# DEVELOPMENT OF A POLY(LACTIC ACID) PACKAGING MATERIAL ABLE TO SCAVENGE CARBON DIOXIDE AND ETHYLENE BY INCORPORATION OF ZEOLITES

Ву

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#### ABSTRACT

## DEVELOPMENT OF A POLY(LACTIC ACID) PACKAGING MATERIAL ABLE TO SCAVENGE CARBON DIOXIDE AND ETHYLENE BY INCORPORATION OF ZEOLITES

By

#### Anna Szwedzińska

Poly(lactic acid) is a biobased polymer and known to biodegrade reasonably quickly in commercial compost. There has been a growing interest in using it as a replacement for petrochemical based polymers due to its environmental-friendliness.

Zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth elements. They can be natural minerals or produced synthetically. Depending on their framework they can have different structures and different pore sizes which makes them sorption-specific systems for various volatiles. There is a growing interest in their application in food packaging as they can adsorb and absorb gases crucial for extending shelf life of fresh produce, like ethylene and CO<sub>2</sub>.

Active packaging systems are efficiently used in food packaging. Studies show that PLA and zeolites can be combined into one material by extrusion. Now the question is if they can act as an efficient active packaging system.

Results obtained showed that two chosen zeolites, natural clinoptilolite and synthetic type 4A, have high sorption capacities for ethylene and carbon dioxide. Experimental conditions were varied, temperatures of 23°C and 7°C, relative humidities of 0% and 100%, headspace gases composed of varying combinations and concentrations of ethylene, carbon dioxide, nitrogen, and oxygen. Although low temperature and the presence of water in the system decreased sorption capacities of the zeolites, most measured amounts of adsorbed ethylene and carbon dioxide were relevant to concentrations

produced and higher than concentrations tolerated by fresh produce, and were promising enough to continue investigating these two zeolites when incorporated into/onto PLA films.

Two techniques to produce PLA/zeolite films were tested, extrusion (followed by injection molding and compression) and bar solution coating. The second method resulted in films with higher sorption potential for the two investigated gases since extrusion resulted in the zeolites being too deeply incorporated into the polymer matrix and having PLA as the polymer with good barrier properties towards ethylene did limit their sorption capacities. Further development of the most efficient coating solution and coating method resulted in production of two zeolite coated PLA films.

The newly developed films were compared in sorption studies to two commercially available bags that are claimed to be ethylene scavengers and as a result to extend fresh produce shelf life. PLA films proved to be comparable to one of the commercial bags comprised of LDPE impregnated with zeolites. The second commercial product did not show significant sorption of either of the two gases of interest. All film samples were tested in two conditions (23°C, 0% RH and 7°C and 100% RH).Although in both cases sorption of ethylene and carbon dioxide was smaller than for powder zeolites, with even higher decrease in low temperature and in the presence of water, the resulting sorbed amounts were still relevant to real life situations. Experiments designed to determine whether those films could be reused showed that both zeolite coated PLA films could be successfully reused in room temperature, the same as for the commercial film. Copyright by ANNA SZWEDZIŃSKA 2015

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#### CHAPTER 1

## **Research Motivation and Goals**

Researchers working in food packaging have always been concerned about using proper packaging materials and systems to minimize food losses and result in safe food products. Lately, there has been a growing interest in providing better quality foods that can stay fresh-like for a much longer time without looking or tasting as if they were packed awhile ago. This resulted in development of active packaging technologies.

In perishables packaging, headspace gas content and its changing concentration are very important in keeping the product fresh like and safe for as long as possible. Gases used during the packaging process (O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>) as well as those produced by food (C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>) play an important role in shelf life. Recently zeolites have been a subject of study as absorbers for many different gases. Since they can act as ethylene and CO<sub>2</sub> scavengers, researchers are investigating their possible utilization in active packaging systems.

Poly(lactic acid) as a biobased and certified compostable in industrial compost systems alternative to petrochemical based polymers is also receiving growing attention in food packaging. For fresh produce purposes it should be modified by additives that will help with sorption of specific gases. Since zeolite/PLA composite materials have been successfully produced in the past, natural development suggests extrapolating their use to food packaging.

