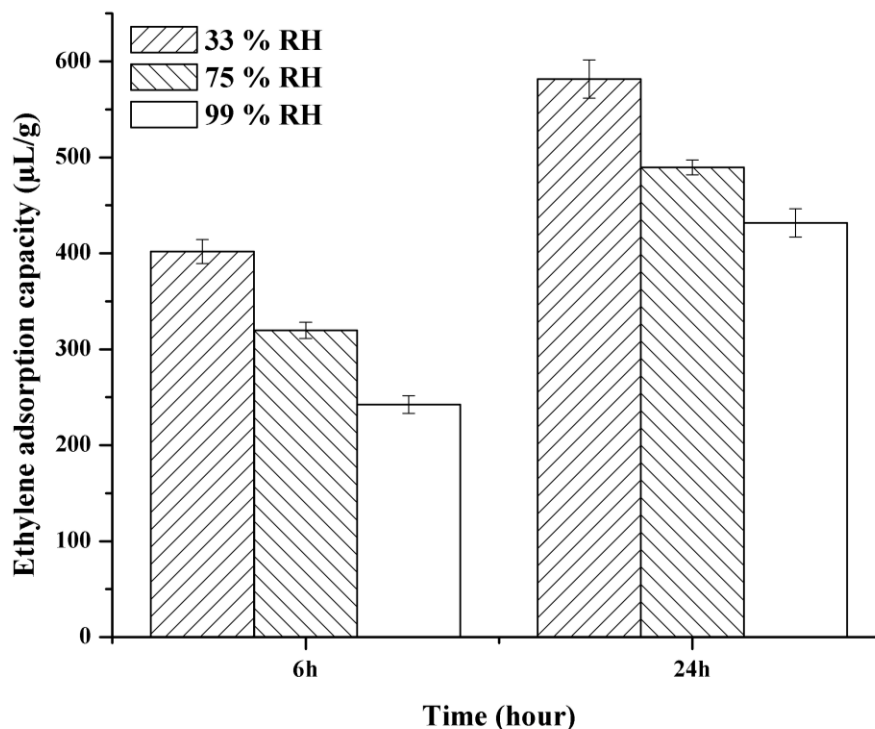


Figure 4.5 The ethylene adsorption capacity of the mixture of pumice (1 g, “< 5 µm”) and KMnO_4 (100 mg) within 6 h and 24 h at different RH

4.4.2.5 FTIR analysis and color change of the mixture

FTIR was used to observe the peak change of spectra before and after the mixture absorbed ethylene, and the results are depicted in Figure 4.6. As for KMnO_4 , there was a sharp peak at 900 cm^{-1} wavenumber, which was associated with the vibration mode of MnO_4^- [31, 32]. The most characteristic peak of pumice was between 1000 cm^{-1} and 1100 cm^{-1} wavenumber caused by stretching vibrations of Si-O and Al-O bonds, and another weak peak around 780 cm^{-1} was attributed to Si-O-Al stretching vibration [33]. For the mixture of pumice and KMnO_4 , the three peaks could still be observed before ethylene absorption. However, the peak at 900 cm^{-1} became small after absorbing ethylene for 24 h, which proved that KMnO_4 oxidized ethylene and itself was reduced. The characteristic peaks of pumice were unchanged because pumice physically adsorbed ethylene, and the chemical structure itself was not changed.

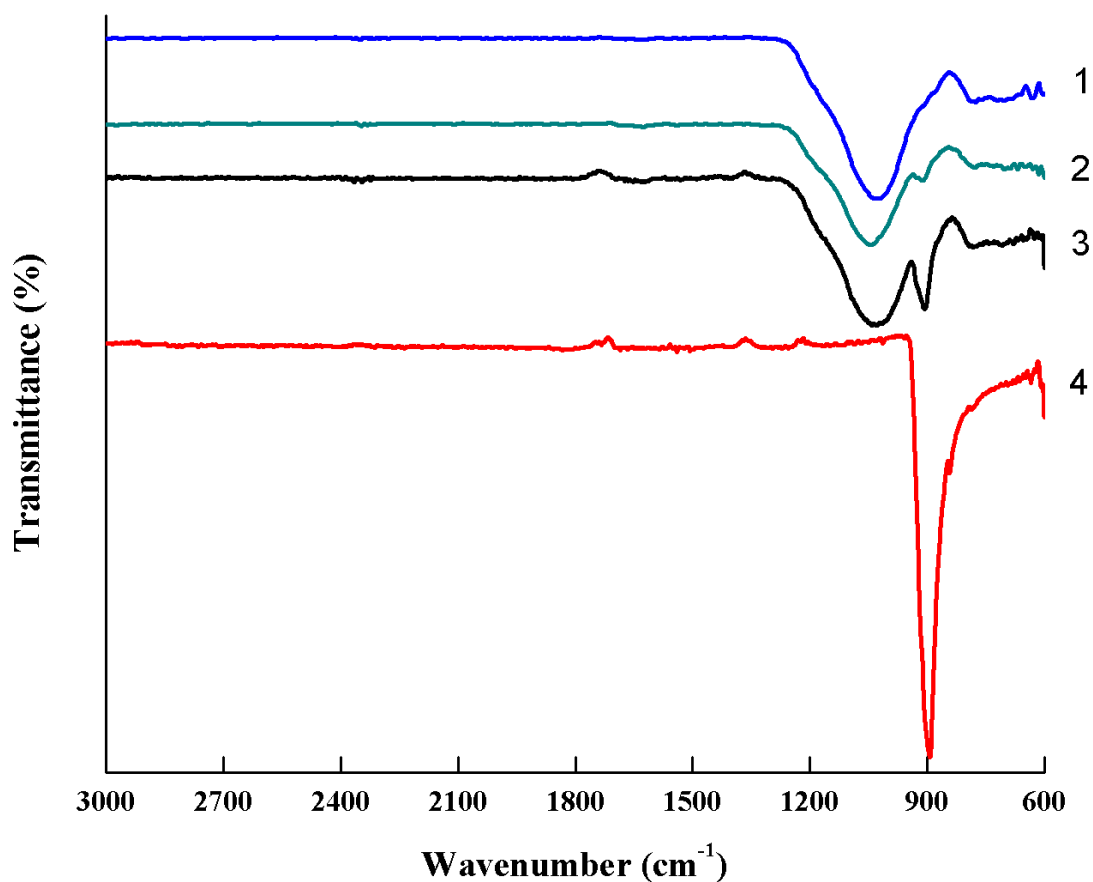


Figure 4.6 FTIR image of (1) pumice (“< 5 μm ”), (2) the mixture of pumice (1 g, “< 5 μm ”) and KMnO_4 (100 mg) after absorbing ethylene for 24 h, (3) the mixture of pumice (1g, “< 5 μm ”) and KMnO_4 (100 mg) without absorbing ethylene, and (4) KMnO_4

The color change of the mixture before and after absorbing ethylene is presented in Figure 4.7. The purple color was exhibited when the mixture did not absorb ethylene, while the color became chocolate after the mixture absorbed ethylene for 24 h. This is because KMnO_4 was uniformly mixed with pumice, so the mixture appeared purple, while the color changed after KMnO_4 reacted with ethylene. When CIE $L^*a^*b^*$ was used to characterize the color change, the initial color (Figure 4.7a) of the mixture before removing ethylene served as a reference color. When the color turned chocolate as presented in Figure 4.7b, the color difference (ΔE^*) index was 29.1, indicating the mixture could still remove ethylene. The ethylene adsorption capacity was completely lost when the ΔE^* index was approximately 45.0, which was introduced in detail in the supplemental information.

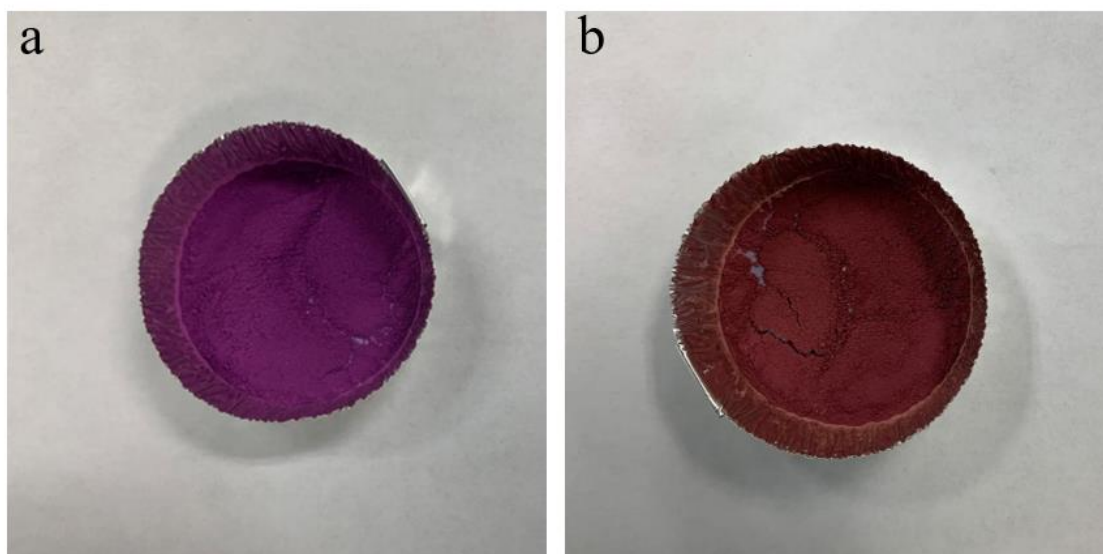


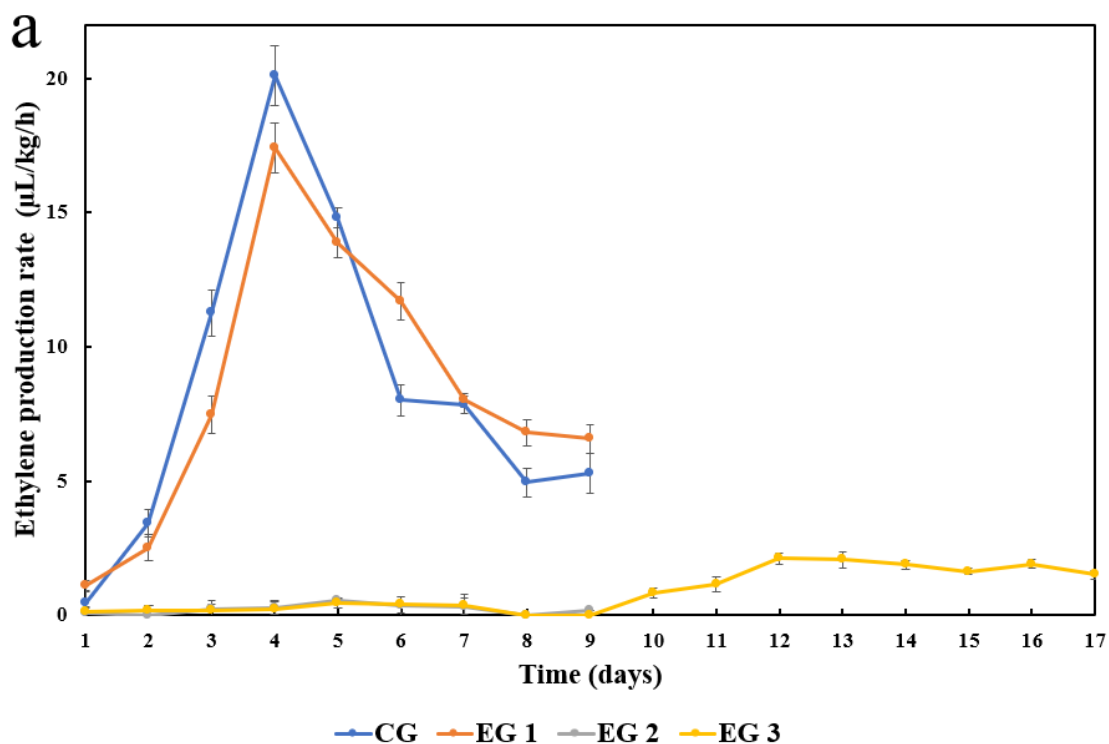
Figure 4.7 Color images of the mixture of pumice (1 g, “< 5 μ m”) and KMnO_4 (100 mg): (a) without absorbing ethylene and (b) absorbing ethylene for 24 h

4.4.3 Effect of ethylene scavenger presence on avocados preservation

4.4.3.1 Ethylene and CO_2 production rates

Figure 4.8 shows the trend of ethylene (a) and CO_2 (b) production rates of avocados from the unripe period until decay. For CG, both ethylene and CO_2 production rates increased rapidly and reached the peaks of 20.09 $\mu\text{L}/\text{kg}/\text{h}$ and 43.75 $\text{mL}/\text{kg}/\text{h}$ respectively on the 4th d. These peaks can be attributed to the fact that avocados belong to climacteric products which generate a climacteric peak of ethylene production rate and respiration rate during ripening [34, 35]. After the climacteric peak, the ethylene production rate of avocado in CG gradually decreased to final 5.29 $\mu\text{L}/\text{kg}/\text{h}$ on the 9th d, and the CO_2 production rate showed a regular fluctuation between 34.74 and 37.80 $\text{mL}/\text{kg}/\text{h}$. Although pumice adsorbed ethylene, its ethylene adsorption capacity was insufficient to scavenge ethylene produced by avocado, which could be explained by ethylene and CO_2 production rates of EG 1 being close to that of CG. In contrast, the ethylene production rate for EG 2 and 3 remained at a low level, nearly 0 $\mu\text{L}/\text{kg}/\text{h}$, within nine days because the ethylene scavenger made up of a mixture of pumice and KMnO_4 removed ethylene produced by avocados. Moreover, the ethylene production rate of the avocado in EG 3 increased to around 2 $\mu\text{L}/\text{kg}/\text{h}$ after nine days, and this value was kept stable until the last day (17 d). In addition, the relatively stable CO_2 production

rate (below 25 mL/kg/h) of EG 2 and 3 demonstrated that the respiration of avocados was restricted on account of ethylene removal by the mixture of pumice and KMnO_4 . However, the CO_2 production rate increased to 36.78 mL/kg/h on the 15th d implying the respiration was disordered and the avocado was starting to be spoiled.



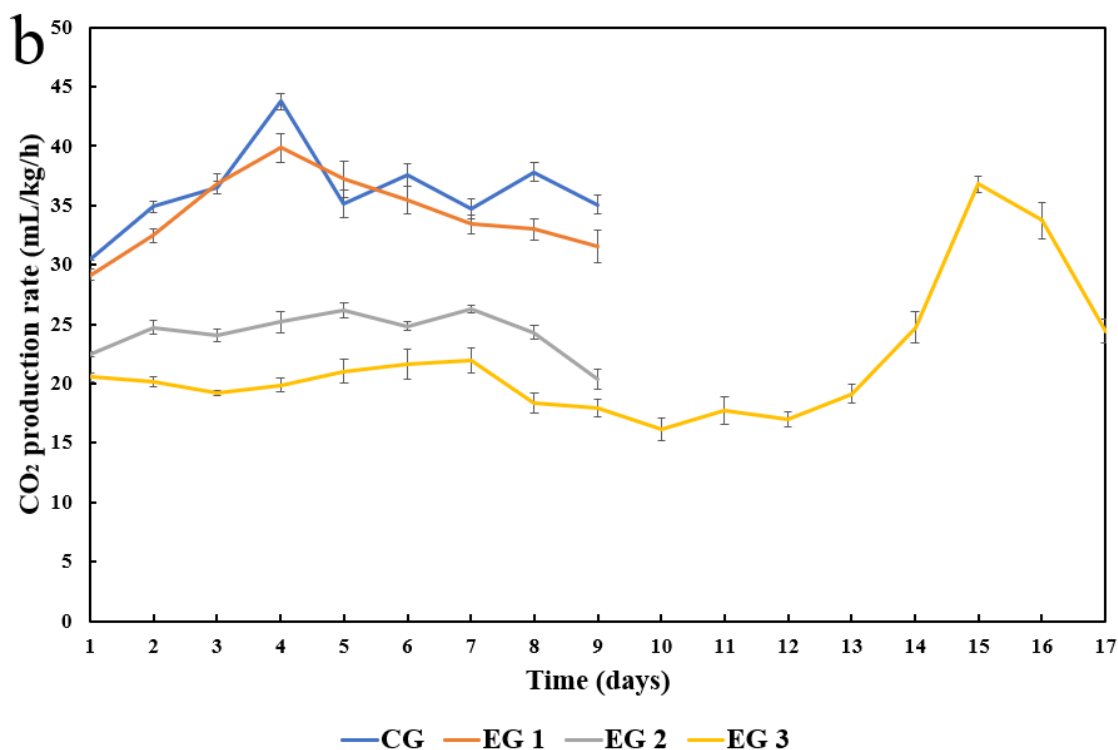


Figure 4.8 (a) Ethylene production rate and (b) CO₂ production rate of avocados from the unripe period until decay (CG: no ethylene scavenger, EG 1: pumice (1 g, < 5 μm) as ethylene scavenger, EG 2 and 3: the mixture of pumice (1 g, < 5 μm) and KMnO₄ (100 mg) as ethylene scavenger) (CG: control group, EG: experimental group)

4.4.3.2 Inner appearance and firmness of avocados

The inner appearance indicated that avocados in CG (Fig. 9a) and EG 1 (Fig. 9b) were spoiled on the 9th d, with corresponding firmness (Fig. 9e) of $0.55 \times 10^5 \text{ N/m}^2$ and $0.62 \times 10^5 \text{ N/m}^2$. Nevertheless, avocados in EG 2 and 3 were still in good condition on the 9th d, as can be observed in Fig. 9c with firmness of $4.04 \times 10^5 \text{ N/m}^2$, and started to be spoiled on the 17th d, as shown in Fig. 9d. In combination with inner appearance and flesh firmness, the mixture of pumice and KMnO₄ as the ethylene scavenger preserved avocados well and extended the shelf life by approximately one week.

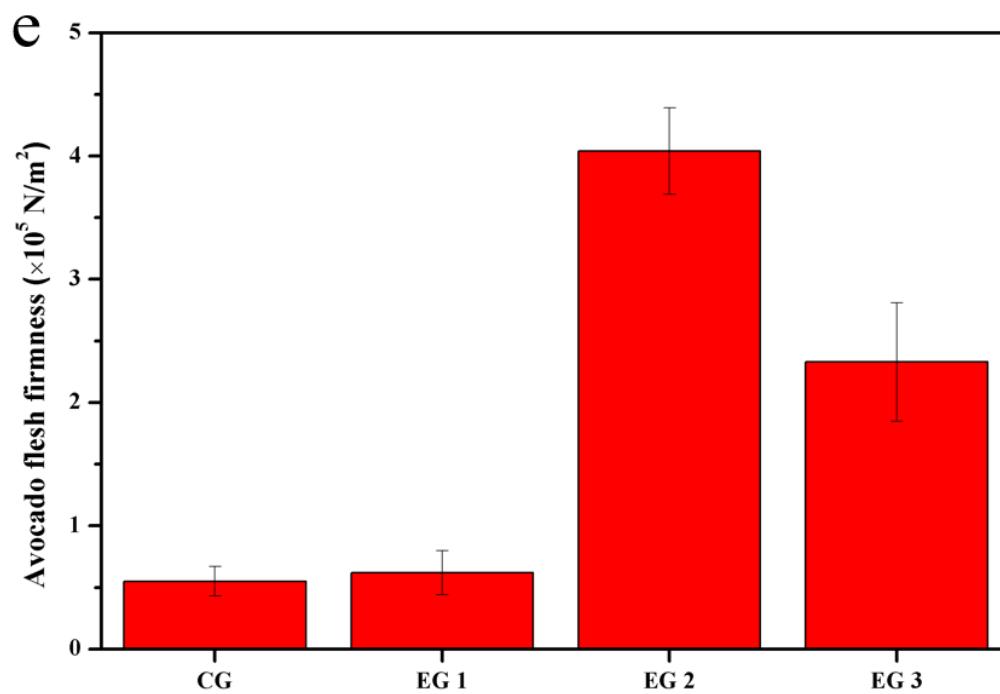


Figure 4.9 The inner appearance of avocados from (a) CG on the 9th d: no ethylene scavenger, (b) EG 1 on the 9th d: pumice (1 g, $< 5 \mu\text{m}$) as ethylene scavenger, (c) EG 2 on the 9th d and (d)

EG 3 on the 17th d: the mixture of pumice (1 g, < 5 μm) and KMnO_4 (100 mg) as ethylene scavenger, and (e) flesh firmness from CG, EG 1, EG 2 and EG 3 on the 9th d and 17th d respectively (CG: control group, EG: experimental group)

4.5 Conclusion

A novel ethylene scavenger made up of pumice and KMnO_4 was successfully developed. When pumice was combined with KMnO_4 , the ethylene adsorption capacity was significantly improved because of the combination of physical adsorption (pumice) and chemical oxidation (KMnO_4) producing a synergistic effect of ethylene removal. The study showed that smaller particle sizes and lower RH were beneficial to ethylene adsorption capacity. The optimal ratio of pumice to KMnO_4 was 1 g to 100 mg, and the ethylene adsorption capacity was approximately 620 $\mu\text{L/g}$ within 24 h at lab room RH (30 %). Moreover, the novel ethylene scavenger effectively restricted ethylene and CO_2 production rates and prolonged the shelf life of avocados by one week compared to those with pumice alone and without ethylene scavenger. This study provided a promising methodology to extend the shelf life of fruit and vegetables.