Zeolites, crystalline aluminosilicates of alkali and alkaline earth elements that are characterized by unique three-dimensional framework structures composed of  $SiO_4$  and  $AlO_4$ , have been successfully used as ethylene and  $CO_2$  scavengers. They have also been used to produce polymer/zeolite films and their adsorption capacities have been investigated. Polymers commonly mixed with zeolites include LDPE, HDPE, PP, PC, and PS but they can also be successfully incorporated into PLA films.

The main goal of this project was to develop a new active packaging system composed of zeolites and PLA, which will be able to act as an ethylene and CO<sub>2</sub> scavenger. The specific objectives were to measure ethylene and CO<sub>2</sub> sorption capacities of two chosen zeolites in the form of powders and to produce and evaluate PLA films coated with zeolites as ethylene and CO<sub>2</sub> scavengers.

The following steps were involved in accomplishing the pursued goals. First, a method and system that could be applied to measuring ethylene and CO<sub>2</sub> sorption for both powder zeolites and PLA films coated with zeolites were developed. This was followed by determination of zeolite sorption of ethylene and CO<sub>2</sub> at various concentrations, temperatures and relative humidities, and also in the presence of additional gases. Then the natural step was to move to producing PLA zeolite films. Coating of PLA film with zeolites was the most successful of the attempted methods. Lastly, these films were investigated as to ethylene and CO<sub>2</sub>sorptionat various concentrations, temperatures and relative humidities, and also in the presence of additional gases.

This project was designed to provide information about how to produce a desired wt% combination of zeolite on PLA film so that the sorption capacity of the zeolites is not inhibited by the high barrier of PLA to ethylene. The goal was to produce not a system that absorbs the most, but rather one that is most efficient in adsorbing concentrations that are most relevant to real life situations, and to compare it to commercially available packages that are claimed to be ethylene scavengers that extend fresh produce shelf life.

#### CHAPTER 2

#### Literature review

#### 2.1. Active Packaging

The main concern of food packaging has always been to use appropriate packaging materials and methods to ensure the safety and health of food products, but also to minimize product losses. As consumers expect high quality, fresh-like quality and easy to access fresh produce, the industry must match these demands. One way to achieve it is by using active packaging technology for perishables.

Active packaging (AP) can be described as a packaging system that enhances shelf life by doing more than simply contain the product. For foods, often this involves incorporating additives as a part of the packaging material or placing them inside of a container to modify or to interact with the headspace in the package and extend the products shelf life. AP has to fulfill consumer demands of high quality, fresh-like quality and safety of food products. This technology involves interactions between the package or package component and the food or internal gas atmosphere. The main purpose of many active packaging technologies is to extend the shelf life of fresh produce while preventing loss of nutritional quality and freshness, and at the same time inhibiting the growth of pathogens and spoilage microorganisms. The market for active packages has been rapidly growing in the last several decades[1-3, 89].

Two mechanisms by which active packaging works are based on where and how the active element is incorporated. It can be placed inside the package but separate from the food, for example as a sachet, or it can be incorporated into the packaging material [1,4-5].

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The classification of active packaging systems depends on their principle of operation. They might be scavenging or emitting systems. Within these two actions, AP might work with different gases (oxygen, carbon dioxide, ethylene, ethanol, etc.) by both absorption and release. But also moisture control, antimicrobial and antioxidant releasing, flavor releasing and absorbing, light absorbing or regulating, and color containing systems are known. Advanced AP systems might have dual or multiple functionality since fresh produce will be influenced by many factors and will need or produce more than one gas. For instance, a popular combination is oxygen scavengers with carbon dioxide emitters, or sometimes also releasing antimicrobials. Often these combined systems will complement each other. For example, an oxygen absorber when combined with ethanol (C<sub>2</sub>H<sub>5</sub>OH) and antimicrobial release will be more effective than the oxygen scavenger alone [1-8].

Until now, the most popular way of creating an active packaging system was to place additives in the form of a sachet, sheet, label or closure liner inside of a package. Sachets may not be the safest due to the danger of being eaten or ruptured and allowing active components to contact the food. Also contents of these sachets have not always been safe. For example, the most common ethylene absorbing system consists of potassium permanganate imbedded in silica. First silica absorbs ethylene which is then oxidized by potassium permanganate to ethylene glycol. It is a very popular scavenger due to its low cost and the ease of placing a sachet with an active compound inside a package. Unfortunately, potassium permanganate is toxic, so it should not be in direct contact with any food products [1, 7-8].