CRedit authorship contribution statement

Chunyu Wang: Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Roles/Writing – original draft. Abdellah Ajji: Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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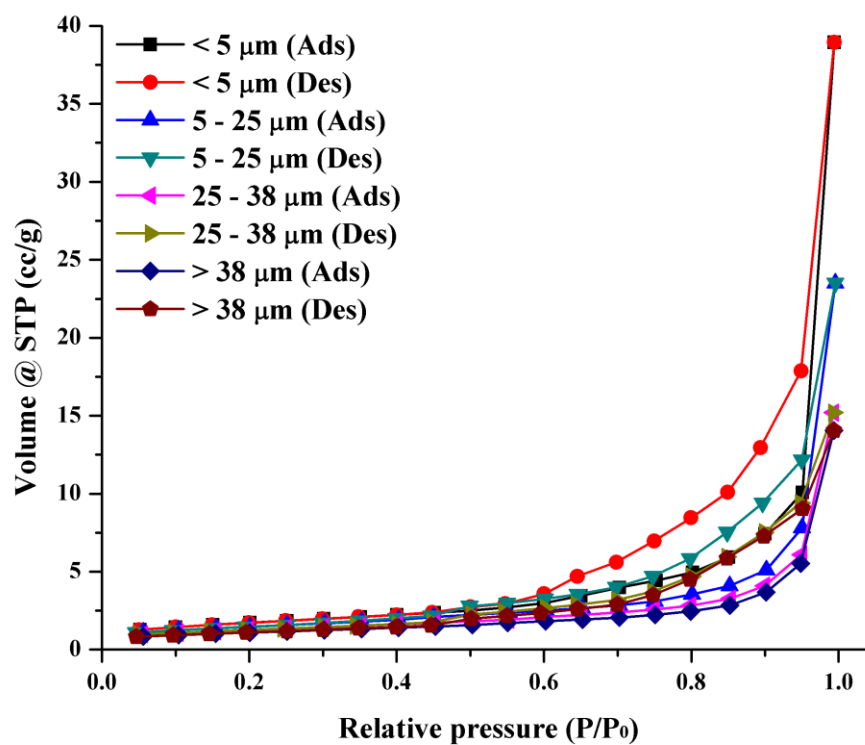


Figure S4.2 Nitrogen adsorption and desorption isotherms of pumice with different particle sizes
(Ads: adsorption, Des: desorption)

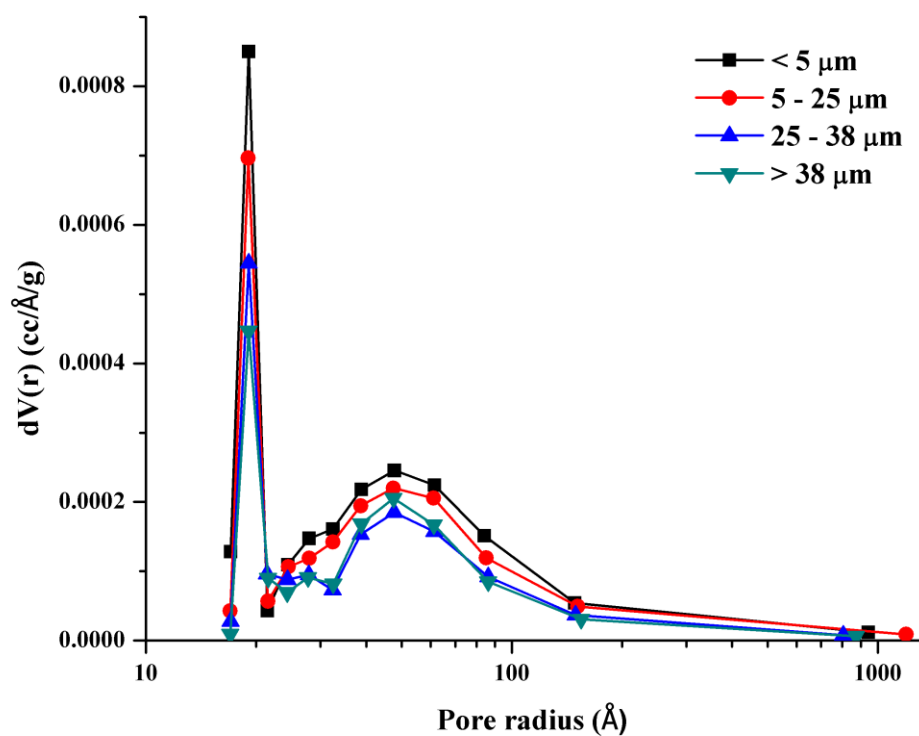


Figure S4.3 The pore size distribution of pumice with different particle sizes

A large index means significant color change, while a small index stands for little color change. The color of the ethylene scavenger changes during its application in preserving avocados, so the ΔE^* index can scientifically reflect the color change. Herein, the color of the ethylene scavenger before preserving avocados was employed as a reference color, and the change of the ΔE^* index was plotted in Figure S4.4. On day 0, the ethylene scavenger was purple, and the corresponding ΔE^* index was 0. The color turned brown, and the ΔE^* index was 33.0 after preserving avocado for one day. It is observed that the ΔE^* index increased slowly from day 2 and reached 39.4 on the 8th d when the color of the ethylene scavenger became dark brown. Since then, it has been difficult to distinguish the color of the scavenger with the naked eye. The ΔE^* index was 43.1 on the 14th d and correspondingly CO_2 production rate of avocado started to increase rapidly, implying the avocado started to be spoiled.

If color change was correlated with a percentage of chemical oxidation in KMnO_4 , a ΔE^* index of 45.0 (in consideration of error) could be regarded as maximum, meaning 100 % of chemical oxidation in KMnO_4 . Thus, 73.33 %, 87.56 %, and 95.78 % of chemical oxidation in KMnO_4 corresponded to 33.0, 39.4, and 43.1 of ΔE^* index on the 1st, 8th, and 14th d, respectively.

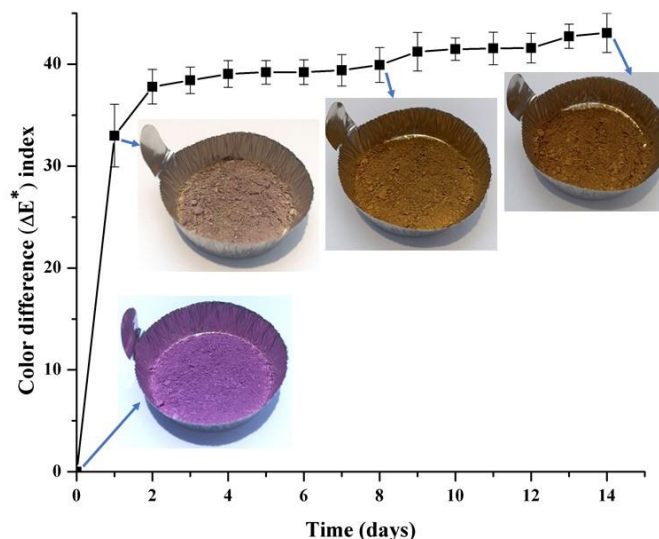


Figure S4.4 The ΔE^* index of ethylene scavenger and its color change during preserving avocados

Ethylene adsorption through pumice belongs to physical adsorption, so ethylene can be separated from pumice when an external force is applied. According to experimental verification, the pumice used alone in the experiment could be recycled after vacuum drying. Pumice (1g, size < 5 μm) having adsorbed ethylene for 24 h was dried at 80 °C in a vacuum oven for 24 h and then, ground to uniformity. Compared to the first cycle, its ethylene adsorption capacity in the second cycle was almost unchanged, approximately 50 $\mu\text{L/g}$ within 6 h and 80 $\mu\text{L/g}$ within 24 h at lab room RH (30%). After vacuum drying, pumice could continue to be employed and combined with KMnO_4 as an ethylene scavenger. However, the mixture of pumice and KMnO_4 was not able to be recycled because it was difficult to separate pumice from the mixture, and KMnO_4 was transformed to MnO_2 and KOH after oxidizing ethylene. To our knowledge, there was no methodology to achieve this goal.

Supporting references:

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CHAPTER 5 ARTICLE 2 : ETHYLENE SCAVENGING FILM BASED ON LOW-DENSITY POLYETHYLENE INCORPORATING PUMICE AND POTASSIUM PERMANGANATE AND ITS APPLICATION TO PRESERVE AVOCADOS

Chunyu Wang, Abdellah Ajjj*

3SPack, Research Center for High Performance Polymer and Composite Systems (CREPEC),
Chemical Engineering Department, Polytechnique Montréal, Montréal, Québec, H3C 3A7, Canada

* Corresponding author

E-mail addresses: chunyu.wang@polymtl.ca (C. Wang), abdellah.ajji@polymtl.ca (A. Ajjj).

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5.1 Abstract

An ethylene scavenging film was developed for the sake of extending the shelf life of fresh fruit and vegetables. This film consisted of low-density polyethylene (LDPE) as matrix, the mixture of pumice and potassium permanganate (KMnO_4) (weight ratio: 10 to 1) as active agents, and maleic anhydride grafted polyethylene (PE-g-MA) as compatibilizer. SEM, FTIR, DSC, mechanical, oxygen and water vapor barrier, and ethylene scavenging properties of the ethylene scavenging films with different loading of active agents were investigated. The study showed that a low loading (1 wt.% and 3 wt.%) of active agents were evenly distributed in the LDPE films and improved the mechanical property, crystallinity, and gas barrier performance against oxygen and water vapor. In addition, the film (thickness: 60 μm) incorporating 3 wt.% active agents had an ethylene scavenging capacity of 7.31 $\mu\text{mol}/(25 \text{ in}^2)$ within 12 d at 25 °C. Further, the ethylene scavenging film with 3 wt.% active agents preserved avocados well for 20 d at 25 °C, inhibited the ethylene and CO_2 concentrations in the packaging headspace, and reduced the flesh firmness loss, while the shelf life of avocados packaged with pure LDPE film was only 10 d.

Keywords: active agents, pumice, KMnO_4 , avocados, ethylene scavenging

5.2 Introduction

The loss of fruit and vegetables is a troublesome problem around the world because a large proportion of postharvest products turn rotten during transportation, storage, and sale. In the process of maturation, fruit and vegetables can release ethylene, which in turn accelerates their ripening and senescence [1, 2]. Hence, the shelf life of fruit and vegetables would be extended if ethylene produced in the packaging headspace could be scavenged [3, 4]. Active packaging technology is a suitable method to scavenge ethylene to preserve fruit and vegetables [5, 6]. The difference between active packaging and regular packaging technologies is that active agents are involved in the former [7, 8]. These active packaging films are equipped with ethylene scavenging ability by incorporating active agents.

KMnO_4 is an effective active agent that oxidizes ethylene into water and carbon dioxide (CO_2) [9, 10]. Although active packaging films were developed by embedding KMnO_4 into LDPE, where the film not only had improved oxygen barrier performance but also prolonged the shelf life of bananas [11], it was rare to apply KMnO_4 as active agent alone because the ethylene-oxidizing efficiency is related to the surface area of KMnO_4 exposed to ethylene [12, 13]. Therefore, KMnO_4 is generally combined with inert materials with high specific surface area to serve as active agents [14-16]. Indeed, an ethylene scavenging film prepared by loading KMnO_4 -impregnated halloysite into LDPE was recently developed to lower ethylene and CO_2 production rate of cherry tomatoes [17]. LDPE, one of the most common polymers, is used as packaging films owing to good flexibility, durability, mechanical and gas barrier properties, as well as some advantages including nontoxicity, low cost, and abundant resources [18-20]. In addition, pumice possesses some advantages, including low cost, high porosity, good adsorption property, easy availability, and eco-friendly nature [21-23]. In the system of pumice and KMnO_4 , pumice can physically adsorb ethylene and increase specific surface area of KMnO_4 exposed to ethylene [13].

In this study, the mixture of pumice and KMnO_4 was employed as active agents, LDPE as matrix, and PE-g-MA as compatibilizer to develop the ethylene scavenging film to preserve avocados. First, active packaging films with different content of active agents were prepared via twin-screw extruder. Then, properties including the dispersion of active agents, ethylene scavenging capacity, gas permeability, thermal and mechanical performance of prepared films were characterized and

compared. Finally, these active packaging films were applied to preserve avocados, and gas composition in packaging headspace and the flesh firmness were further analyzed. To the best of our knowledge, the preparation of ethylene scavenging films by incorporating pumice and KMnO_4 into LDPE films has not been studied yet.

5.3 Experimental

5.3.1 Materials

Pumice (size: $2\ \mu\text{m} \sim 45\ \mu\text{m}$) was supplied by Hess Pumice Company, Idaho, USA. KMnO_4 was purchased from Thermo Fisher Scientific, Canada. Ethylene was from Air Liquide, Canada. LDPE (NOVAPOL® LF-0219-A, density ($23\ ^\circ\text{C}$): $0.918\ \text{g}/\text{cm}^3$, melt index ($190\ ^\circ\text{C}/2.16\ \text{kg}$): $2.3\ \text{g}/10\ \text{min}$) was acquired from Nova Chemical Corporation, Alberta, Canada. PE-g-MA (BYNELTM 4206, density ($23\ ^\circ\text{C}$): $0.92\ \text{g}/\text{cm}^3$, melt index ($190\ ^\circ\text{C}/2.16\ \text{kg}$): $2.5\ \text{g}/10\ \text{min}$) was acquired from Dow Chemical Company, Ontario, Canada. Avocados (Delicia avocado, Mexico) without visual defects were collected from Walmart supermarket and selected to ensure uniformity in terms of shape and weight ($180 \pm 10\ \text{g}$). When choosing avocados, one should make sure that they had the following features, hard texture when squeezing, tough mouthfeel, green flesh, and unripe odor [24].

5.3.2 Sample preparation

Pumice was sieved with mesh sieve (opening: 2500, pore size: $5\ \mu\text{m}$) to obtain particles size in the range of $2 \sim 5\ \mu\text{m}$. Then, pumice and KMnO_4 , with a weight ratio of 10 to 1, were mixed and ground for at least 30 min through grinding ball mill (SPEX Sample Prep 8000 Series Mixer), until achieving uniformity. LDPE and PE-g-MA were dried at $70\ ^\circ\text{C}$ overnight in a vacuum oven before melt blending. Next, LDPE, PE-g-MA, and the mixture of pumice and KMnO_4 were extruded by twin-screw extruder (Leistritz Extrusionstechnik GmbH, ZSE18HP-40D, screw diameter: 18 mm) and made into films via a casting die at a screw speed of 50 rpm and temperature profile of $150 \sim 170\ ^\circ\text{C}$. Herein, the amount of mixture (pumice and KMnO_4) was 1 wt.%, 3 wt.%, 5 wt.%, and 10 wt.%, respectively. A corresponding PE-g-MA content of 1 wt.%, 3 wt.%, 5 wt.%, and 10 wt.%, respectively, was also added for better dispersion. Finally, the thickness of the films was controlled at approximately $60\ \mu\text{m}$. For the sake of convenient presentation, these LDPE-based films were

denoted as LDPE-1%PKM, LDPE-3%PKM, LDPE-5%PKM, and LDPE-10%PKM, respectively, and pure LDPE film was prepared as control.

5.3.3 Packaging avocados with films

The application of the ethylene scavenging films prepared earlier was to preserve avocados at 25 °C and 30 % of relative humidity. Cut films to the same size of 20 × 8 in², and then packaged avocados with the aid of 20'' Impulse Sealer (Model NO. H-1029). Each film was prepared as two replicates assigned #1 and #2. Ethylene, CO₂, and O₂ concentration in packaging headspace were measured every two days using F-950 Three Gas Analyzer (Felix Instruments, USA) through silicone septa stuck on the film. The avocados were cut open and their inner appearance observed, and flesh firmness tested on the 10th d for #1 and 20th d for #2. A simple experimental process is displayed in the supplemental information.

5.3.4 Characterization

5.3.4.1 Scanning Electron Microscopy (SEM)

SEM (Hitachi TM3030Plus equipment) was used to observe the cross-section of cryo-fractured films at a voltage of 15 kV. Samples were treated with liquid nitrogen for 15 min and then snapped before being observed by SEM.

5.3.4.2 Surface color

The surface color of LDPE-based films was measured using CR20 Colorimeter (Hangzhou CHNSpec Technology co. ltd, China) with a measuring aperture of 4 mm in diameter. The parameters of L*, a*, and b* represent lightness, redness/greenness, and yellowness/blueness respectively. Herein, the white plate (L* = 91.76, a* = -1.20, b* = -1.86) was chosen as the reference used to compare the color change of films. The color difference (ΔE^*) was calculated according to the equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Where $\Delta L^* = L^* \text{ reference} - L^* \text{ test sample}$, $\Delta a^* = a^* \text{ reference} - a^* \text{ test sample}$, $\Delta b^* = b^* \text{ reference} - b^* \text{ test sample}$.

5.3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrophotometer (PerkinElmer) was used to monitor the difference of prepared LDPE-based films. Samples were scanned from 4000 to 600 cm^{-1} at a scanning resolution of 4 cm^{-1} and the spectra between 630 and 3300 cm^{-1} were analyzed.

5.3.4.4 Differential scanning calorimetry (DSC)

DSC (Q1000, TA Instrument) was conducted to analyze the thermal behavior of films under nitrogen atmosphere. Samples were heated from 40 °C to 160 °C to eliminate thermal history, at a heating rate of 10 °C/min. After isothermal equilibrium for 5 min, samples were cooled to 40 °C at a cooling rate of 10 °C/min and then were heated again to 160 °C at a heating rate of 10 °C/min.

5.3.4.5 Mechanical properties

The mechanical properties of the films were obtained by a universal testing machine (Bluehill Instron) with a sample strip width of 0.5 cm, a load cell 50 kgf, a gauge length of 50 mm, and a crosshead speed of 500 mm/min. Each film was tested ten times and all data including Young's modulus, tensile strength, and elongation at break were reported.

5.3.4.6 Gas barrier properties

The oxygen transmission rate (OTR) of LDPE-based films was measured using MOCON OX-TRAN Model 2/21 (Minneapolis, USA) at 23 °C, 0 % relative humidity, and 1 atm pressure. The water vapor transmission rate (WVTR) was tested via MOCON AQUATRAN Model 1 (Minneapolis, USA) at 38 °C, 90 % relative humidity, and 1 atm pressure. The units of OTR and WVTR were $\text{cc}/[\text{m}^2 \cdot \text{day}]$ and $\text{g}/[\text{m}^2 \cdot \text{day}]$ respectively.

5.3.4.7 Ethylene scavenging capacity

All LDPE-based films with the same thickness of nearly 60 μm were cut to a size of $5 \times 5 \text{ in}^2$. Subsequently, these films were placed in sealed containers with a volume of 1 L at 25 °C and 30 % relative humidity, followed by injecting 200 μL of ethylene with a syringe into the containers, and testing ethylene content each day through rubber stoppers using F-950 Three Gas Analyzer (Felix Instruments, USA). This analyzer has gas inlet and outlet connecting sampling probes. During detection, the gas in the headspace is pumped into the analyzer at a sampling flow rate of 70 mL/min and a sampling volume of 35 mL. After detection, the gas is pumped back to the

headspace to prevent vacuum from occurring. Finally, ethylene scavenging capacity was obtained by calculating the difference between the initial amount of ethylene and the remaining amount in containers, and the unit was expressed as $\mu\text{mol}/(25 \text{ in}^2)$.

5.3.4.8 Gas composition in packaging headspace and avocado firmness

Ethylene, O₂, and CO₂ concentrations were measured every two days by F-950 Three Gas Analyzer. According to the operating principles mentioned above, not only ethylene content could be obtained, but also CO₂ and O₂ content were obtained. Finally, ethylene concentration was expressed as $\mu\text{mol/L}$, while O₂ and CO₂ concentrations were converted to mmol/L .

Avocado flesh firmness was measured using GY series fruit penetrometer (Shanghai Jingsheng Scientific Instruments Corporation, China) with a probe of 3.5 mm in diameter. Five testing points for each avocado were randomly measured after avocados were cut open and the firmness unit was converted to N.

5.3.4.9 Statistical analysis

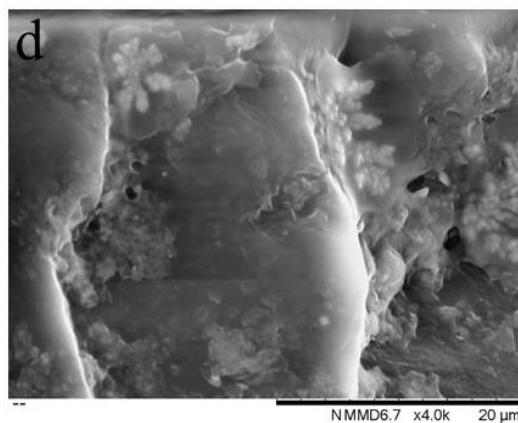
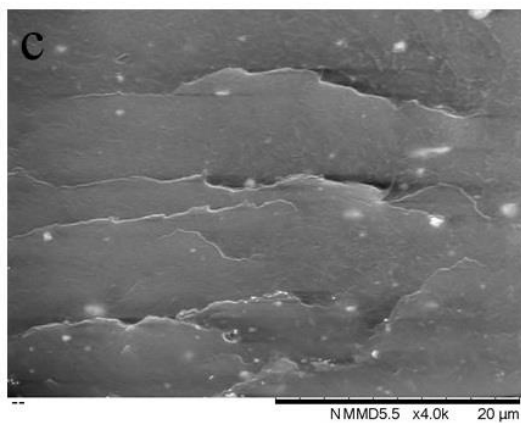
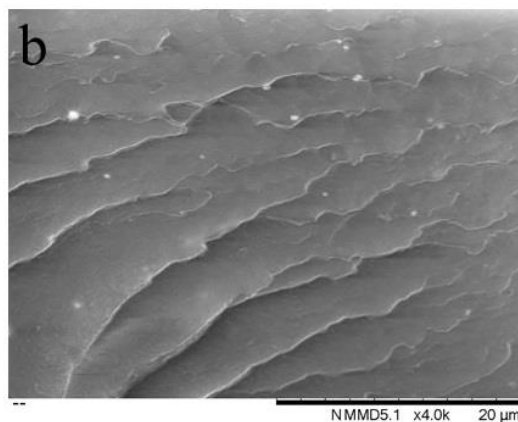
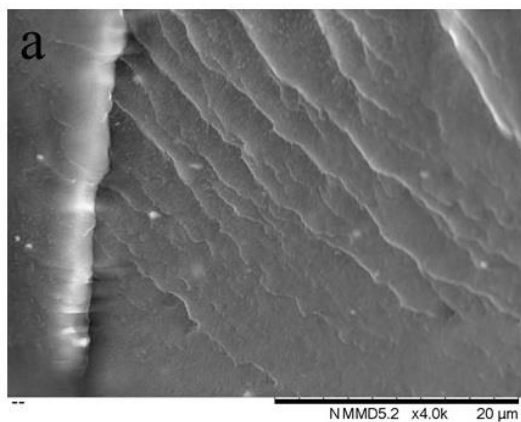
All experiments were carried out in three replicates and the statistical analysis of experimental data was performed using Minitab software (Minitab® 19 for windows, Minitab LLC, USA) according to one-way ANOVA with Tukey's test to ensure a significance level of $p \leq 0.05$. Graphs in this report were plotted in accordance with mean values and error bars were designed according to standard deviation.

5.4 Results and discussion

5.4.1 SEM and color analysis of films

Figure 5.1 shows SEM cross-sectional images and surface color of LDPE-based films containing different content of active agents. There was no obvious aggregation observed in the cross-section of films when 1 wt.% and 3 wt.% of active agents were incorporated, as presented in Figure 5.1 (a) and (b). This is because PE-g-MA, as compatibilizer, was added to facilitate dispersion of active agents in LDPE matrix [25, 26]. When 5 wt.% of active agents was added, aggregation, i.e., the larger particles, appeared as depicted in Figure 5.1 (c). Furthermore, Figure 5.1 (d) shows that clearly visible aggregation occurred in LDPE-10%PKM, even though PE-g-MA was also added,

illustrating excess active agents were not able to achieve homogeneous dispersion. Therefore, choosing the appropriate loading of active agents is of great importance during the process of melt blending because the degree of particle dispersion has a significant impact on the performance of extruded films, including thermal, mechanical, and gas barrier properties [27-29].



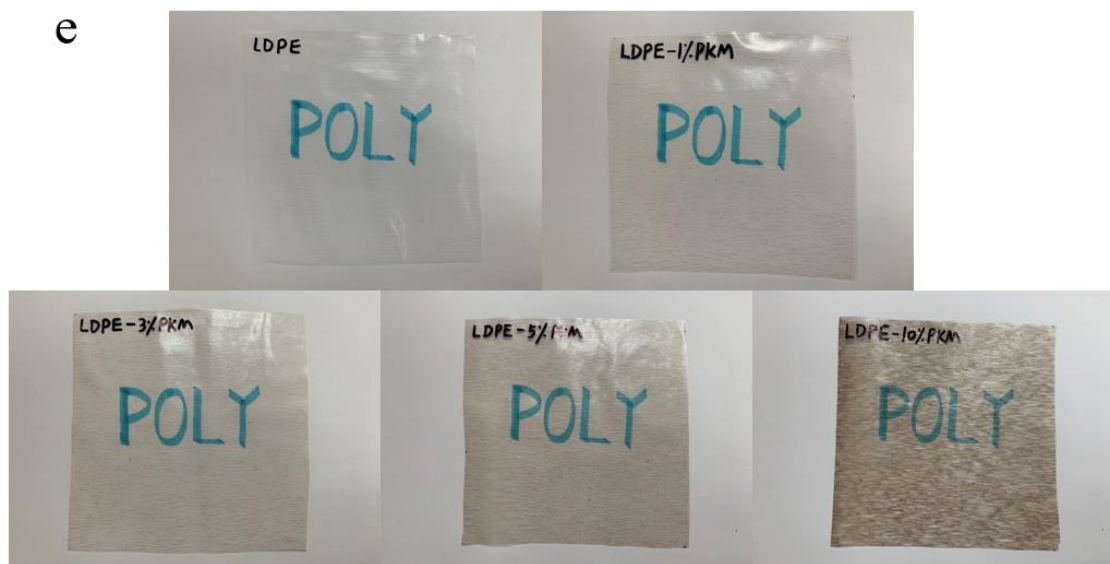


Figure 5.1 SEM cross-sectional images of LDPE-based films: (a) LDPE-1%PKM, (b) LDPE-3%PKM, (c) LDPE-5%PKM, and (d) LDPE-10%PKM; (e) photographs of films

The surface color of packaging films is an important marketing parameter, and it is usually preferable if one can see the food quality through packaging films. As shown in Figure 5.1 (e), pure LDPE film is transparent, and the active LDPE-based films gradually become rough and opaque with the content of active agents, which could be associated with their dispersion in the films as presented in Figure 5.1 (a) (b) (c) and (d). Therefore, the color difference (ΔE^*) between the films was more and more prominent as the loading of active agents increased [30, 31]. The ΔE^* based on reference was as follows, 5.30 for LDPE, 7.04 for LDPE-1%PKM, 9.54 for LDPE-3%PKM, 15.56 for LDPE-5%PKM, and 26.08 for LDPE-10%PKM. The other color indices are summarized in the supplemental information.

5.4.2 FTIR

In order to figure out the influence of the addition of active agents and PE-g-MA to LDPE, FTIR spectra of prepared LDPE-based films and the mixture of pumice and KMnO_4 , shown in Figure 5.2, were collected and analyzed. Regarding FTIR spectra of pure LDPE, five characteristic peaks were as follows, the peaks at 2850 and 2915 cm^{-1} were attributed to CH_2 asymmetric stretching, the peak at 1375 cm^{-1} was caused by CH_3 symmetric deformation, and the peaks at 1465 and 720 cm^{-1} were assigned to bending deformation and rocking deformation, respectively [32]. There was

a broad peak at 1030 cm^{-1} caused by stretching vibrations of O-Si-O bonds coming from pumice [33]. However, the absorbance peak moved to 1070 cm^{-1} when pumice was incorporated into films. This shift is interpreted as possibly the result of the interaction between the hydroxyl groups of pumice and the maleic anhydride groups of PE-g-MA [34]. The detail of the interaction is explained in the supplemental information. In addition, the peak of KMnO_4 at 900 cm^{-1} was not observed in the films [35, 36], because KMnO_4 content was too low.

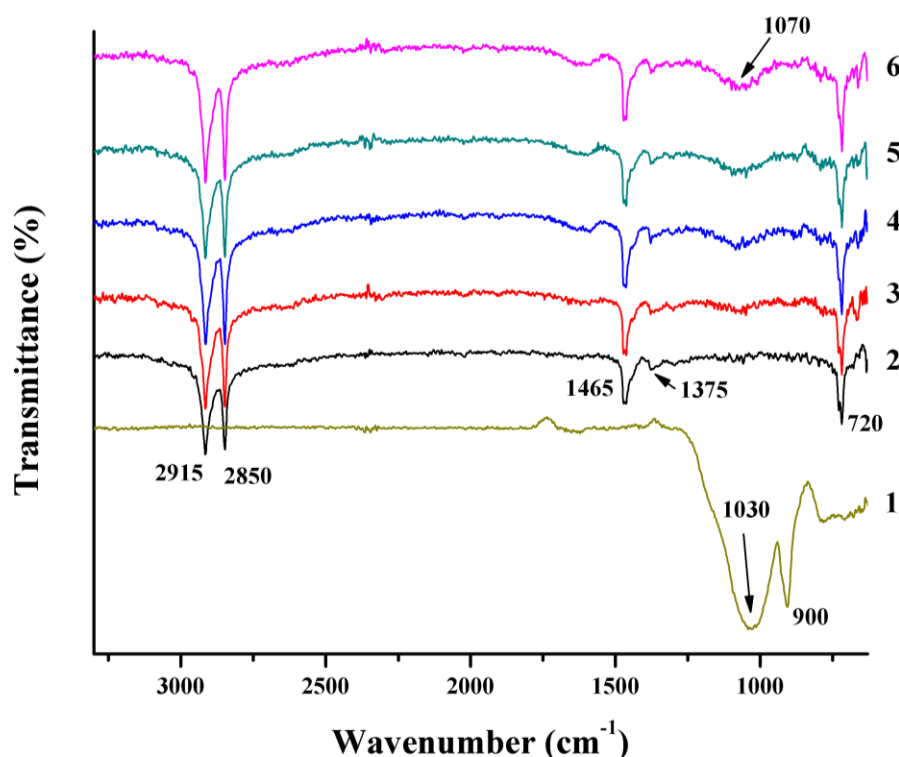


Figure 5.2 FTIR spectra of (1) mixture of pumice and KMnO_4 , (2) pure LDPE, (3) LDPE-1%PKM, (4) LDPE-3%PKM, (5) LDPE-5%PKM, and (6) LDPE-10%PKM

5.4.3 DSC

Melting temperature (T_m) and melting enthalpy (ΔH_m) of LDPE-based films were determined through DSC thermograms. Crystallinity (X_c) was calculated according to the equation, $X_c = \frac{\Delta H_m}{\Delta H_f^0} \times 100\%$ [17], where ΔH_f^0 is the heat of fusion taken as 293 J/g based on 100% crystalline LDPE [37]. The result in terms of T_m , ΔH_m , and X_c are summarized in Figure 5.3. T_m at a stable

value of 108 ~ 109 °C, was not influenced a lot after the addition of active agents. Compared with 61.4 J/g for pure LDPE, ΔH_m of LDPE-1%PKM increased to 66.6 J/g, and then ΔH_m was gradually reduced with the content increase of active agents. Correspondingly, X_c displayed the same trend, rising from 20.9 % for pure LDPE to the maximal value at 22.7 % for LDPE-1%PKM and then going down, which demonstrated that the loading of active agents had a direct effect on crystallinity degree. At lower loading (1 wt.% and 3 wt.%), the active agents acted as nucleating agents to induce crystallization of LDPE molecular chains due to uniform dispersion [29], however, the nucleating efficiency was diminished at higher loading (5 wt.% and 10 wt.%) because of particle aggregation [17].

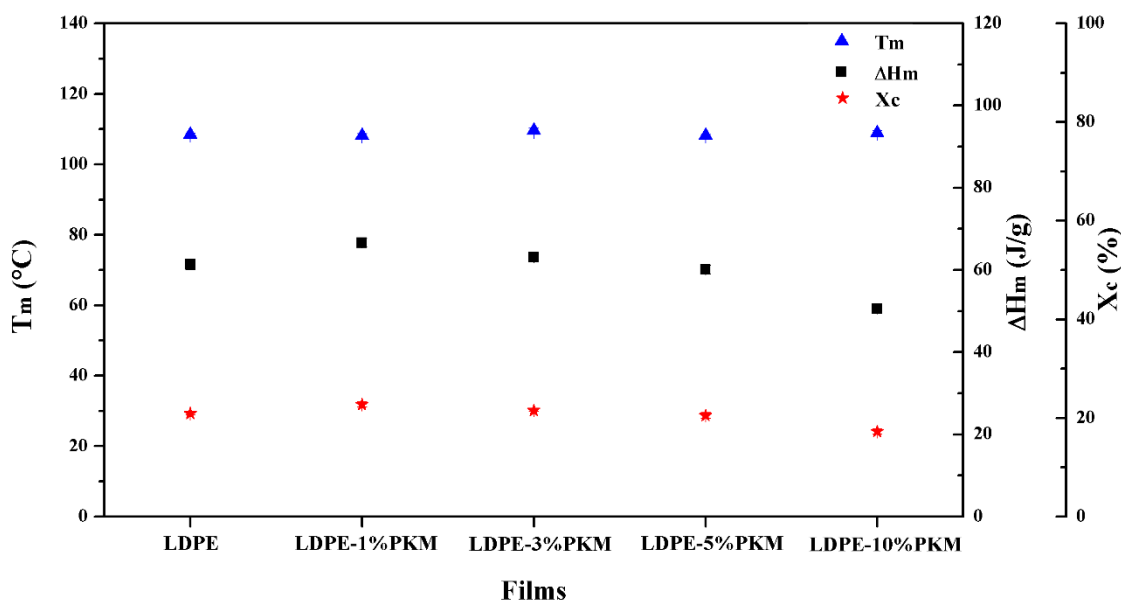


Figure 5.3 Summary of DSC results for LDPE-based films

5.4.4 Mechanical properties

Mechanical properties of LDPE-based films were characterized, and the results are shown in Figure 5.4. It is apparent that LDPE-3%PKM, compared with other films, exhibited optimum Young's modulus, tensile strength, and elongation at break, followed by LDPE-1%PKM, demonstrating that 1 wt.% and 3 wt.% of pumice and KMnO₄ improved mechanical performance of LDPE films. Relevant studies have reported that a small amount of clay additives with a good dispersion in polymer films could result in an enhancement of mechanical properties [38-40]. However,

mechanical performances were significantly diminished for LDPE-5%PKM and especially for LDPE-10%PKM because excess active agents led to poor dispersion and particle aggregation in the LDPE matrix as discussed above from the microscopy results.

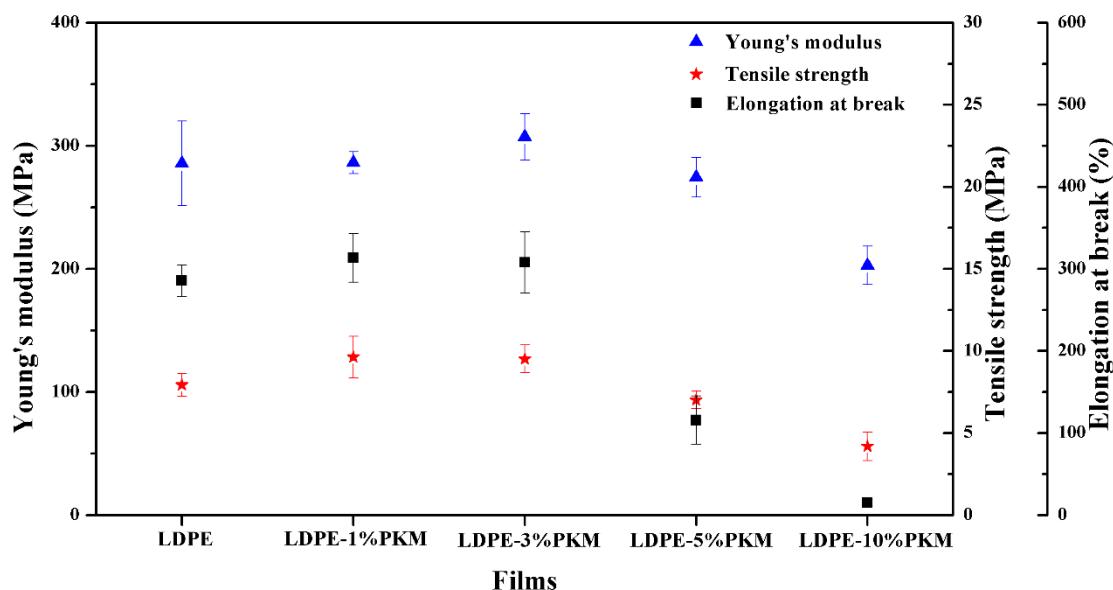


Figure 5.4 Summary of mechanical properties for LDPE-based films

5.4.5 Gas barrier properties

Gas barrier properties of the LDPE-based films were evaluated by detecting their OTR and WVTR and the results are presented in Figure 5.5. Throughout all LDPE-based films, it is obvious that LDPE-3%PKM possessed the lowest OTR (1465.58 cc/[m²·day]) and WVTR (24.31 g/[m²·day]), meaning the film incorporated with 3 wt.% active agents had better oxygen and water vapor barrier properties. Besides, the barrier performance of LDPE-1%PKM was slightly lower than that of LDPE-3%PKM, and a similar result was reported that 1 wt.% and 3 wt.% of alkaline halloysite nanotubes greatly enhanced the gas barrier properties of LDPE films [41]. This result was expected because the tortuous paths for gas diffusion in the LDPE matrix were formed due to well-dispersed pumice and KMnO₄ at lower loadings (1 wt.% and 3 wt.%) [42, 43]. On the contrary, higher loading of pumice and KMnO₄ resulted in the formation of aggregation, especially evident at 10 wt.% loadings, so that some voids may have been generated, leading to higher gas permeability and poor barrier performance [17, 29].