The newer option is to incorporate active elements directly into the material or on the surface of it. The choice of proper polymer will also play a critical role in the efficiency of such a system. If a polymer has high barrier properties to the gas which is to be absorbed, having an active element too deep into the polymer matrix will inhibit its sorption capacity. But having the element on the surface will permit adsorption. This way the characteristics of the active element will be the least affected by the polymer material itself. Incorporating of active elements, for example zeolites, into polymer film might be done by using different production processes, extrusion from a masterbatch, lamination or coating, etc [1,7-8].

Table 2.1 shows a variety of active packaging systems with their mechanism of action (active element) and food applications. It can be seen that with these already known systems we can successfully control concentrations of headspace gases along with moisture content, temperature, etc. Foods for which those AP systems can be applied seem to be very vast.

AP system	Active element	Food		
Oxygen scavengers	Iron based Bread, cakes, cooked			
	Metal/acid	biscuits, pizza, pasta,		
	Nylon MXD6	cheese, cured meats and		
	Metal (e.g. platinum) catalyst	fish, coffee, snack foods,		
	Ascorbate/metallic salts	dried foods and beverages		
	Enzyme based			
Carbon dioxide	Iron oxide/calcium hydroxide	Coffee, fresh meats and fish,		
scavengers/emitters	Ferrous carbonate/metal halide	Nuts		
	Calcium oxide/activated charcoal			
	Ascorbate/sodium bicarbonate			
Ethylene scavengers	Potassium permanganate	Fruit, vegetables		
	Activated carbon			
	Activated clays/zeolites			
Ethanol emitters	Encapsulated ethanol	Pizza crusts, cakes, bread,		
		biscuits, fish and bakery products		
Moisture absorbers	Activated clays and minerals	Fish, meats, poultry, snack		
	Silica gel	foods, cereals, dried foods,		
		sandwiches, fruits and		
		Vegetables		
Flavor/odor	Acetylated paper	Fruit juices, fish, cereals,		
Absorbers	Citric acid	poultry, dairy products		
	Ferrous salt/ascorbate	and fruit		
	Activated carbon/clays/zeolites			

Table 2.1. Some examples of active packaging systems, adapted from [4].

Active packaging technology is still developing and will be based on advances in packaging material science but also on new consumer demands. Although active and intelligent packaging was first introduced in Japan in the mid 70s and 20 years later became an interest in industry in Europe and in the USA, this market is still growing. In 2001, active and intelligent packaging was worth 1.1 M US\$ with only two technologies accounting for80% of it - oxygen scavenging and moisture absorbents. The global value increased to 1.8 M US\$ by 2005 with 40% still taken by oxygen scavengers. Predictions for 2010 (forecasted in 2007) showed a growing trend in global market value, shown in figure 2.1. It should be also noticed that ethylene and CO<sub>2</sub> scavenging are still one of the smallest market shares, with just a few percent of the total, presented in figure 2.2 [7-8].



Figure 2.1. Global market value (million US \$) of active and intelligent packaging [7].



Figure 2.2. Global market share (%) of active and intelligent packaging [7].

Many of the AP systems used nowadays are still expensive and do not compensate for the cost with the benefits they bring. Handling of these packages can also cause issues, because having limited sorption/emission capacity of active components, it is not desirable for them to start to work before the product is packed. And most of all, consumers have to accept industrially applied solutions. Sachets and other foreign bodies inside the package may be a concern for consumers, especially with small children. AP with the active element incorporated into the polymer might be a more acceptable option [7-8].

## 2.2. Ethylene (C<sub>2</sub>H<sub>4</sub>)

Ethylene is a naturally occurring gas that works as a plant hormone and can cause different physiological effects in fresh produce. Ethylene accelerates ripening and senescence, and causes early maturity and softening of climacteric fruits and vegetables by increasing their respiration rate. It is a colorless gas, which is produced by plants. It can also induce yellowing of green vegetables. Too high levels of ethylene during storage can shorten shelf life and also produce some defects of the harvest like textural and color changes or even tissue degradation, for example russet spotting on lettuce and scald on apples. Not all ethylene effects are unwanted; some can be positive like degreening of citrus fruits or induction of flowering in pineapples [1-4, 9, 13-14].