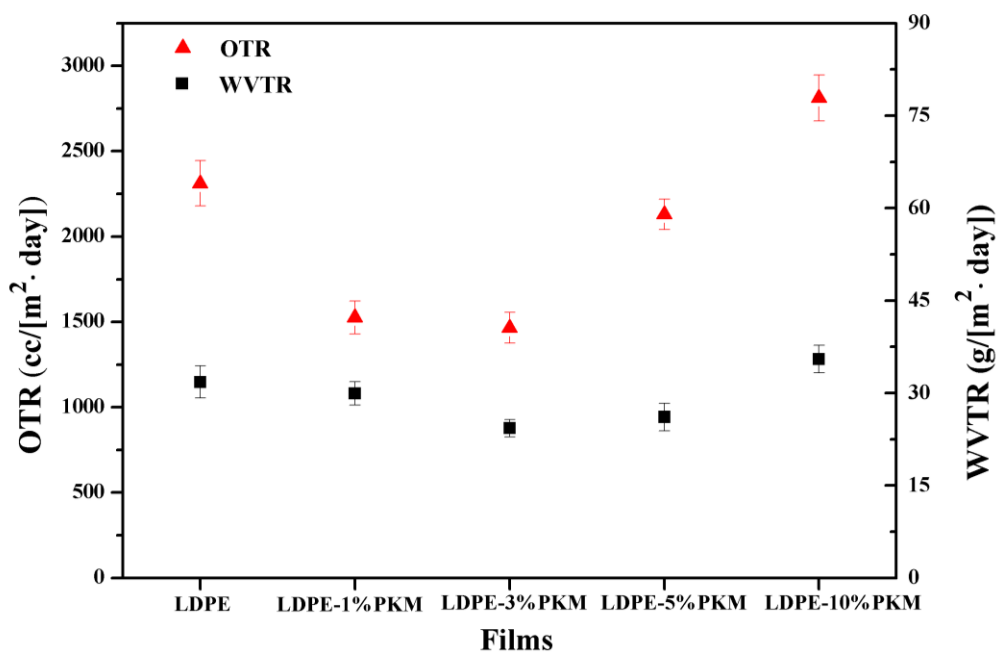


Figure 5.5 Summary of OTR and WVTR for LDPE-based films

5.4.6 Ethylene scavenging analysis

Figure 5.6 shows ethylene scavenging capacity results of LDPE-based films incorporating different contents of pumice and KMnO_4 within 12 d. According to those results, it can be concluded that the ethylene scavenging capacity of LDPE-based films is correlated to the content and the dispersion of active agents [17, 27]. In the case of little difference of dispersion, the content of active agents determined the ethylene scavenging capacity of films, so LDPE-3%PKM could scavenge more ethylene than LDPE-1%PKM, and the same for LDPE-5%PKM and LDPE-10%PKM, as can be observed in Figure 5.6. In addition, the ethylene scavenging capacity of LDPE-1%PKM and LDPE-3%PKM are superior to that of LDPE-5%PKM and LDPE-10%PKM, which should be caused by a uniform dispersion of low active agents loading and the particle aggregation of high loading. Taken together, 3 wt.% of active agents are the most beneficial to the films with regards to scavenging ethylene. During a period of 12 d, LDPE-3%PKM had a ethylene scavenging capacity of $7.31 \mu\text{mol}/(25 \text{ in}^2)$, followed by LDPE-1%PKM ($6.38 \mu\text{mol}/(25 \text{ in}^2)$), LDPE-10%PKM ($5.08 \mu\text{mol}/(25 \text{ in}^2)$) and LDPE-5%PKM ($4.78 \mu\text{mol}/(25 \text{ in}^2)$). The LDPE-based films could scavenge ethylene because the incorporation of active agents, of which pumice

physically adsorbed ethylene and KMnO_4 chemically oxidized ethylene [13]. The result indicates that the LDPE-3%PKM may serve as an ethylene scavenging film for fruit and vegetables.

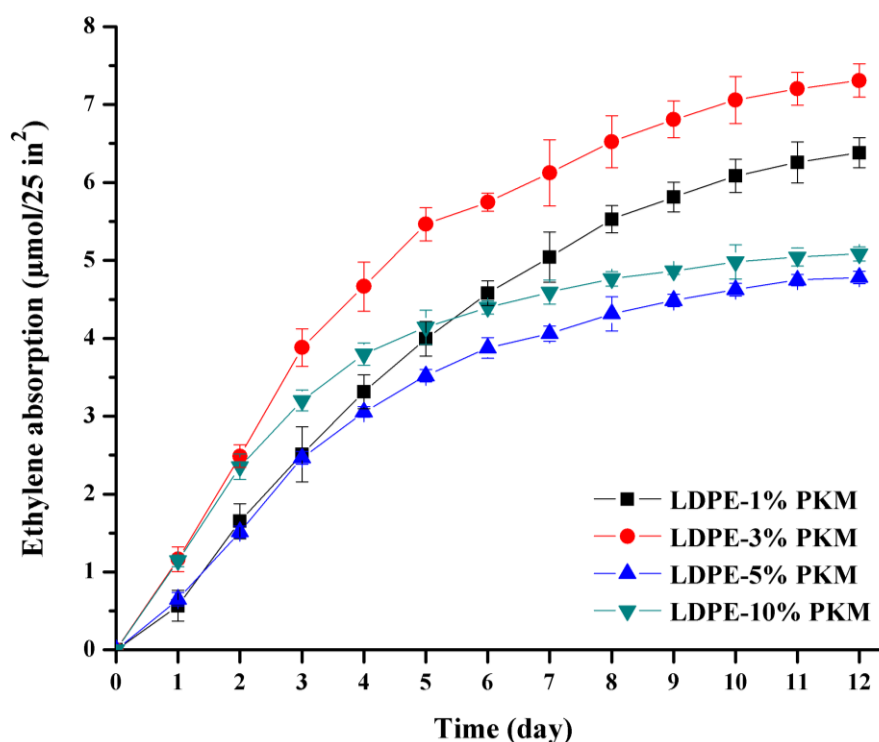


Figure 5.6 Ethylene scavenging capacity of LDPE-based films

5.4.7 Preservation of avocados through ethylene scavenging films

5.4.7.1 Gas composition in packaging headspace

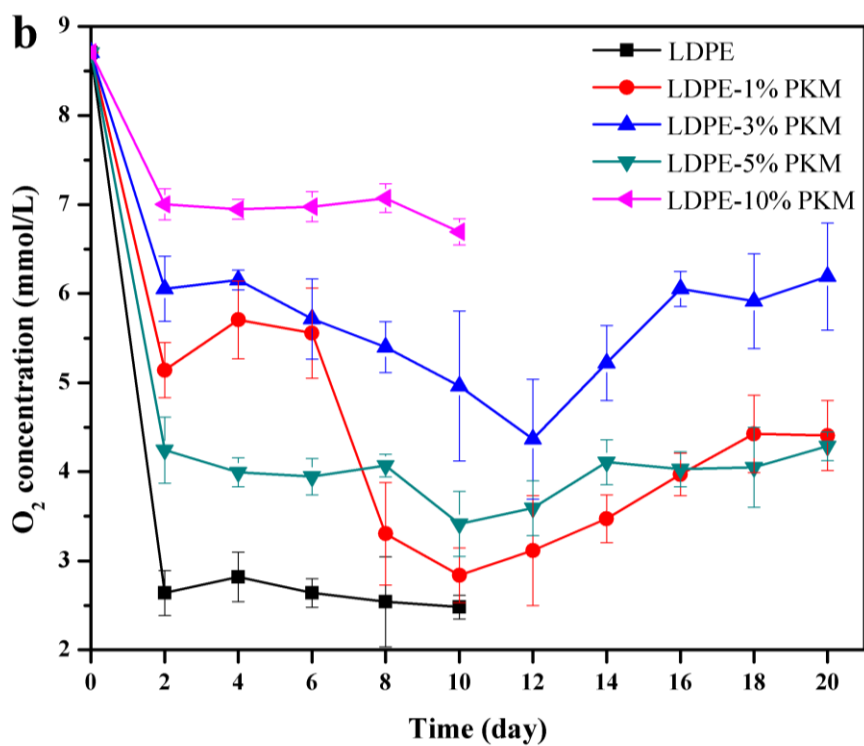
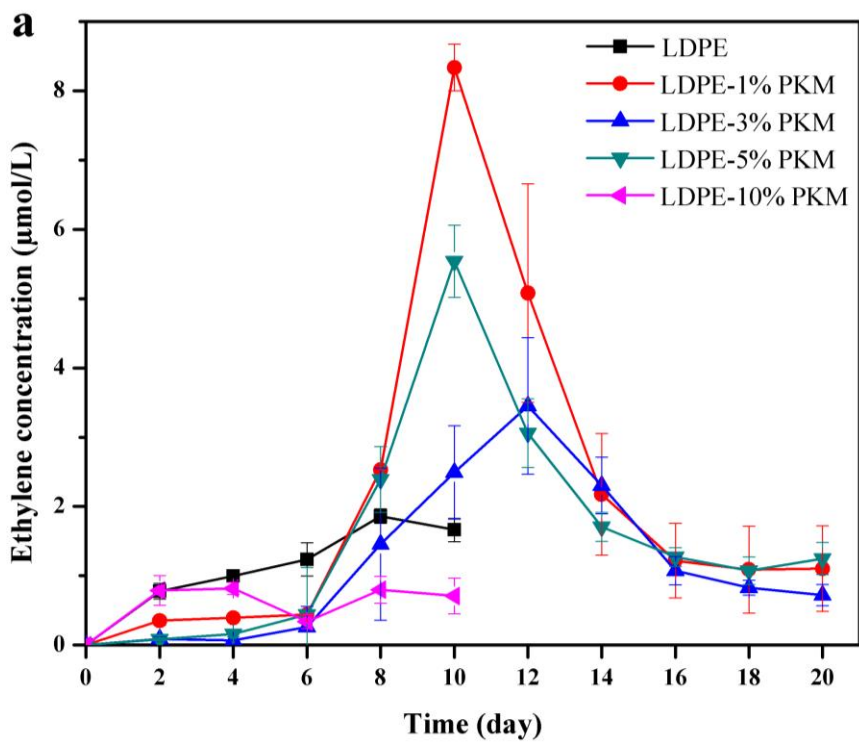
Gas composition is an important indicator to evaluate fruit status and three gases including ethylene, O_2 , and CO_2 are involved during their ripening process. Herein, ethylene, O_2 , and CO_2 concentrations in the packaging headspace, as shown in Figure 5.7 (a), (b), and (c), respectively.

In principle, avocado belongs to climacteric fruit meaning there is a climacteric stage for respiration rate and ethylene production rate [10, 44]. For LDPE-1%PKM and LDPE-5%PKM packaging, ethylene concentration gradually increased and quickly peaked at $8.33 \mu\text{mol/L}$ and $5.53 \mu\text{mol/L}$ respectively on the 10th d, and then decreased until spoilage. Although a similar trend was found for LDPE-3%PKM packaging, the period of ethylene concentration reaching the peak was

postponed to 12 d and the value was 3.44 $\mu\text{mol/L}$. In addition, the ethylene concentration in the packaging headspace of LDPE and LDPE-10%PKM did not show significant fluctuation over time as can be observed in Figure 5.7 (a). Their gas composition detection continued for 10 d but were spoiled after. By comparison, LDPE-3%PKM demonstrated a better performance controlling ethylene concentration due to its excellent ethylene scavenging property.

The changes of O_2 and CO_2 concentrations are reversed because CO_2 is produced when O_2 is consumed, as can be seen in Figure 5.7 (b) and (c). As control, O_2 concentration in the packaging headspace of LDPE was kept at a low level around 2.63 mmol/L while CO_2 concentration was high, increasing from 4.90 mmol/L to 6.28 mmol/L. As for LDPE-10%PKM, the poor gas barrier resulted in strong gas exchange between packaging headspace and surrounding atmosphere so that a high O_2 concentration (nearly 7.07 mmol/L) and a low CO_2 concentration (below 1.99 mmol/L) were measured. In LDPE-1%PKM packaging, O_2 concentration significantly decreased to 2.83 mmol/L and CO_2 concentration rapidly increased to 6.67 mmol/L on the 10th d, whereas the corresponding value was 3.41 mmol/L and 4.86 mmol/L in LDPE-5%PKM packaging. Nonetheless, the minimal O_2 concentration and maximal CO_2 concentration were detected on the 12th d in LDPE-3%PKM packaging, at 4.36 mmol/L and 4.05 mmol/L, respectively.

According to the analysis above, a loading of 3 wt.% active agents was the most favorable for the control of gas composition owing to good ethylene scavenging property and excellent gas barrier performance. Moreover, LDPE-3%PKM delayed the arrival of the peak for each gas composition to 12 d illustrating it effectively postponed the climacteric stage. In addition, the changing trend of gas composition shown in Figure 5.7 (a), (b), and (c) demonstrated that ethylene, O_2 , and CO_2 concentrations are interconnected because ethylene was a product of metabolism during fruit respiration.



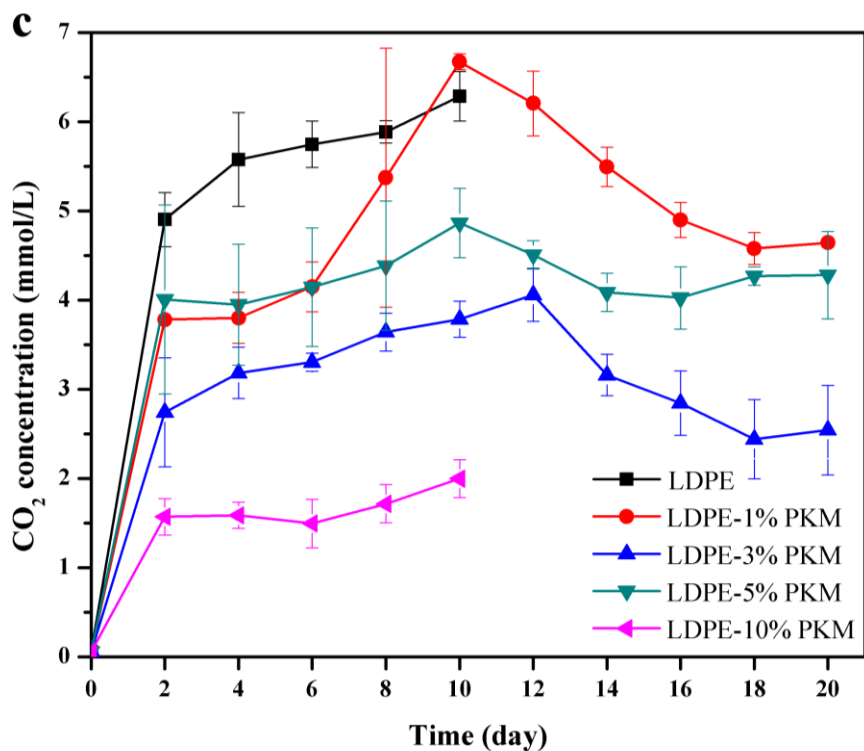
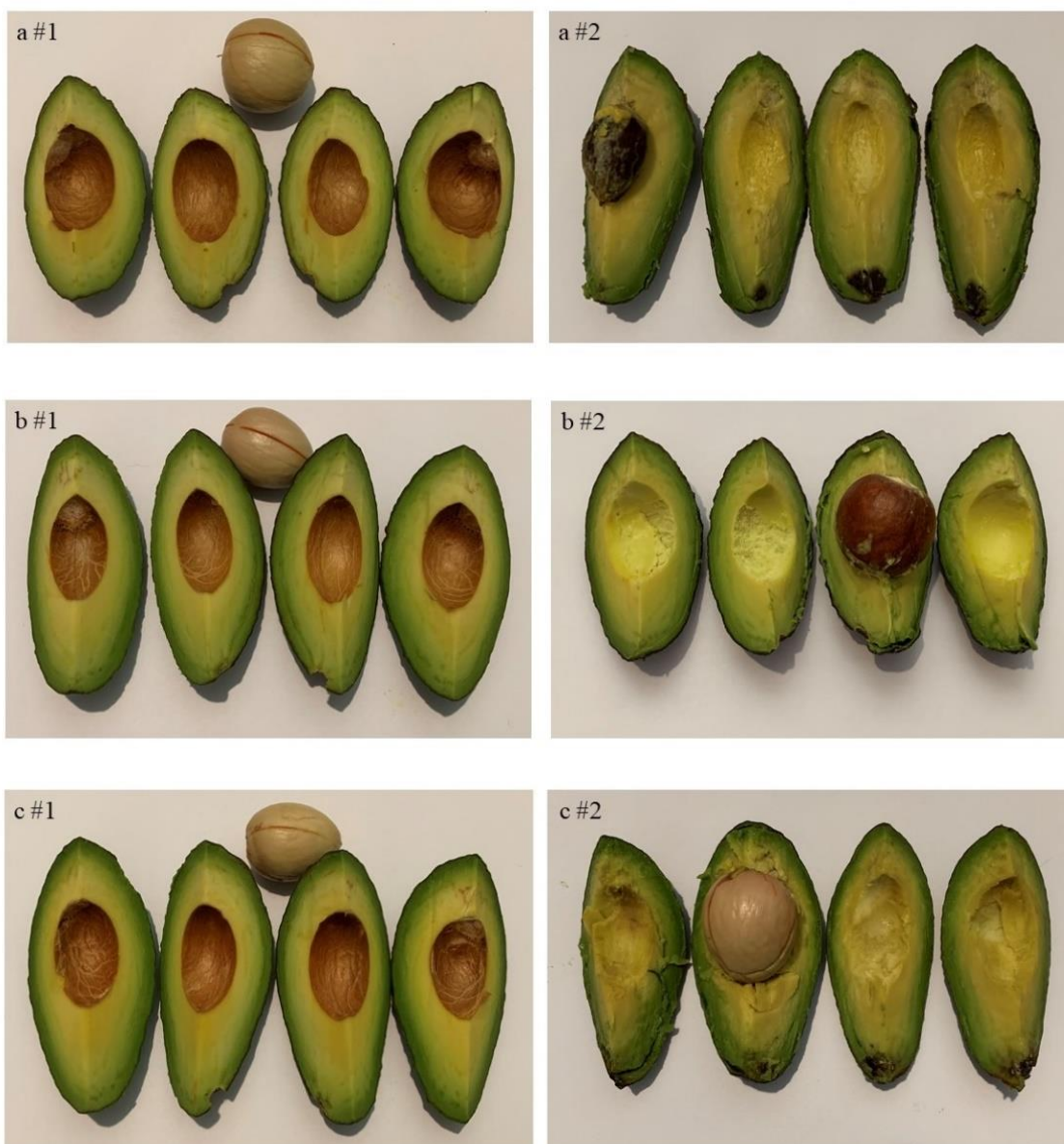


Figure 5.7 Gas composition (a: ethylene, b: O₂, c: CO₂) in packaging headspace at 25 °C up to 20 d

5.4.7.2 Shelf life and firmness of avocados

The shelf life of avocados was determined by inner appearance and flesh firmness. It is apparent that avocados packaged with LDPE-10%PKM and LDPE were spoiled after 10 d of preservation according to the inner appearance in Figure 5.8 (d #1) and (e #1). In contrast, the inner appearance as is shown in Figure 5.8 (a #1) (b #1) and (c #1) demonstrated that avocados packaged by LDPE-1%PKM, LDPE-3%PKM, and LDPE-5%PKM for 10 d were still in good condition. It can be attributed that LDPE could not scavenge ethylene produced by avocado, while LDPE-10%PKM had poor gas barrier performance, meaning gas exchange between packaging headspace and atmosphere was uncontrolled and the respiration of avocado happened as under normal conditions. However, LDPE-1%PKM, LDPE-3%PKM, and LDPE-5%PKM not only scavenged ethylene but also had good gas barrier performance, which ensured avocados were well preserved. Undoubtedly, LDPE-10%PKM and LDPE were not able to protect avocado for 20 d as can be observed in Figure 5.8 (d #2) and (e #2). On the 20th d, black spots appeared on the bottom of flesh for avocados

packaged with LDPE-1%PKM and LDPE-5%PKM as is presented in Figure 5.8 (a #2) and (c #2), nevertheless, inner appearance was free of defects regarding the avocado packaged with LDPE-3%PKM as can be seen in Figure 5.8 (b #2). On the one hand, LDPE-3%PKM showed the best gas barrier properties among all films, on the other, its ethylene scavenging capacity was superior. Overall, both gas barrier properties and ethylene scavenging capacity of LDPE-based films should be taken into consideration regarding packaging avocados.



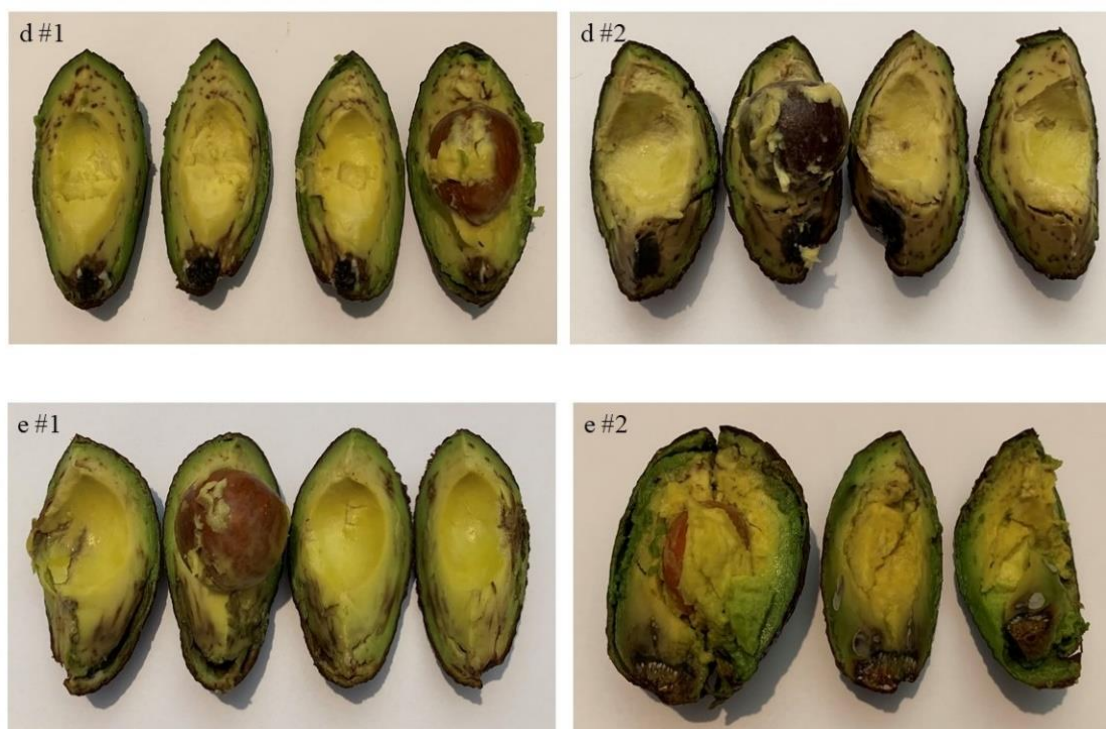


Figure 5.8 Inner appearance of avocados packaged with (a) LDPE-1%PKM, (b) LDPE-3%PKM, (c) LDPE-5%PKM, (d) LDPE-10%PKM and (e) LDPE films (#1: preservation for 10 d, #2: preservation for 20 d)

Besides, flesh firmness, summarized in Figure 5.9, can partly reflect whether avocados are spoiled or not [24, 45], because the firmness gradually decreased from unripe period to decay. The flesh firmness was approximately 0.50 N for avocados packaged with LDPE and LDPE-10%PKM for 10 d. For those packaged by LDPE-1%PKM, LDPE-3%PKM, and LDPE-5%PKM, their flesh firmness was 5.56 N, 5.69 N, and 5.52 N respectively after 10 d of preservation, which decreased by 63.6 %, 61.4 %, and 62.5 %, respectively, 20 d later. In combination with inner appearance and flesh firmness, LDPE-10%PKM and LDPE were not appropriate to preserve avocados, while LDPE-1%PKM and LDPE-5%PKM could preserve avocados at least 10 d but less than 20 d. The optimum film was LDPE-3%PKM which extended the shelf life of avocados to 20 d or more.

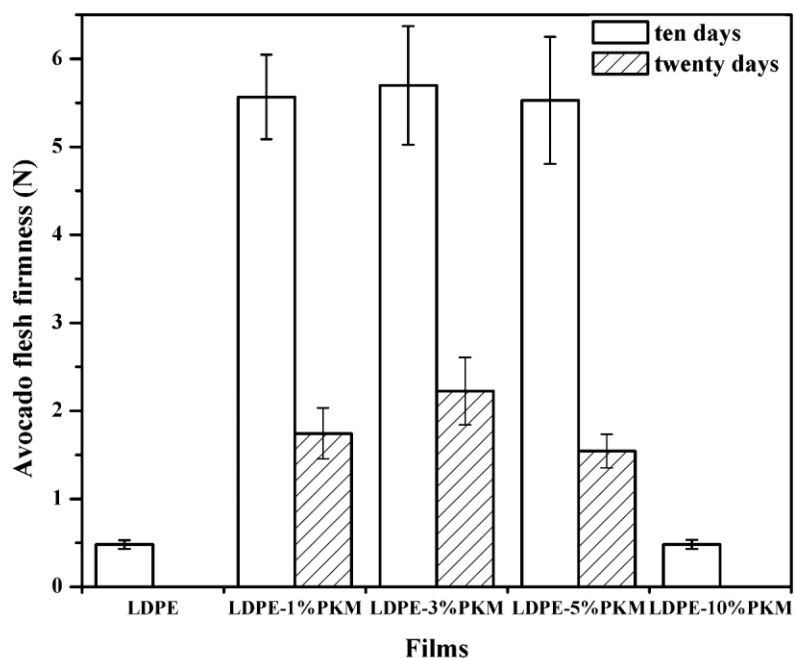


Figure 5.9 Flesh firmness of avocados packaged with LDPE-based films for 10 d and 20 d

5.5 Conclusion

An ethylene scavenging film containing LDPE as matrix and the mixture of pumice and KMnO_4 as active agents was prepared to extend the shelf life of fruit and vegetables. A low loading (1 wt.% and 3 wt.%) of active agents could disperse uniformly within LDPE matrix with the aid of PE-g-MA, resulting in improved performances in terms of thermal, mechanical, and gas barrier properties. Moreover, LDPE-3%PKM showed superior ethylene scavenging performance compared with other films. Hence, the preservation of fruit and vegetables by scavenging ethylene could be achieved through LDPE-3%PKM, showing that it extended the shelf life of avocados to 20 d, controlled ethylene and CO_2 concentrations in the packaging headspace, and reduced the flesh firmness loss. LDPE-based films incorporating pumice and KMnO_4 have a promising prospect for applications as active packaging, and further research is needed to assess safety during the actual application.

CRediT authorship contribution statement

Chunyu Wang: Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Roles/Writing – original draft. Abdellah Ajji: Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

5.6 Acknowledgements

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5.8 Supporting information

Ethylene scavenging film based on low-density polyethylene incorporating pumice and potassium permanganate and its application to preserve avocados

Chunyu Wang, Abdellah Ajjj*

3SPack, Research Center for High Performance Polymer and Composite Systems (CREPEC), Chemical Engineering Department, Polytechnique Montréal, Montréal, Québec, H3C 3A7, Canada

* Corresponding author

E-mail addresses: chunyu.wang@polymtl.ca (C. Wang), abdellah.ajji@polymtl.ca (A. Ajjj).

Figure S5.1 is a simple packaging illustration. For each LDPE-based film, two replicates were prepared. For example, one avocado was packaged by LDPE-3%PKM named #1, and another avocado was packaged by LDPE-3%PKM named #2. The avocado #1 was cut to observe its inner appearance on the 10th d, but the avocado #2 was carried on the 20th d.

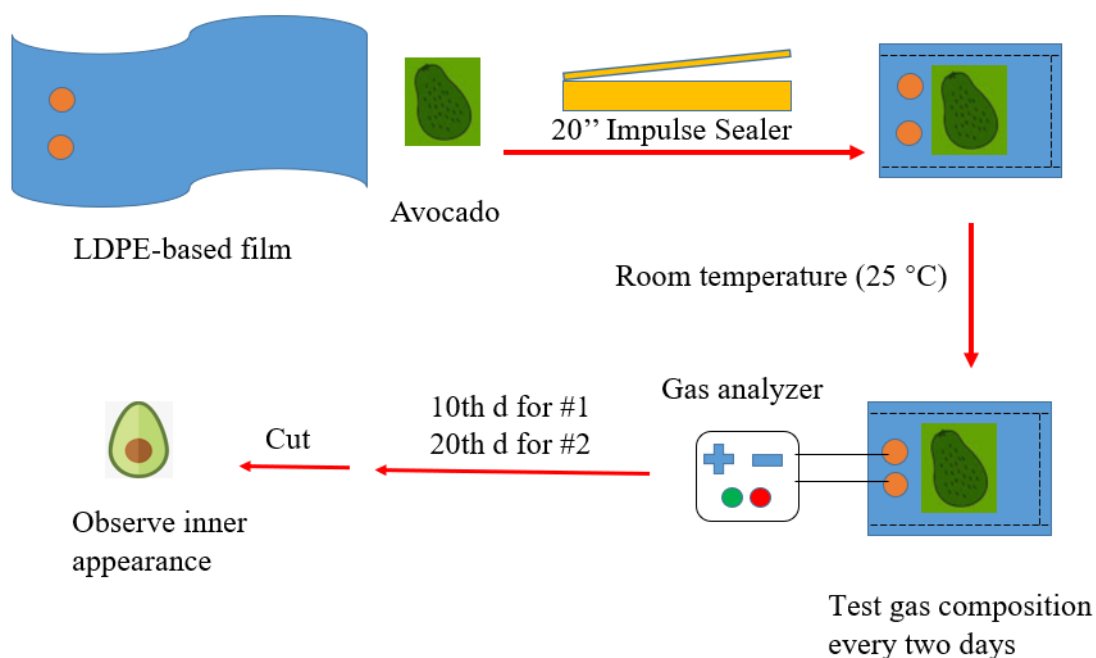


Figure S5.1 The experimental process of packaging avocados

The color index was expressed as mean value \pm standard deviation, and the color difference (ΔE^*) was calculated based on the reference ($L^* = 91.76$, $a^* = -1.20$, $b^* = -1.86$). The following table concluded the surface color index of all films. The incorporation of active agents made the surface

of LDPE film rough and opaque, so the lightness (L^*) of films decreased with the content of active agents increasing. When the loading of active agents was low (1 wt.% and 3 wt.%), L^* had a small decrease compared to LDPE film, but a higher loading (5 wt.% and 10 wt.%) led to a significant decrease of L^* . In addition, the increasing a^* and b^* meant more redness and yellowness were displayed. Overall, ΔE^* increased with the content of active agents increasing.

Table S5.1 Surface color index of LDPE-based films

Samples	L^*	a^*	b^*	ΔE^*
LDPE	86.46 ± 0.90	-1.26 ± 0.10	-1.93 ± 0.16	5.30 ± 0.57
LDPE-1%PKM	85.13 ± 0.75	-0.86 ± 0.07	0.50 ± 0.01	7.04 ± 0.40
LDPE-3%PKM	82.73 ± 0.83	-0.53 ± 0.06	1.13 ± 0.07	9.54 ± 0.48
LDPE-5%PKM	77.36 ± 1.33	0.60 ± 0.01	3.76 ± 0.13	15.56 ± 0.99
LDPE-10%PKM	67.66 ± 1.90	2.06 ± 0.17	7.56 ± 0.12	26.08 ± 1.56

According to the study about PP-g-MA and silica nanoparticles [1], the interaction between PE-g-MA and pumice is illustrated as the following Fig.S2. There are many hydroxyl groups on the surface of pumice [2], which can react with the maleic anhydride groups of PE-g-MA. Once bound on PE-g-MA, the dispersion of pumice in the LDPE film will be significantly improved, as can be observed in SEM images. Therefore, a small amount of active agents could improve the thermal, mechanical and gas barrier properties.

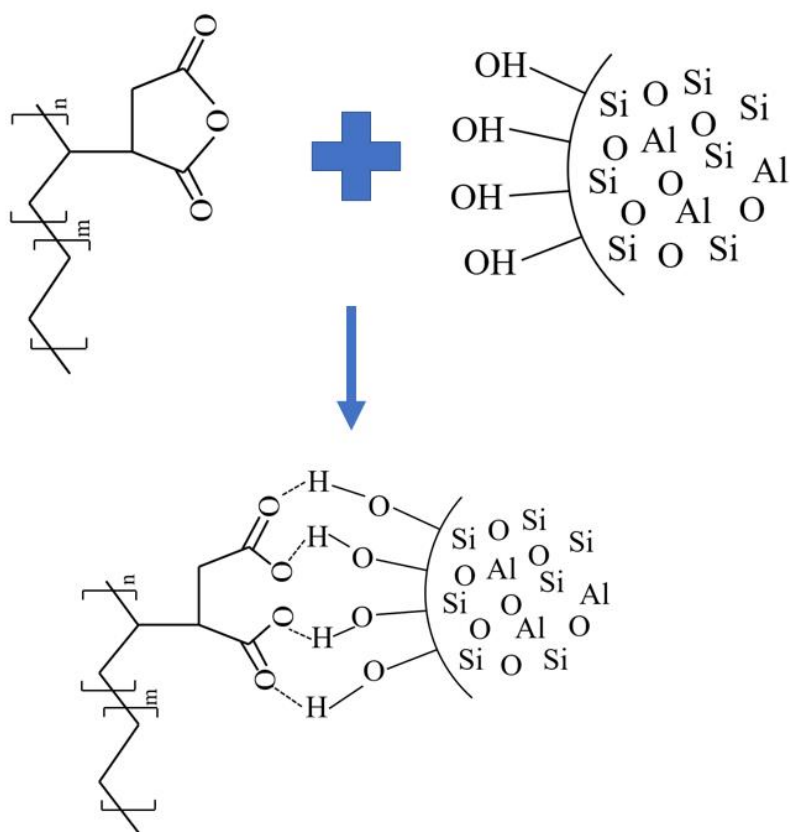


Figure S5.2 The interaction between PE-g-MA and pumice

Supporting references:

- [1] D. N. Bikiaris, A. Vassiliou, E. Pavlidou, and G. P. Karayannidis, "Compatibilisation effect of PP-g-MA copolymer on iPP/SiO₂ nanocomposites prepared by melt mixing," *European Polymer Journal*, vol. 41, no. 9, pp. 1965-1978, 2005, doi: 10.1016/j.eurpolymj.2005.03.008.
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CHAPTER 6 ARTICLE 3 : DEVELOPMENT AND APPLICATION OF LDPE-BASED MULTILAYER FILM INCORPORATING KMNO₄ AND PUMICE FOR AVOCADO PRESERVATION

Chunyu Wang, Abdellah Ajjj*

3SPack, Research Center for High Performance Polymer and Composite Systems (CREPEC),
Chemical Engineering Department, Polytechnique Montréal, Montréal, Québec, H3C 3A7, Canada

* Corresponding author

E-mail addresses: chunyu.wang@polymtl.ca (C. Wang), abdellah.ajji@polymtl.ca (A. Ajjj).

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6.1 Abstract

This study aimed to develop a low-density polyethylene based multilayer active packaging film with three layers. The core layer was an active layer containing pumice and potassium permanganate, while the skin layer was the barrier layer impregnated with sodium chloride. The multilayer film showed an ethylene scavenging capacity of 1.6 $\mu\text{mol}/(25 \text{ in}^2)$ within 8 d at 25 °C and was endowed with water absorption capacity. In addition, the oxygen and water vapor permeability of the multilayer film were improved in comparison to the neat one. Further, the multilayer film extended the shelf life of avocado from less than 10 d to 16 d at 25 °C, controlled ethylene and carbon dioxide concentrations, and caused a reduction in the loss of flesh firmness and weight. More importantly, according to migration testing, active agents in the core layer would not migrate to avocado peel, which ensured that avocados would not be contaminated.

Keywords: multilayer film, potassium permanganate, ethylene scavenging, avocados, migration testing

6.2 Introduction

Avocados are a very popular fruit all over the world and avocado-producing countries such as Mexico and Peru produce and export millions of tons of avocados every year [1, 2], but their perishable feature with a short shelf life is the most challenging problem to tackle. Nowadays, cold storage is the most widely adopted method to preserve avocados during the transportation process after harvest [2]. Nevertheless, cold storage may lead to chilling injury of avocados and the risk increases with the extension of cold storage time [3, 4]. In addition, it is not realistic to always preserve avocados through cold storage, especially when they are sold at grocery stores and fruit markets or brought to home kitchens. Hence, the investigation on the preservation of avocados at room temperature is of great significance. As a climacteric tropic fruit, the ripeness and senescence of avocados are closely affected by ethylene and respiration rate [2, 5]. Thus, active food packaging is a possible method that can be used to extend the shelf life of avocados by removing ethylene and adjusting gas composition in the packaging headspace [6]. In general, the avocado quality is associated with the level of ripeness (firmness) and inner defects (browning or bruising) [7, 8], so one can make a judgement of the quality by means of flesh appearance and firmness. In the past few years, active packaging films applied to maintain food quality were attracting more and more attention [6, 9-11].

To equip active packaging film with ethylene absorption property, active agents that can scavenge ethylene, play an essential role. On the one hand, porous materials such as zeolite and halloysite with high specific surface area and sufficient adsorption sites could serve as active agents incorporated into low-density polyethylene (LDPE) to prepare active packaging films [12, 13]. On the other, potassium permanganate (KMnO_4) is a well-known active agent that can oxidize ethylene to water and carbon dioxide [14, 15]. More recently, active packaging films containing both porous materials and KMnO_4 as synergistic active agents has already been investigated to preserve fruit and vegetables. [16, 17]. Pumice is a volcanic rock with a porous structure, and it is a potential material in the field of active packaging due to its good adsorption capacity, low cost, easy availability, and eco-friendly merits [18, 19]. In our past study, pumice has been successfully employed in combination with KMnO_4 as the ethylene scavenger to extend the shelf life of avocados [20]. In addition, sodium chloride (NaCl) is deliquescent salt with humidity regulating

property and can be applied as an additive in packaging films to protect fruit and vegetables by absorbing and desorbing water vapor depending on equilibrium relative humidity [21, 22].

Although active packaging films could extend the shelf life of fruit and vegetables, potential safety hazard exists. In brief, films are in direct contact with food, so active agents may migrate to food surface and cause food contamination [23-25]. Then, it may cause health issues if the contaminated food is ingested and digested. To prevent the migration of active agents, multilayer packaging technology is a promising method, in which a barrier layer can be employed to isolate food from the active layer containing active agents. This method has been declared to be feasible in Regulation 450/2009/EC published by the Official Journal of the European Union [24].

This study was to develop a LDPE-based multilayer film to preserve avocados. The multilayer film had three layers, i.e., one core layer sandwiched by two skin layers. Pumice and KMnO_4 acted as active agents embedded in the core layer, while NaCl was incorporated into skin layers. The cross-section structure, thermal property, mechanical property, gas permeability, ethylene scavenging capacity, and water absorption capacity of the multilayer film were characterized. As for avocado preservation, gas composition in the packaging headspace, the inner appearance, flesh firmness and weight loss of avocados, and migration testing of active agents were analyzed. To our knowledge, no such research about multilayer film containing pumice and KMnO_4 as active agents was performed before.

6.3 Experimental

6.3.1 Materials

Low-density polyethylene (LDPE, NOVAPOL® LF-0219-A, density (23 °C): 0.918 g/cm³, melt index (190 °C/2.16 kg): 2.3 g/10 min) was acquired from Nova Chemical Corporation, Alberta, Canada. Pumice (2 ~ 45 μm) was purchased from Hess Pumice Company, Idaho, USA. Potassium permanganate (KMnO_4) was obtained from Thermo Fisher Scientific, Canada. Polyethylene grafted maleic anhydride (PE-g-MA, BYNELTM 4206, density (23 °C): 0.92 g/cm³, melt index (190 °C/2.16 kg): 2.5 g/10 min) was supplied by Dow Chemical Company, Ontario, Canada. Sodium chloride (NaCl) was purchased from a supermarket. Nitric acid (HNO_3 , 70 %, trace metal basis) was purchased from Sigma-Aldrich. Avocados (Delicia avocado, Mexico) without visual

defects were collected from Walmart supermarket and selected to ensure uniformity in terms of shape and weight (180 ± 10 g). In addition, avocados used in the experiment should have the following features, hard texture when squeezing, tough mouthfeel, green flesh, and unripe odor [26].

6.3.2 Sample preparation

Pumice powder, with particle size in the range of $2 \sim 5$ μm , was obtained by a mesh sieve (opening: 2500) with 5 μm pores. Then pumice and KMnO_4 were mixed according to a weight ratio of 10 to 1 [20], and subsequently ground by a grinding ball mill (SPEX Sample Prep 8000 Series Mixer) for at least 30 min until uniformity.