Although ethylene is naturally occurring in plant tissues, the main sources of ethylene in the atmosphere are climacteric fruits and damaged or rotten produce. It is also produced by internal combustion engines, smoke and other sources of pollution. Climacteric fruits are fruits with high respiration rates that after harvest increase very rapidly during ripening and decrease during senescence. An increase in ethylene production is observed as the fruits ripen. Non-climacteric fruits have low respiration rates after harvest, which also decrease over time and are not influenced much by the presence of ethylene. Table 2.2 provides a list of climacteric and non-climacteric fruits and vegetables [9, 13-14].

Climacteric	Non-climacteric
Apple	Blackberry
Blueberry	Cherry
Nectarine	Cranberry
Peach	Cucumber
Pear	Grape
Plum	Raspberry
Tomato	Strawberry
	Watermelon

Table 2.2. Fresh produce classification based on respiratory behavior during ripening, adapted from[13].

For climacteric fruits, lowering ethylene concentration can delay ripening, but without it normal ripening cannot occur. For instance, tomatoes need ethylene to develop a red color and to soften. Although different fruits have different production rates of ethylene, when stored together with other fruits they can be affected by high ethylene levels produced by the other fruits. Table 2.3 shows differing ethylene production rates of fruits and vegetables [9, 13-15].

		Fresh produce	
Class	(20°C) (μ C₂H₄/kg h)		
Verylow	Less than 0.1	Cauliflower, cherry, citrus fruits, grape,	
veryiow		strawberry, pomegranate, potato	
		Blackberry, blueberry, cranberry,	
Low	0.1 - 1.0	cucumber, pineapple, pumpkin,	
		raspberry, watermelon	
Moderate	1.0 - 10.0	Banana, fig, mango, tomato	
High	10.0 - 100.0	Apple, avocado, nectarine, papaya,	
півц	10.0 - 100.0	peach, pear, plum	
Very high	more than 100.0	Mammee apple, passion fruit	

# Table 2.3. Commodities classified according to ethylene production rates, adapted from [13].Production rate at 68°F

Even very low concentrations of ethylene, at the level of parts per billion (ppb) and parts per million (ppm), can be critical. Table 2.4 shows how small amounts of ethylene are produced by given perishables and also lists their ethylene sensitivity [13].

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Table 2.4. Ethylene production and sensitivity of some fresh produce, adapted from [13].

Fresh produce	Ethylene production	Ethylene sensitivity (ppm)
Climacteric Fruit		
Apple, kiwifruit, pear	High	high (0.03 - 0.1)
Avocado, passion fruit	High	medium (> 0.4)
Banana, mango	Medium	high (0.03 - 0.1)
Nectarine, papaya, peach, plum, tomato	Medium	medium (> 0.4)
Vegetables and non-climacteric fruit		
Broccoli, Brussels, cabbage, carrot,		
cauliflower, cucumber, lettuce, potato,	Low	high (0.01 - 0.02)
spinach, strawberry		
Asparagus, celery , citrus	Low	medium (0.04 - 0.2)
Berries, cherry, grape, pineapple	Low	low (> 0.2)

Exposure to ethylene can bring positive or negative effects. The effect may also depend on when exposure to this plant hormone occurs. Ethylene effects can be very different like physiological disorders (chilling injury, russet spotting, superficial scald, internal browning), abscission, bitterness, toughness, off-flavors, sprouting, color changes (yellowing or discoloration) and softening [9, 13-14, 16]. Some examples are listed in table 2.5.

 Table 2.5. Positive and negative effects of the same ethylene response, adapted from [13].