Masterbatch pellets were prepared using a twin-screw extruder (Leistritz Extrusionstechnik GmbH, ZSE18HP-40D, screw diameter: 18mm) with a pelletizing die by melting blending LDPE (matrix), 9 wt.% PE-g-MA (compatibilizer) and 9 wt.% active agents (pumice and KMnO_4). The extruding process was operated at a temperature profile of $150 \sim 170$ $^\circ\text{C}$ and a screw speed of $40 \sim 50$ rpm. In addition, another masterbatch was prepared under the same extruding condition, composed of LDPE, 9 wt.% PE-g-MA and 9 wt.% NaCl.

A lab-scale Multilayer-Layer Blown Film Extrusion Line (Labtech Engineering Co., Ltd, LF-400-COEX) was utilized to produce multilayer films by diluting masterbatch with pure LDPE pellets, where two single screw extruders having a screw diameter of 20 mm and L/D of 30 were used. The temperature profile and screw speed were set at $160 \sim 170$ $^\circ\text{C}$ and 40 rpm respectively. The thickness of the films was controlled at $60 \sim 80$ μm by adjusting the speeds of nips, windup rollers, and the blow-up ratio. The multilayer film has a three-layer structure in which a core layer is sandwiched between two skin layers. Herein, three multilayer films were prepared, LDPE-AA/LDPE, LDPE-AA/LDPE-NaCl, and LDPE/LDPE (control), whose compositions of the core and skin layers are presented in Table 6.1.

Table 6.1 Multilayer films and their compositions

Multilayer film sample	Core layer	Skin layer
LDPE/LDPE	LDPE	LDPE

LDPE-AA/LDPE	LDPE, 3 wt.% PE-g-MA, 3 wt.% active agents (weight ratio of pumice and KMnO ₄ : 10 to 1)	LDPE
LDPE-AA/LDPE-NaCl	LDPE, 3 wt.% PE-g-MA, 3 wt.% active agents (weight ratio of pumice and KMnO ₄ : 10 to 1)	LDPE, 3 wt.% PE-g-MA, 3 wt.% NaCl

6.3.3 Characterization of multilayer films

6.3.3.1 Scanning Electron Microscopy (SEM) and surface color

After cryo-fractured treatment, the cross-section structure of multilayer films was observed through SEM (Hitachi TM3030Plus equipment) under an electron voltage of 15 kV. Samples were treated with liquid nitrogen for 15 min and then snapped before SEM observation.

CR20 Colorimeter (Hangzhou CHNSpec Technology co. ltd, China) was used to test the surface color of multilayer films by means of a measuring aperture of 4 mm in diameter. The parameters of L*, a*, and b* represent lightness, redness/greenness, and yellowness/blueness respectively. Herein, all samples were placed upon a white plate to test color parameters and the white plate (L* = 91.8, a* = -1.2, b* = -1.9) served as the reference to compare the color change of films. The color difference (ΔE^*) was calculated using the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Where $\Delta L^* = L^* \text{ reference} - L^* \text{ test sample}$, $\Delta a^* = a^* \text{ reference} - a^* \text{ test sample}$, $\Delta b^* = b^* \text{ reference} - b^* \text{ test sample}$.

6.3.3.2 Differential scanning calorimetry (DSC) and mechanical properties

DSC (Q1000, TA Instrument) was used to measure the melting point, melting enthalpy, and crystallinity degree of the multilayer films. DSC experimental procedures were set as follows, the temperature was first increased from 40 °C to 160 °C at a heating rate of 10 °C/min to eliminate previous history, then it was decreased to 40 °C at a cooling rate of 10 °C/min, and finally increased again to 160 °C/min at the same heating rate.

A universal testing machine (Bluehill Instron) was used to measure the mechanical properties of the multilayer films, including Young's modulus, tensile strength, and elongation at break. All samples were cut into strips of 0.5 cm in width. Other parameters were set as follows, a gauge length of 5 cm, a crosshead speed of 500 mm/min, and a load cell of 50 kgf. Each multilayer film was tested ten times.

6.3.3.3 Gas barrier properties

The oxygen permeability (OP) of the multilayer films was analyzed by MOCON OX-TRAN Model 2/21 (Minneapolis, USA) at 23 °C, 1 atm pressure, and 0 % relative humidity. The water vapor permeability (WVP) was measured using MOCON AQUATRAN Model 1 (Minneapolis, USA) at 38 °C, 1 atm pressure, and 99 % relative humidity. The units of OP and WVP were expressed as cc·mil/m²·day·atm and g·mil/m²·day·atm respectively.

6.3.3.4 Ethylene and water absorption capacities

The multilayer films were cut into 5 × 5 in² sizes, then placed in a sealed container with 1 L of volume. Then, 50 μL of ethylene was injected into the container through a rubber stopper with the aid of a syringe and stored at 25 °C and 30 % relative humidity for ethylene scavenging analysis. The ethylene concentration in the headspace of the container was measured each day utilizing F-950 Three Gas Analyzer (Felix Instruments, USA) with the ethylene detection range of 0-200 ppm, whose operating principle was explained in section 6.3.4.1. The ethylene scavenging capacity (%) of multilayer films was calculated by the following equation:

$$\text{Ethylene scavenging capacity (\%)} = \frac{\text{initial concentration} - \text{remaining concentration}}{\text{initial concentration}} \times 100$$

As for water absorption capacity, the multilayer films were cut into 5 × 5 in² sizes, then weighed with a weighing balance before being placed in a sealed container with 1 L of volume at 25 °C, where a small vial full of distilled water to create an environment of high relative humidity (99 %) [22] was put inside in advance. The films were taken out two weeks later and weighed immediately. Water absorption capacity was obtained by calculating the weight difference of film on the first day and the last day, divided by film area, and the unit was expressed as mg/(25 in²).

6.3.4 Avocado preservation with multilayer films

Avocados (weight: 180 ± 10 g) were packaged using multilayer films that were cut into 20×8 in² sizes and sealed with the aid of a 20'' Impulse Sealer, and then these sealed packages were placed under the lab environment at 25 °C and relative humidity at 30%. Each multilayer film was prepared as two replicates denoted as #1 and #2. The gas composition, including ethylene, oxygen (O₂), and carbon dioxide (CO₂) concentration in packaging headspace, was measured every two days using F-950 Three Gas Analyzer (Felix Instruments, USA) through silicone septa stuck on the film, the simple scheme is shown in Figure 6.1. Then the avocados were cut open, observed the inner appearance, and tested the flesh firmness on the 10th d for #1 and 16th d for #2.

6.3.4.1 Gas composition in packaging headspace

Ethylene, O₂, and CO₂ concentrations were measured every two days by F-950 Three Gas Analyzer. This analyzer has a gas inlet and outlet connecting sampling probes. During detection, the gas in the headspace is pumped into the analyzer at a sampling flow rate of 70 mL/min and a sampling volume of 35 mL. After detection, the gas is pumped back to the headspace to prevent a vacuum from occurring, and simultaneously, ethylene, O₂, and CO₂ content was recorded. Finally, ethylene concentration was expressed as $\mu\text{mol/L}$, while O₂ and CO₂ concentrations were expressed as mmol/L.

6.3.4.2 Inner appearance, firmness, and weight loss

The inner appearance of avocados packaged with multilayer films was observed by cut them open and then photographs were taken to compare the differences between multilayer packaging.

GY series fruit penetrometer (Shanghai Jingsheng Scientific Instruments Corporation, China) was utilized to test avocado flesh firmness with a probe of 3.5 mm in diameter. Five testing points for each sample were randomly measured, and the firmness unit was converted to N.

The weight loss of avocados was obtained by the following equation, where W₀ is the weight of avocados on the first packaging day, and W_n is the weight on the last packaging day.

$$\text{Weight loss (\%)} = \frac{W_0 - W_n}{W_0} \times 100$$

6.3.4.3 Migration testing

Inductively coupled plasma-mass spectrometry (ICP-MS, PerkinElmer, NexION 300X) was employed to test the concentration of manganese (Mn), silicon (Si), aluminum (Al), and sodium (Na) to investigate whether active agents and NaCl would migrate to the peel of avocados. After 16 d, the whole avocado packaged with multilayer film was soaked in 200 mL of nitric acid solution (2 %, v/v) for 24 h, and then 20 mL of solution was extracted to test. To figure out if active agents would remain on the surface of the film, the entire film after packaging avocado for 16 d was also soaked in nitric acid solution and treated with the same process as that of peel. The simple scheme was depicted in Figure S6.1. The instrument parameters were as follows, nebulizer gas flow: 1.0 L/min, auxiliary gas flow: 1.2 L/min, plasma gas flow: 18 L/min, ICP radio frequency power: 1600 W, sweeps/reading: 20, integration time: 1000 ms.

6.3.5 Statistical analysis

The Minitab software (Minitab® 19 for windows, Minitab LLC, USA) was used to statistically analyzed the experimental data according to one-way ANOVA with Tukey's test to ensure a significance level of $p \leq 0.05$. All experiments were carried out in three replicates and the results were displayed as mean value \pm standard deviation.

6.4 Results and discussion

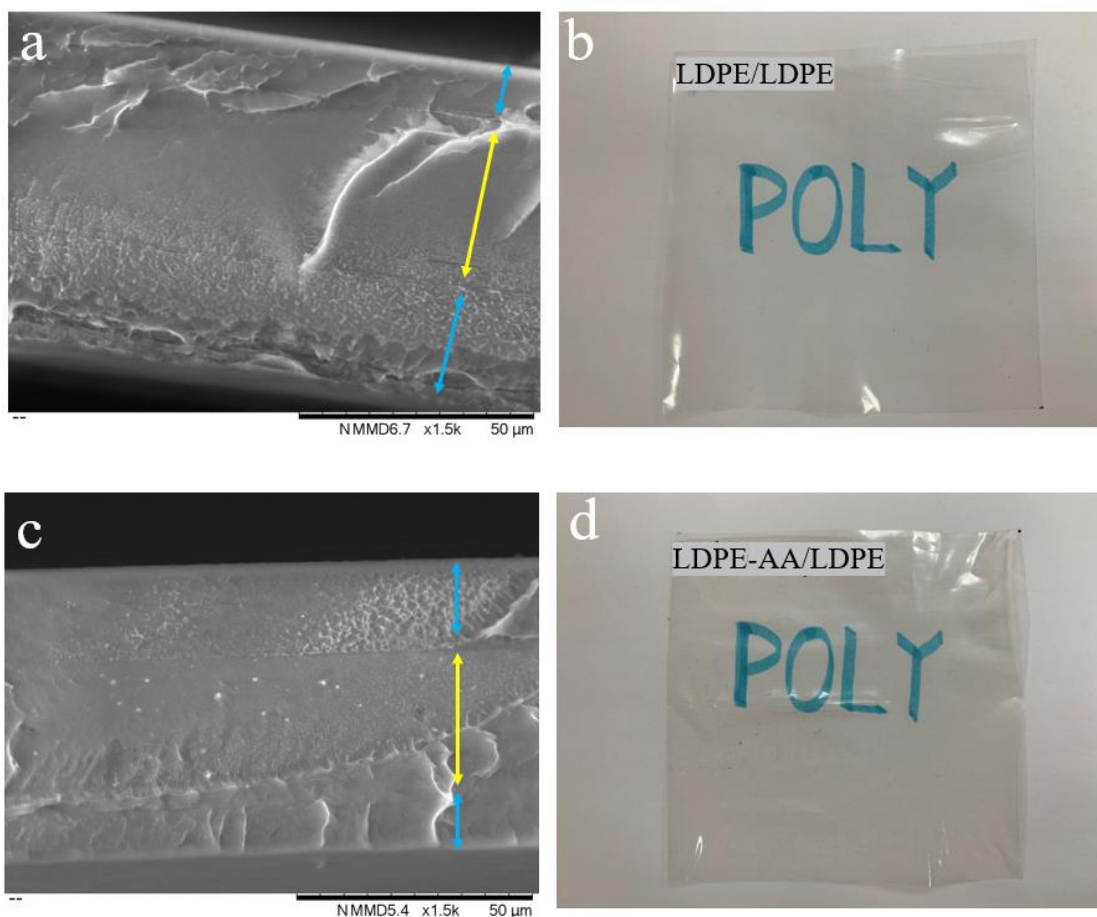
6.4.1 Properties analysis of multilayer films

6.4.1.1 SEM and surface color

The three-layer structures and surface photographs of multilayer films are presented in Figure 6.1 in which the thickness can be seen as in the range of 60 ~ 80 μm . There are no particles observed in LDPE/LDPE films as shown in Figure 6.1 (a), and particles of active agents uniformly dispersed in the core layer of LDPE-AA/LDPE (Figure 6.1 (c)) and LDPE-AA/LDPE-NaCl (Figure 6.1 (e)) with the aid of the PE-g-MA [27, 28]. The maleic anhydride groups of PE-g-MA could bind with surface hydroxyl groups of pumice [29], which facilitated the dispersion of active agents in the films. In addition, NaCl particles were agglomerated in the skin layers of LDPE-AA/LDPE-NaCl as can be observed in Figure 6.1 (e). The presence of NaCl not only improved the gas permeability

of the multilayer films, but also endowed the films with hydrophilic property, which will be introduced in the section 6.4.1.3 and 6.4.1.4 respectively.

The surface color is an important parameter for packaging films in both marketing and applications because this determines whether the state of food can be visually observed [30]. According to the surface photographs in Figure 6.1 (b) (d) and (f), all three multilayer films are transparent, confirming the addition of active agents and NaCl only slightly influenced the transparency. Table S6.1 listed the color indices (L^* , a^* , b^*) of multilayer films. Based on the reference color ($L^* = 91.8$, $a^* = -1.2$, $b^* = -1.9$), the color difference (ΔE^*) of LDPE/LDPE, LDPE-AA/LDPE, and LDPE-AA/LDPE-NaCl was 4.8, 6.6, and 7.0, respectively. Although the lightness (L^*) showed a small reduction and yellowness (b^*) had a slight increase with the addition of active agents and NaCl, ΔE^* of multilayer films was not significant, illustrating active agents and NaCl did not cause a significant change with respect to the surface color of multilayer films.



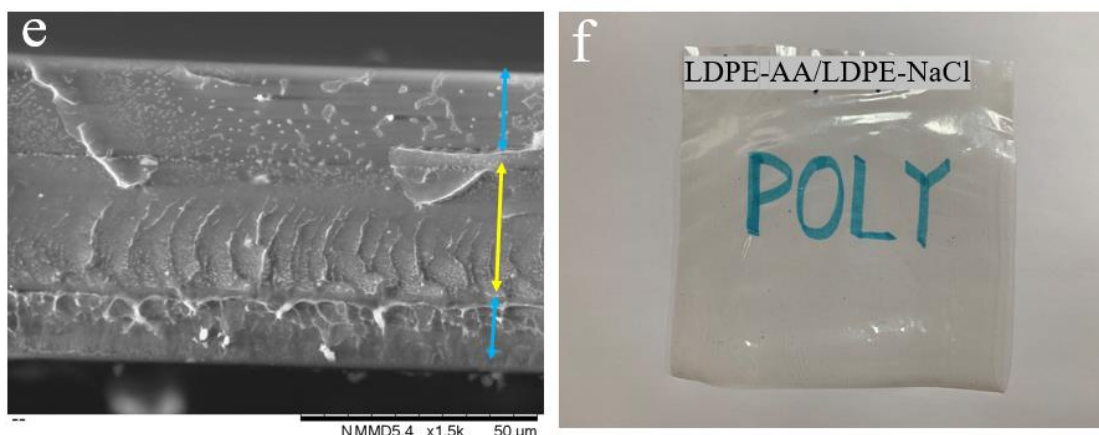


Figure 6.1 SEM cross-sectional images of multilayer films: (a) LDPE/LDPE, (c) LDPE-AA/LDPE, (e) LDPE-AA/LDPE-NaCl, and corresponding surface photographs: (b) (d) (f)

6.4.1.2 DSC and mechanical properties

Melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (X_c) collected from DSC are summarized in Table S6.2. T_m did not show a noticeable difference among multilayer films, illustrating that the addition of active agents and NaCl would not significantly influence T_m of films. ΔH_m of LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl decreased by 14.2 % and 18.3 % respectively than that of LDPE/LDPE. The change of X_c was the same as ΔH_m because X_c was calculated according to the equation, $X_c = \frac{\Delta H_m}{\Delta H_f^0} \times 100\%$ [16], where ΔH_f^0 is the heat of fusion taken as 293 J/g based on 100% crystalline LDPE [31]. The decrease of ΔH_m and X_c might be caused by particle agglomeration, which restricted the crystallization of LDPE molecular chains [12, 16].

All Mechanical properties of LDPE/LDPE, LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl multilayer films were depicted in Figure S6.2. Compared with LDPE/LDPE multilayer film, the Young's modulus of LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl rose and fell slightly to 139.0 MPa and 126.0 MPa respectively. Both tensile strength and elongation at break decreased from 12.4 MPa and 458.0 % of LDPE/LDPE to 11.6 MPa and 411.2 % of LDPE-AA/LDPE, and to 10.6 MPa and 362.9 % of LDPE-AA/LDPE-NaCl, respectively. Taken together, although the LDPE/LDPE multilayer film possessed the optimum mechanical properties, the addition of active agents and NaCl caused a mild effect on the mechanical properties. A similar decrease in terms of

tensile strength and elongation at break due to the presence of particles in LDPE films was ever reported in other research [12, 16, 32].

6.4.1.3 Gas barrier properties

According to the results shown in Figure 6.2 (a), oxygen permeability (OP) and water vapor permeability (WVP) of multilayer films increased with the incorporation of active agents and NaCl. The OP and WVP of LDPE/LDPE multilayer films were measured as 2.1×10^3 cc·mil/m²·day·atm and 30.6 g·mil/m²·day·atm respectively. An addition of 3 wt.% active agents in the core layer increased OP and WVP by 5.0 % and 4.6% respectively over that of LDPE/LDPE. However, the increasing rate of OP and WVP was 28.6 % and 37.9 % respectively when 3 wt.% NaCl was contained in the skin layers. By comparison, the presence of NaCl generated a more pronounced impact than active agents. As discussed in the section 3.1, NaCl agglomerated in the skin layer, which might form interfacial voids at the agglomeration/polymer interface making it easier for gas to pass through the film [12, 16, 33]. Overall, the LDPE-AA/LDPE-NaCl multilayer film had the OP of 2.7×10^3 cc·mil/m²·day·atm and WVP of 42.2 g·mil/m²·day·atm.

6.4.1.4 Ethylene and water absorption

As is well-known, LDPE/LDPE was not equipped with ethylene scavenging capacity, but LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl could scavenge ethylene owing to the incorporation of active agents in the core layer. Figure 6.2 (b) demonstrates that LDPE-AA/LDPE-NaCl scavenged more ethylene than LDPE-AA/LDPE, and both of their ethylene scavenging capacities gradually reached a plateau after 8 d. The ethylene scavenging capacity per 25 in² of LDPE-AA/LDPE-NaCl film was 75.4 %, corresponding to 1.6 $\mu\text{mol}/(25 \text{ in}^2)$ within 8 d, higher than that of LDPE-AA/LDPE film with 37.3 %, corresponding to 0.9 $\mu\text{mol}/(25 \text{ in}^2)$. This is because the agglomeration of NaCl in the skin layers increased gas permeability as mentioned above, so ethylene was more likely to pass through the skin layer and then was scavenged by active agents in the core layer.

In addition, the water absorption capacity of LDPE/LDPE, LDPE-AA/LDPE, and LDPE-AA/LDPE-NaCl within 14 d at high relative humidity was 0, 12.8 mg/(25 in²), and 179.1 mg/(25 in²), respectively. LDPE is considered a hydrophobic polymer; however, it is hydrophilic when combined with deliquescent NaCl, which can absorb water vapor at high relative humidity (≥ 75 %) and desorb water vapor when relative humidity is low [22]. Moreover, there are reports

demonstrating that films incorporating NaCl could regulate humidity and keep it at a high level [21, 34], which was beneficial to postharvest preservation by preventing moisture loss [35].