Ethylene response	Positive effect	Negative effect
Accelerates chlorophyll loss	Degreening of citrus	Yellowing of green vegetables
Promotes ripening	Ripening of climacteric fruit	Overly soft and mealy fruit

In the horticultural industry different methods have been applied to reduce ethylene's impact on fresh produce during both storage and distribution. The most common ones are low temperatures and controlled atmospheres but also using filters/scrubbers to remove ethylene present around stored fruits and vegetables. Low temperature is proven to lower the respiration rate of fresh produce, and controlled atmosphere utilizes low oxygen and high carbon dioxide concentrations which will also result in lowering respiration rates. But not all of these technologies can be used when dealing with closed packages where ethylene will be accumulating [1-4, 9].

Packaging technologies involving control of ethylene inside packages are based on scavenging it. The most widely used systems involve sachets. As mentioned before, these might contain potassium permanganate, which is toxic and causes concerns about KMnO<sub>4</sub> migration into the produce. The second most common sachet-based C<sub>2</sub>H<sub>4</sub>scavenging system involves activated carbon with a metal catalyst. These systems can effectively remove ethylene from air passing over the sachet. Unfortunately, they require heat and moving gases, so they are not appropriate for closed packages. However activated charcoal impregnated with a palladium catalyst inside a paper sachet was proven to scavenge ethylene from kiwi, banana, broccoli and spinach [16].

Recently, there has been a focus on replacing sachets by incorporating active compounds directly into the package. Many of these newly developed polymer films consist of polyethylene impregnated with finely dispersed minerals. Often these minerals are local kinds of clay, zeolites or Japanese oya stone. They are produced as bags and are commercially available. Many of these companies are Japanese or Korean, but there are also some from the United States and Australia. A few of these companies and their packaging systems are listed in table 2.6 [9, 16].

Producer	Country	Market name	Active element	Packaging form
Air repair Products, Inc.	USA	N/A	Potassium permanganate	Sachets/blankets
Ethylene Control, Inc.	USA	N/A	Potassium permanganate	Sachets/blankets
Extenda Life Systems	USA	N/A	Potassium permanganate	Sachets/blankets
Mitsubishi Gas Chem. Co. Ltd	Japan	Sendo-Mate	Activated carbon	Plastic film
Cho Yang Heung San Co. Ltd	Korea	Orega	Activated clays/zeolites	Plastic film
Evert-Fresh Corporation	USA	Evert-Fresh	Activated zeolites	Plastic film
Odja Shoji Co. Ltd	Japan	BO Film	Crysburite ceramic	Plastic film
Peakfresh Products Ltd	Australia	Peakfresh	Activated clays/zeolites	Plastic film
Grofit Plastics	Israel	Bio-fresh	Activated clays/zeolites	Plastic film
Food Science Australia	Australia	N/A	Tetrazine derivatives	Plastic film

 Table 2.6. Commercially available ethylene scavenger systems, adapted from [16].

Manufacturers offering bags made of minerals dispersed within the film advertise their products as ethylene adsorbing products, often reusable ones. To prove that their product works as described they provide results from shelf life experiments where normal polyethylene bags are compared to their mineralized bags. Often the results presented show extension of shelf life or lowering of the ethylene concentration in the headspace. The explanation might not be so obvious as ethylene absorption by the minerals. As is the case for any finely distributed material within the bag, these minerals will also open pores in the plastic and influence barrier properties for different gases, including ethylene. Ethylene as a small molecule will diffuse more easily through open pores in the plastic than through the plastic itself. Also exchange of oxygen and carbon dioxide will be altered by the pores. O<sub>2</sub> will enter the bags while CO<sub>2</sub> will leave them. All of these processes will extend shelf life and decrease the concentration of ethylene inside the package, no matter the sorption activity of the mineral dispersed within the plastic bag. Even though many minerals have sorption capacity for ethylene, the biggest challenge is not to inhibit it when dispersing the minerals within the polymer matrix. Polymers with high barriers for ethylene will not allow any ethylene to get into such a mineral fast enough to extend the shelf life of fresh produce. This is why it is important to focus on methodologies of incorporating ethylene scavengers as close to the surface of the plastic as possible. Also experiments which are supposed to support ethylene absorption of a given system should be run in closed systems where part of plastic bag is placed and there will be no doubt that such a product removes ethylene from the headspace. Also conditions of such tests should mimic real conditions applied when packing perishables, i.e. low temperatures and high humidity, since it is known that temperature and humidity influences not only the production of ethylene by fruits but also influences sorption capacities of active compounds [1-4, 9, 13-14].