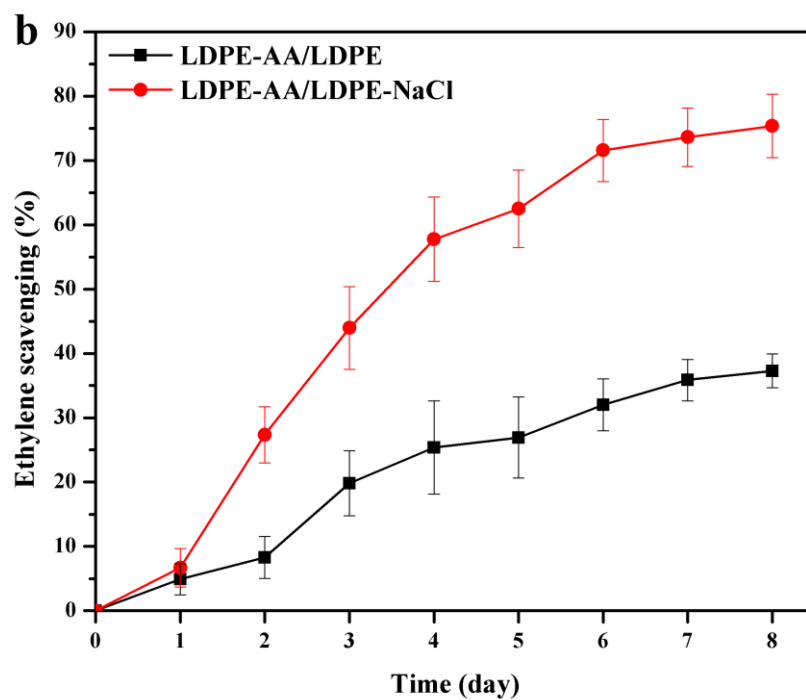
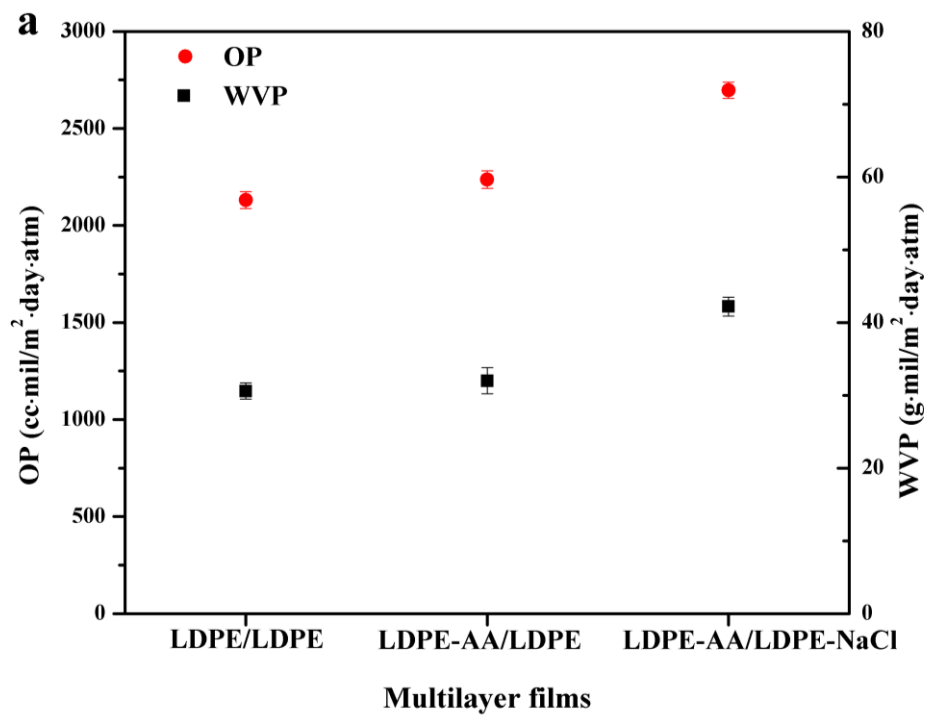


Figure 6.2 Ethylene scavenging capacity of multilayer films

6.4.2 Quality analysis of Avocado preservation

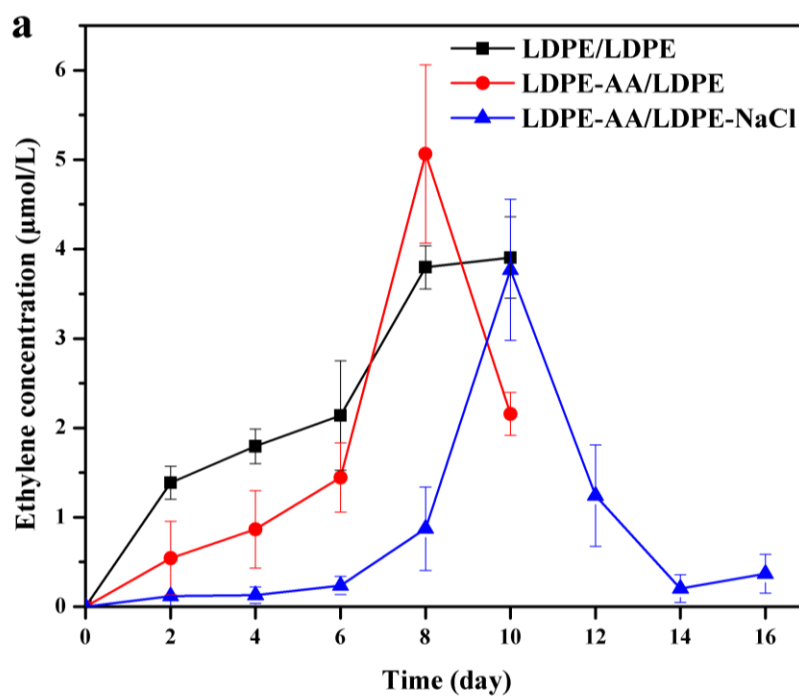
6.4.2.1 Gas composition in packaging headspace

Three leading gases, including ethylene, O₂, and CO₂, are involved in fruit ripening and senescence because O₂ is consumed and CO₂ is produced through respiration, and ethylene is released simultaneously. Figure 6.3 shows gas composition in LDPE-AA/LDPE-NaCl packaging headspace up to 16 d, whereas testing continued 10 d for LDPE/LDPE and LDPE-AA/LDPE because avocados were spoiled by then.

LDPE/LDPE film had low gas permeability and did not possess ethylene scavenging performance, so the beginning ethylene concentration on the 2nd d was high at 1.4 μmol/L, and then increased to 3.9 μmol/L on the 10th d as shown in Figure 6.3 (a) when the avocado was spoiled. As for LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl packaging, ethylene concentration displayed a similar trend, increasing initially and decreasing afterward, and a climacteric peak appeared [15, 36]. However, the climacteric stage was postponed from 8 d in the LDPE-AA/LDPE packaging to 10 d in the LDPE-AA/LDPE-NaCl packaging, as can be observed in Figure 6.3 (a). The former climacteric peak was at 5.1 μmol/L while the latter was at 3.8 μmol/L. Compared with two other films, LDPE-AA/LDPE-NaCl kept ethylene concentration at a low level because of suitable ethylene scavenging property and gas permeability. In Figure 6.3 (b), O₂ concentration in LDPE/LDPE and LDPE-AA/LDPE packaging headspace was low within 10 d, between 0.5 mmol/L and 1.4 mmol/L, while LDPE-AA/LDPE-NaCl held O₂ concentration at approximately 5.0 mmol/L. LDPE/LDPE packaging had a higher CO₂ concentration (Figure 6.3 (c)), followed by LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl. Overall, LDPE-AA/LDPE-NaCl controlled ethylene and CO₂ concentrations lower than the other two films and retained a higher O₂ concentration in the packaging headspace, which is due to the good ethylene scavenging capacity and improved gas permeability.

In general, low O₂ concentration and high CO₂ concentration are beneficial to the storage of avocados [3, 37]. However, too low O₂ concentration (<2%) can lead to anaerobic respiration [38], and too high carbon CO₂ concentration (>15%) can cause physiological injury [39]. According to the report by Meir, et al. [40], the optimal modified atmosphere packaging (MAP) conditions are 2-6% O₂ (corresponding to 0.89-2.68 mmol/L) and 3-10% CO₂ (corresponding to 1.35-4.50

mmol/L) at 5 °C and 7 °C. Although the O₂ concentration in LDPE/LDPE and LDPE-AA/LDPE packaging was low between 0.5-1.5 mmol/L, the CO₂ concentration was high, which may be the reason why LDPE/LDPE and LDPE-AA/LDPE could not preserve avocados for a long shelf life. As for LDPE-AA/LDPE-NaCl packaging, the CO₂ concentration was below 4.50 mmol/L but the O₂ concentration was approximately 5.0 mmol/L, and it is believed that the shelf life of avocados could be further extended if O₂ was controlled to the lower level.



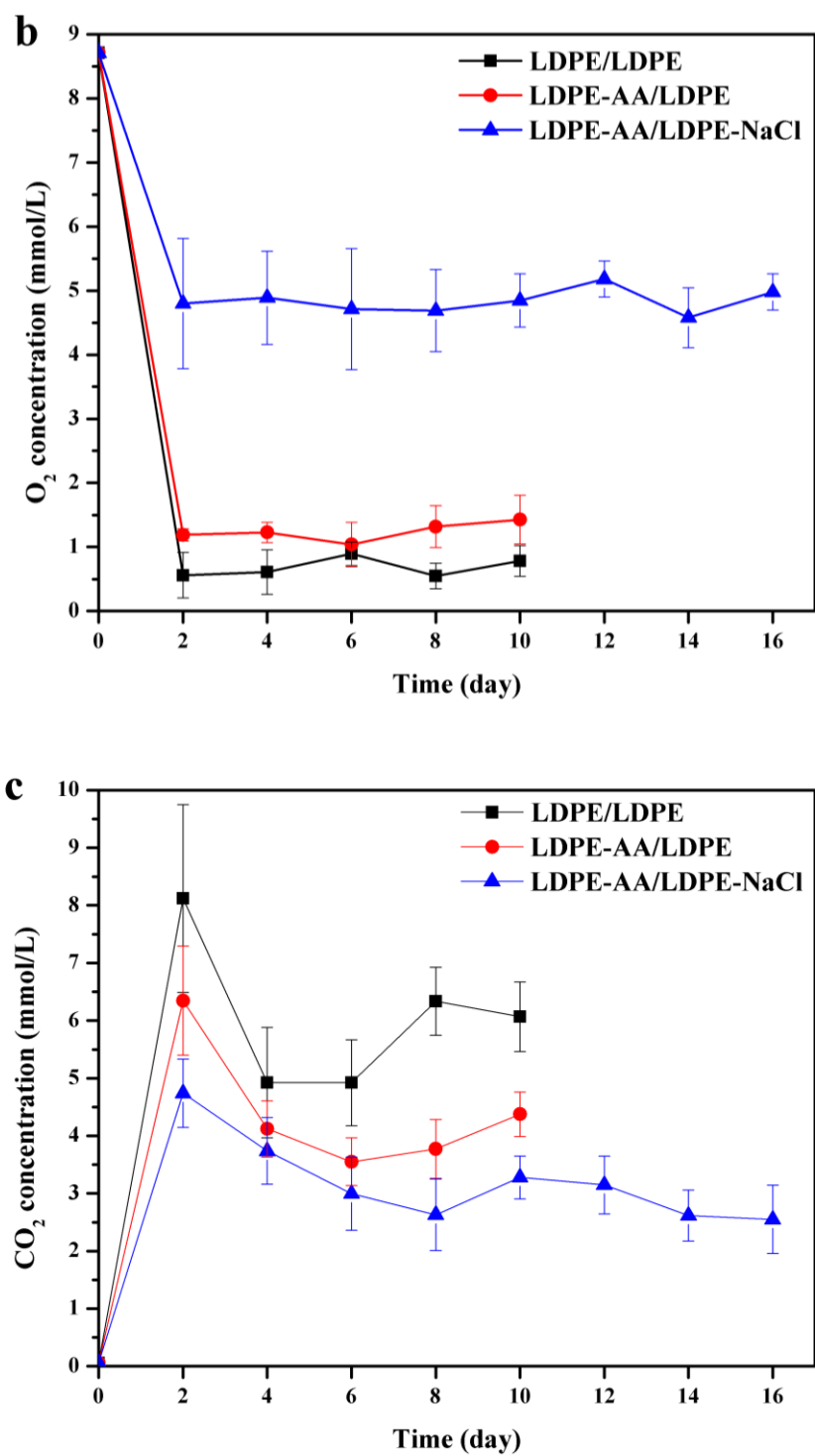


Figure 6.3 Gas composition (a: ethylene, b: O₂, c: CO₂) in packaging headspace at 25 °C up to 16

d

6.4.2.2 Inner appearance, firmness, and weight loss

Inner appearance (Figure 6.4) of avocados can directly reflect if they are spoiled, and flesh firmness (Figure S6.3) is also an important indicator to evaluate fruit status [7, 8]. One can easily make judgments when combining the inner appearance and flesh firmness. The initial appearance before packaging is displayed in Figure S6.4. The avocados packaged in LDPE/LDPE and LDPE-AA/LDPE for 10 d were spoiled, as can be observed in Figure 6.4 (a #1) (b #1), with the flesh firmness of 6.17 N and 6.25 N respectively. On the 16th d, Figure 6.4 (a #2) (b #2) displayed spoiled avocados with the firmness of 0.49 N. Under the preservation of LDPE-AA/LDPE-NaCl, the avocado remained fresh for 10 d, as can be seen in Figure 6.4 (c #1), and its flesh firmness was 6.53 N. When packaged for 16 d, the avocado was still good, as presented in Figure 6.4 (c #2), but its firmness was low, only 0.91 N. In addition, after 10 d, the weight losses of avocados packaged in LDPE/LDPE, LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl were 1.97 %, 1.50 % and 1.21 % respectively, and the values corresponded to 3.51 %, 2.96 % and 2.11 % respectively after 16 d. This can be attributed to the presence of NaCl, which could regulate the humidity of packaging headspace as aforementioned, so LDPE-AA/LDPE-NaCl achieved a minimum weight loss of avocados [21, 34, 35]. Taken together, the shelf life of avocados was extended from less than 10 d to until 16 d under the preservation of LDPE-AA/LDPE-NaCl.

a #1



a #2



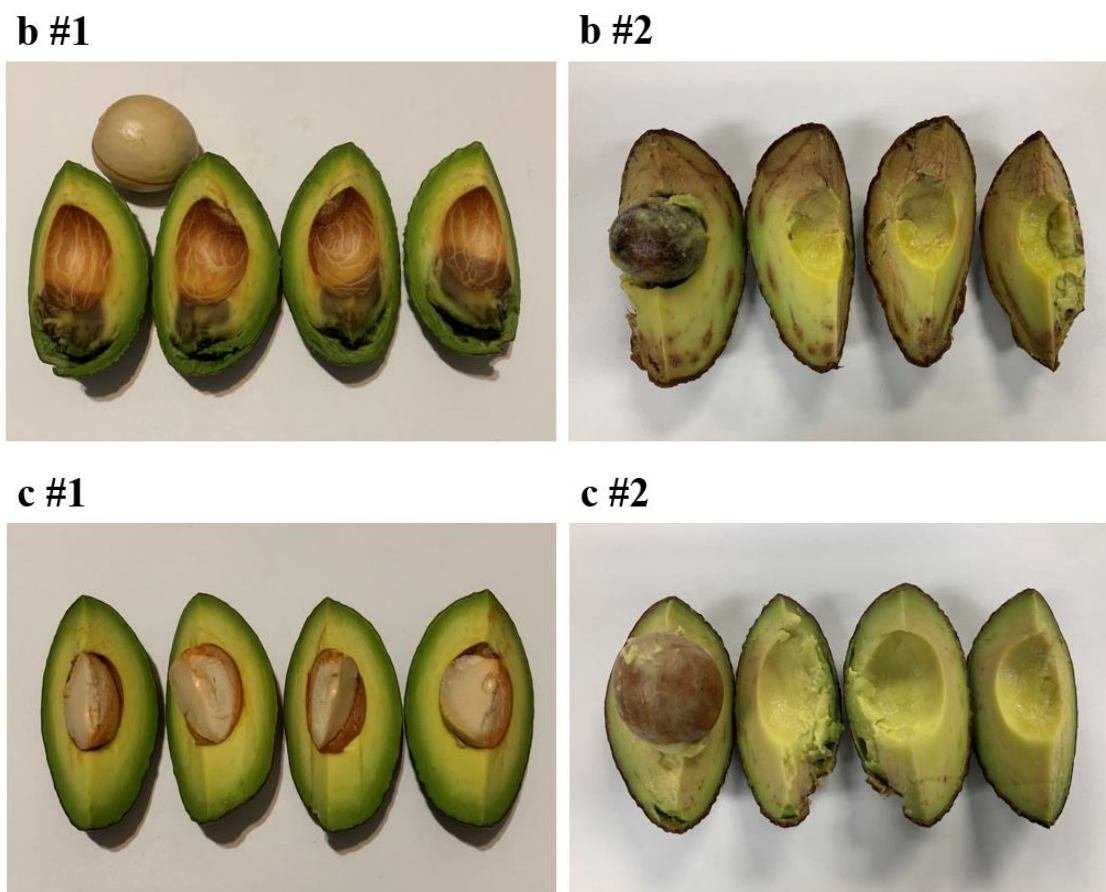


Figure 6.4 The inner appearance of avocados packaged with (a) LDPE/LDPE, (b) LDPE-AA/LDPE, and (c) LDPE-AA/LDPE-NaCl films at 25 °C (#1: preservation for 10 d, #2: preservation for 16 d)

6.4.2.3 Migration testing

The summary of the migration testing results is listed in Table 6.2. Elements of Mn represent KMnO_4 , Si and Al represent pumice, and Na represents NaCl. Concentrations of Mn, Si, and Al in HNO_3 solution for samples of peels are very close, illustrating that KMnO_4 and pumice did not migrate from the core layer to the peels of avocados. In addition, HNO_3 solution soaking of packaged films did not show a large difference in concentrations of Mn, Si, and Al, demonstrating that pumice and KMnO_4 in the core layer did not migrate to the skin layer. As for NaCl, it did not migrate to the peel of avocados according to concentrations of Na for samples of peels, but a high concentration of Na was tested for the sample of the film (LDPE-AA/LDPE-NaCl) because NaCl was deliquescent and incorporated in the skin layer. Moreover, NaCl is safe and food grade, so

there is no need to worry that it may cause food safety problems. The fact that the concentrations of elements of HNO₃ solution (blank) were lower than that of peel and film samples might result from the samples (peels and films) themselves, proving the HNO₃ solution would not influence the migration detection.

According to COMMISSION REGULATION (EU) 2016/1416, the migration limits of Al and Mn are 1 mg/kg food and 0.6 mg/kg food, respectively. By calculation, the migration of Al and Mn from LDPE-AA/LDPE-NaCl to avocado is below the limits, at 0.074 mg/kg and 0.005 mg/kg respectively (Conditions: solution volume 200 mL, Al 67.1 µg/L, Mn 5.0 µg/L, avocado weight 180 g).

Table 6.2 The concentration of elements after treating avocado and packaged film with HNO₃ solution

Samples	Mn (µg/L)	Si (µg/L)	Al (µg/L)	Na (µg/L)
Blank (HNO ₃ solution)	0.04	< LoD	38.30	65.57
Peel (LDPE/LDPE)	7.0 ± 1.6	108.7 ± 12.9	69.5 ± 7.4	61.3 ± 4.0
Peel (LDPE-AA/LDPE)	8.3 ± 1.7	115.8 ± 24.5	61.9 ± 5.2	63.8 ± 6.0
Peel (LDPE-AA/LDPE-NaCl)	5.0 ± 0.7	105.1 ± 12.5	67.1 ± 4.2	60.3 ± 6.2
Film (LDPE/LDPE)	26.8 ± 3.0	78.5 ± 5.9	36.8 ± 2.1	322.2 ± 12.7
Film (LDPE-AA/LDPE)	21.5 ± 1.6	68.3 ± 8.1	35.8 ± 3.3	311.3 ± 16.5
Film (LDPE-AA/LDPE-NaCl)	34.7 ± 6.2	51.4 ± 7.8	40.4 ± 4.2	4119.5 ± 26.4

Note: Peel (LDPE/LDPE) means the sample was HNO₃ solution (2 %, v/v) soaking peel of avocado packaged by LDPE/LDPE film. Film (LDPE/LDPE) means the sample was HNO₃ solution (2 %, v/v) soaking LDPE/LDPE film. LoD: limit of detection.

6.5 Conclusion

The multilayer film (LDPE-AA/LDPE-NaCl) was successfully developed to extend the shelf life of fruit and vegetables. The film was constituted of three layers, one core layer containing pumice and KMnO_4 as the active layer and two skin layers containing NaCl as a barrier. Although the thermal and mechanical properties of LDPE-AA/LDPE-NaCl showed mild reduction compared with LDPE/LDPE, it was endowed with better gas permeability, ethylene scavenging, and water absorption performances. Moreover, LDPE-AA/LDPE-NaCl extended the shelf life of avocados to 16 d, compared to less than 10 for LDPE/LDPE. Most importantly, LDPE-AA/LDPE-NaCl was confirmed to be safe when applied as packaging material, which settled a matter of active agents migrating from packaging film to food. This study provided a promising prospect for active packaging, and further research on food quality and safety needs to be explored. Future perspectives are recommended to increase ethylene scavenging capacity of multilayer films because it is a challenge to make ethylene pass through skin layer (barrier layer) to core layer (active layer). On top of that, the development of multilayer films with both ethylene scavenging and antimicrobial or antioxidant properties is also a research gap.

CRedit authorship contribution statement

Chunyu Wang: Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Roles/Writing – original draft. **Abdellah Ajji:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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6.8 Supporting information

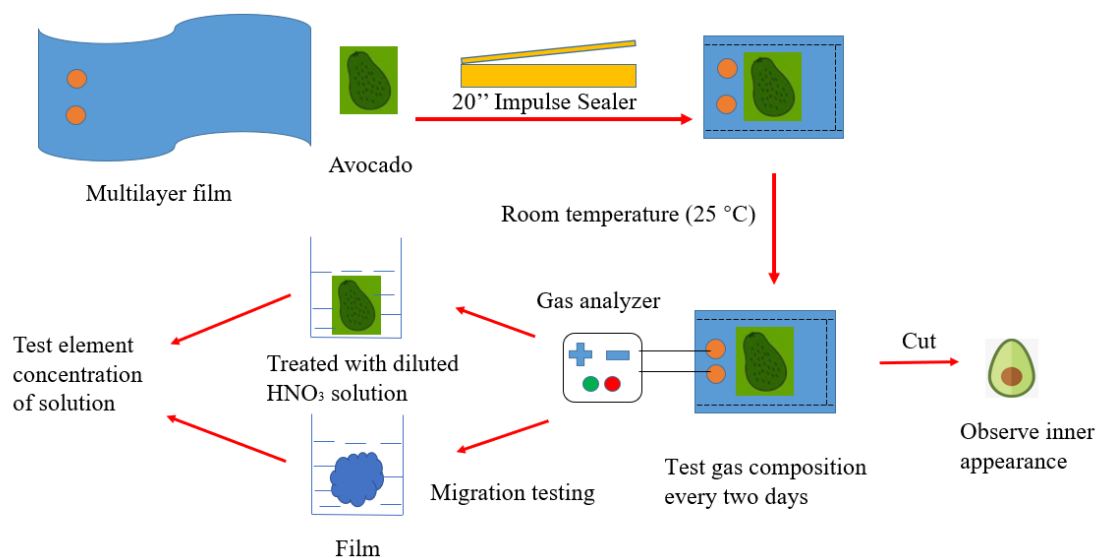


Figure S6.1 The scheme of avocado preservation and migration testing

Table S6.1 The color indices of multilayer films

Multilayer films	L^*	a^*	b^*	ΔE^*
LDPE/LDPE	87.0 ± 0.6	-1.4 ± 0.1	-1.5 ± 0.3	4.8 ± 0.5
LDPE-AA/LDPE	85.6 ± 1.1	-1.2 ± 0.1	0.6 ± 0.1	6.6 ± 0.9
LDPE-AA/LDPE-NaCl	85.3 ± 0.4	-1.4 ± 0.2	0.8 ± 0.5	7.0 ± 0.2

Table S6.2 Summary of DSC results for multilayer films

Multilayer films	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	Xc (%)
LDPE/LDPE	107.3 ± 0.3	66.1 ± 2.2	22.6 ± 0.8
LDPE-AA/LDPE	107.1 ± 0.4	56.7 ± 2.8	19.4 ± 1.0
LDPE-AA/LDPE-NaCl	106.8 ± 0.4	54.0 ± 1.5	18.4 ± 0.5

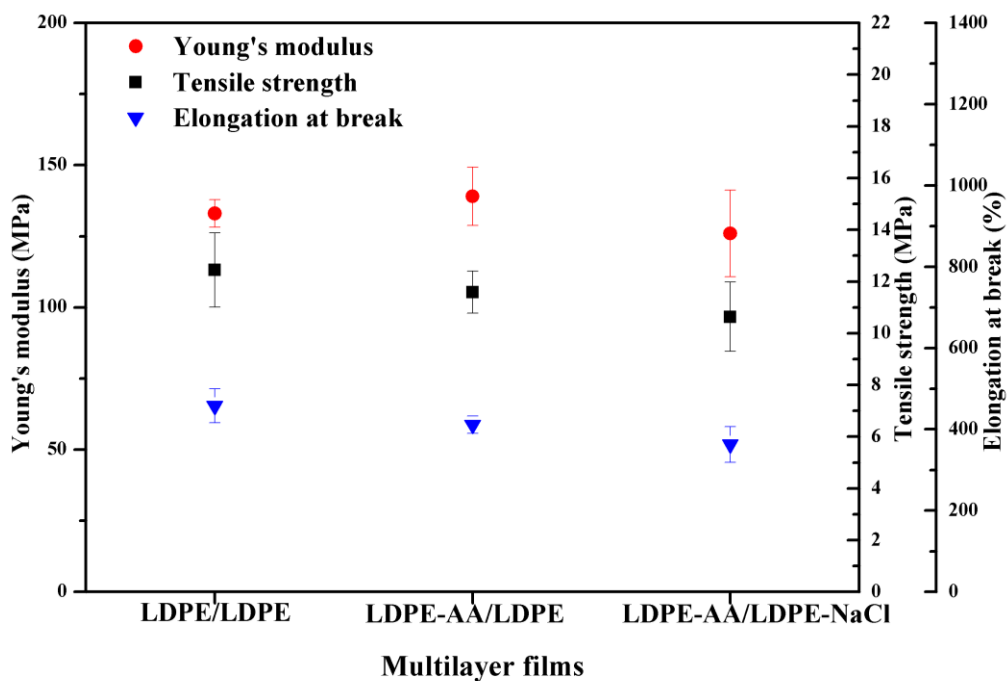


Figure S6.2 Summary of mechanical properties for multilayer films

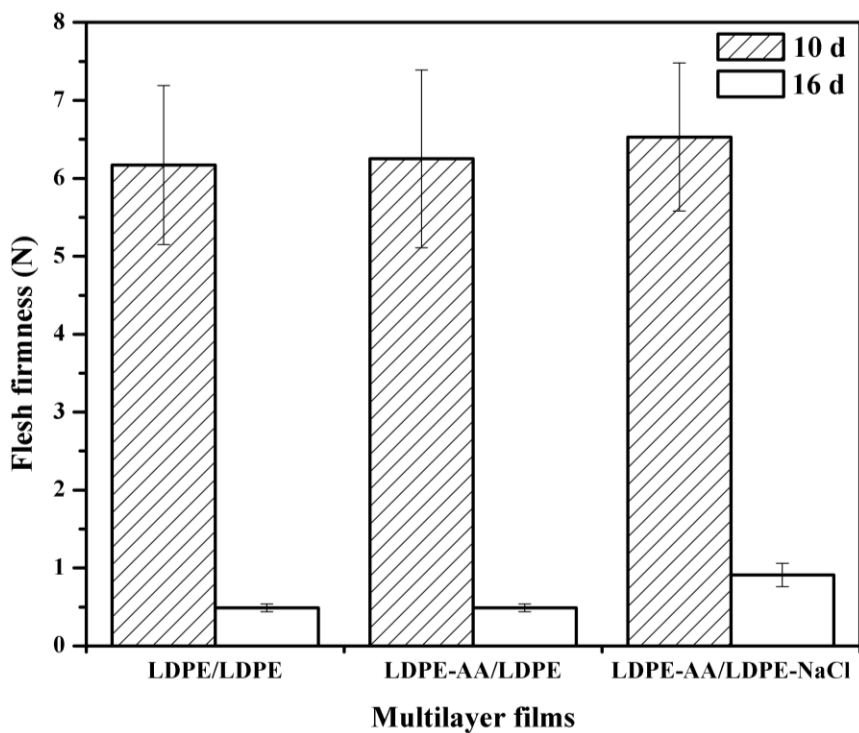


Figure S6.3 Flesh firmness of avocados packaged with multilayer films for 10 d and 16 d

The initial quality of avocados is the same without difference, which means the initial quality in three packaging groups (LDPE/LDPE packaging, LDPE-AA/LDPE packaging, and LDPE-AA/LDPE-NaCl packaging) is the same, as illustrated in the following Figure S6.4, and the initial firmness is between 10-12N. So we chose to directly compare the quality of avocados during storage.



Figure S6.4 Initial appearance of avocado before packaging

CHAPTER 7 GENERAL DISCUSSION

Removing ethylene produced in the packaging headspace can extend the shelf life of fruits and vegetables. Therefore, developing efficient ethylene scavengers is of great significance for reducing food loss and even economic loss. The focus of this work is to systematically develop ethylene scavengers, starting with the research of pumice and KMnO_4 , then combining with LDPE films, ending up with the preparation of the multilayer films. Herein, the thesis is discussed according to two aspects; the first aspect is to discuss the properties of ethylene scavengers including sachets and films, and the second is to discuss the effect of ethylene scavengers on avocado preservation.

7.1 Properties of ethylene scavengers

In the field of ethylene scavenging filed, much attention was paid on the combination of KMnO_4 and its support. KMnO_4 is a strong oxidant with high efficiency to scavenge ethylene. However, it is rare to apply KMnO_4 alone to remove ethylene [114, 115]. To increase its contacting area, KMnO_4 usually needs to be supported by a material with relatively high specific surface area [52, 57, 116]. Pumice is such a material with good gas adsorption, easy availability, cost-efficient and eco-friendly properties [67, 71, 117]. Hence, it is believed that the combination of KMnO_4 and pumice can perform an extraordinary efficacy.

In the first part of this thesis, the ethylene scavenger made up of pumice and KMnO_4 was developed, and three main targets were studied. The first one was to figure out the influence of the size of pumice to ethylene adsorption, and it was found that the ethylene scavenging capacity increased with the size decreasing because the smaller size means larger specific surface area, which is favorable to ethylene adsorption. The second one was to determine the optimal weight ratio of pumice to KMnO_4 , and a weight ratio of 10 to 1 was confirmed to present the highest ethylene scavenging capacity. The last target was to explore the synergistic effect of pumice and KMnO_4 , and it was certified by the fact that the ethylene scavenging capacity of the mixture of pumice and KMnO_4 exhibited a significant increase compared to pumice or KMnO_4 alone. To our knowledge, this is the first time to study the synergistic effect of KMnO_4 and its support by forming the adsorption-oxidation system. In addition, the ethylene scavenging capacity of the ethylene

scavenger decreased when RH was higher due to the competitive relationship between moisture and ethylene for the adsorption sites on the pumice surface.

LDPE is a popular polymer matrix applied in packaging films with excellent performance like high flexibility, chemical resistance, heat sealability, and clarity [90, 118, 119]. In the second part of the thesis, the mixture of pumice and KMnO_4 served as active agents and was incorporated into LDPE films by melt blending through a twin-extruder. In order to improve the dispersion of active agents, PE-g-MA was selected as the compatibilizer; this is due to the hydroxyl groups on the pumice surface can react with maleic anhydride groups of PE-g-MA, which favors the compatibility of active agents and LDPE matrix. A good dispersion of active agents can improve the performance of films, including transparency, crystallinity, mechanical properties, and gas barrier properties. The SEM images showed that a low content of active agents (1 wt.% and 3 wt.%) had a uniform dispersion but on the contrary, active agents agglomerated the content of 5 wt.% and 10 wt.%. According to the surface color analysis, the lightness and transparency of the films reduced as the loading of active agents increased. Compared with pure LDPE film, the crystallinity and mechanical properties were improved with 1 wt.% and 3 wt.% active agents but were reduced with 5 wt.% and 10 wt.% active agents. The film incorporating 3 wt.% active agents possessed the best gas barrier against oxygen and water vapor, followed by the film with 1 wt.% active agents.

Although a small amount of KMnO_4 is usually utilized in sachets or packaging films and it is easy to clean it using water [26], food contamination and safety hazard are always a concern to people especially when sachets are broken or KMnO_4 migrates from films to food surface [1, 41, 111]. Therefore, avoid the migration of KMnO_4 , the third part of this thesis was aimed to develop a multilayer active packaging film through a multilayer extrusion line. There are three layers, one core layer sandwiched between two skin layers; the core layer is an active LDPE-layer containing 3 wt.% active agents, while the skin layer is the LDPE-layer containing 3 wt.% NaCl. The multilayer film could scavenge ethylene relying on the core layer and absorb water by means of the skin layer. According to the surface color analysis, the lightness and transparency of the multilayer film showed a slight reduction with the addition of active agents and NaCl. In addition, the presence of active agents and NaCl has little influence on the melting temperature of the film but caused a mild reduction in crystallinity and mechanical properties. More importantly, no significant change of Mn, Si, and Al elements were detected in migration testing, illustrating active

agents did not migrate from the core layer to the avocado surface. As a consequence, the multilayer film can avoid the safety hazard caused by the contact between active packaging film and food.

For the same amount of pumice and KMnO_4 , the ethylene scavenging capacity of sachets is larger than films. This is because ethylene can be directly adsorbed and oxidized by sachets, however, ethylene needs to firstly be adsorbed on the surface of films and then be oxidized when passing through films. As for monolayer films, LDPE-3%PKM showed the highest ethylene scavenging capacity, which is associated to the good dispersion of 3 wt.% active agents. Compared to the monolayer films, the gas permeability of the multilayer films significantly decreased. Therefore, it is a challenge for gas pass through the skin layer to the core layer, meaning it is difficult to scavenge ethylene. The issue can be tackled by the incorporation of NaCl in the skin layer because the agglomeration of NaCl increased the gas permeability, making it easier for ethylene to go through skin layer and be removed in core layer.

7.2 Avocado preservation with ethylene scavengers

Avocados are a climacteric fruit, so ethylene production rate and respiration rate have a peak stage during the ripening process [22, 23]. When avocado was not protected by ethylene scavengers, the peak stage appeared on the 4th day, but there is no peak stage when avocado was protected by sachets made up of pumice and KMnO_4 because ethylene produced by avocado was removed immediately and completely. For monolayer ethylene scavenging films, the peak stage was postponed to the 10th day in the packaging of LDPE-1%PKM and LDPE-5%PKM, and to the 12th day in the packaging of LDPE-3%PKM. The multilayer films of LDPE-AA/LDPE and LDPE-AA/LDPE-NaCl delayed peak stage to the 8th day and 10th day, respectively.

All experiments of avocado preservation were carried out under 25 °C. The shelf life of avocado without protection by ethylene scavengers was less than 9 days, but the sachets comprised of pumice and KMnO_4 extended the shelf life to 17 days. As for films, the gas permeability and ethylene scavenging capacity made an effect on the quality of avocados. LDPE films had no ethylene scavenging capacity and LDPE-10%PKM had a high gas permeability, so the avocados preserved by them were spoiled within 10 days. LDPE-1%PKM, LDPE-3%PKM, and LDPE-5%PKM kept avocados fresh more than 10 days; on the 20th day, the avocados preserved by LDPE-1%PKM and LDPE-5%PKM started becoming spoiled, while the avocado packaged with

LDPE-3%PKM was kept well. By comparison, LDPE-3%PKM controlled ethylene and CO₂ concentrations to a lower level because of its lower gas permeability and higher ethylene scavenging capacity. Further, the avocados were preserved well by the multilayer film LDPE-AA/LDPE-NaCl for 16 days, compared to less than 10 days for LDPE/LDPE and LDPE-AA/LDPE. This is because ethylene and CO₂ concentrations were controlled to a lower level due to the addition of active agents in the core layer and NaCl in the skin layer. In summary, the multilayer films prolonged the shelf life of avocados to a shorter period than that of monolayer films because multilayer films had a lower gas permeability and ethylene scavenging capacity.

CHAPTER 8 CONCLUSION AND RECOMMENDATIONS

8.1 Conclusion

This work developed ethylene scavenging systems based on pumice and KMnO_4 to extend the shelf life of avocados in the form of sachets and active packaging LDPE films. To this end, our work was divided into three parts.

The first part was aimed to develop an ethylene scavenger consisting of pumice and KMnO_4 , and the conclusion was made as follows:

1. As for pumice, the smaller size and lower RH favored ethylene adsorption because the specific surface area increased with the size decreasing and water competed with ethylene for adsorption sites on the pumice surface.
2. The optimal weight ratio of pumice to KMnO_4 was 10 to 1, and the ethylene scavenging capacity of the mixture of pumice and KMnO_4 was significantly higher than pumice or KMnO_4 alone, due to the synergistic effect of pumice physically adsorbing ethylene and KMnO_4 chemically oxidizing ethylene.
3. Regarding the application of pumice and KMnO_4 , the shelf life of avocados was extended by one week at 25 °C compared to the control without ethylene scavengers, and the ethylene and CO_2 production rates were inhibited, and the firmness loss was reduced.

The second part was to prepare an ethylene scavenging film comprising LDPE as the matrix, the mixture of pumice and KMnO_4 as active agents, and PE-g-MA as the compatibilizer, by means of melt blending and the conclusion was made as follows:

1. The PE-g-MA could improve the compatibility of active agents and LDPE film, which was proved by the shift of the absorbance peak of O-Si-O bonds in FTIR spectra; however, the improvement of compatibility became unobvious when the content of active agents was high, especially at 10 wt.%.
2. The low loading of active agents (1 wt.% and 3 wt.%) evenly dispersed in the LDPE film, while agglomeration occurred at high loading (5 wt.% and 10 wt.%); the increasing content of active agents resulted in a reduction in the transparency and lightness of the films.

3. The film with 3 wt.% active agents showed the most pronounced mechanical properties and gas barrier performance against oxygen and water vapor, and its ethylene scavenging capacity was higher than other films within 12 days at 25 °C.

4. The avocados preserved by the film with 3 wt.% active agents performed better than the others in terms of ethylene and CO₂ concentrations in the packaging headspace, and inner appearance and firmness loss of avocados; the shelf life of avocados was prolonged to 20 days at 25 °C.

The third part was to prepare a multilayer film consisting of a core layer containing active agents and two skin layers containing NaCl through multilayer extrusion, and the conclusion was made as follows:

1. The addition of active agents and NaCl did not greatly change the transparency of multilayer film but caused a mild reduction in crystallinity and mechanical properties.

2. The incorporation of NaCl in the skin layers enhanced the gas permeability of multilayer film, resulting that more ethylene could be removed; in addition, the film was endowed with water absorption property owing to NaCl.

3. The multilayer film prolonged the shelf life of avocados to 16 days at 25 °C, controlled the ethylene and CO₂ concentrations in the packaging headspace, and reduced the weight loss of avocados.

4. The multilayer film avoided the contact between active agents and avocados and prevented the migration of active agents to the surface of avocados.

8.2 Recommendations

The following subjects are recommended in future investigation:

1. Explore the influence of low temperature on the preservation of fruits and vegetables accompanied by the ethylene scavengers.

2. Study whether the ethylene scavenging process is accompanied with catalysis in the adsorption-oxidation system by means of in situ FTIR.

3. Study the antibacterial effect of the ethylene scavenger during preserving fruits and vegetables.

4. Apply an alternative polymer matrix such as PP or PLA and evaluate the gas barrier properties and ethylene scavenging efficiency.
5. Substitute KMnO_4 with other active agents such as nano- TiO_2 and evaluate the ethylene scavenging efficiency.
6. Investigate other compatibilizer to further improve the dispersion of active agents.
7. Try to test the ethylene permeability of films and study the process of ethylene passing through the films by means of simulation.
8. Try to prepare multilayer film by different methods, such as coating, electrospinning, or solvent casting.

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