PeakFresh bags are marketed as ethylene absorbers. These polyethylene bags impregnated with zeolites have been tested in proper closed systems at 20°C and humidity of at least 40%. During a 24h period they did not absorb any measurable amount of ethylene [17-18].

## 2.3. Carbon dioxide (CO<sub>2</sub>)

Respiration is a metabolic process where organic substrates (carbohydrates, lipids and organic acids) are oxidized to carbon dioxide and water. During respiration  $O_2$  will be consumed and  $CO_2$  will be produced [21]. Different perishables have different respiration rates, which are listed in the table 2.7.

In general, after harvesting the respiration rates will determine how fast or slowly given fruits and vegetables will deteriorate. For commodities with high and very high respiration rates, concentrations of CO<sub>2</sub> inside the package can increase substantially after the packaging process is completed [3, 19-21].

Class	(mg CO <sub>2</sub> /kg h)	Fresh produce	
Very low	Less than 5	Dates, dried fruits and vegetables, nuts	
Low	5 - 10	Apple, celery, cranberry, garlic, grape, onion,	
LOW	5 - 10	papaya, potato (mature), sweet potato, watermelon	
		Banana, blueberry, cabbage, cherry, cucumber, fig,	
Moderate	10 - 20	lettuce (head), nectarine, olive, peach, pear, plum,	
		potato (immature), tomato	
High	20 40	Blackberry, carrot (with tops), cauliflower,	
півіт	20 - 40	lettuce (leaf), raspberry, strawberry	
Very high	40 - 60	Broccoli, Brussels sprouts, green onions	
Extromoly high	Mars than CO	Asparagus, mushroom, parsley, peas, spinach,	
Extremely high		sweet corn	

#### Table 2.7. Fresh produce listed in groups according to their respiration rates, adapted from [13]. Bange at 41°E (5°C)

High levels of  $CO_2$  in the headspace are in general beneficial in many cases due to slowing down respiration and lipid oxidation, reducing color change, and inhibiting growth of molds, yeasts and bacteria. Keeping a high concentration of  $CO_2$  in the package can also prevent it from collapsing. This is why there have been many carbon dioxide emitters used in active packaging systems [1,3].

However, excessive concentrations of CO<sub>2</sub> inside the package might reduce the pH of the product, which will result in development of an acid taste or cause flavor tainting and drip loss. Also if the wrong packaging material is used, especially with high respiration classes of perishables, there is a danger of blowing up the package by excessive package expansion, which is very problematic with packaging of freshly roasted or ground coffee. For rigid packaging, carbon dioxide scavengers will inhibit increasing gas pressure while for flexible packaging. They will reduce volume expansion [23-24].

All perishables have a safe range of oxygen and carbon dioxide, based on tolerances to each gas. Tolerances for  $CO_2$  are listed in the table 2.8. If concentrations of carbon dioxide are too high around fresh produce then damage to the commodities may happen, like unfavorable physiological disorder, for example breakdown of internal tissues. To avoid those changes, keeping CO<sub>2</sub> concentrations below the

CO<sub>2</sub> tolerance limits is desired [3, 9, 21].

Table 2.8.	Commodities gro	ouped according to	o their toleran	ce to CO2 conce	ntrations, ad	apted from
[13].						
Maximu	m CO <sub>2</sub> concentrat	ion				

	Fresh produce		
tolerated (%)	rresh produce		
	Apple (Golden Delicious), Asian pear, European		
2	pear, grape, olive, tomato, pepper (sweet),		
	lettuce, Chinese cabbage, celery, sweet potato		
	Apple (most cultivars), peach, nectarine, plum,		
5	orange, avocado, banana, mango, papaya,		
5	kiwifruit, cranberry, pea, pepper (chili),		
	cauliflower, cabbage, Brussels sprouts, carrot		
	Grapefruit, lemon, lime, pineapple, cucumber,		
10	asparagus, broccoli, parsley, green onion, dry onion,		
	garlic, potato		
1 5	Strawberry, raspberry, blackberry, blueberry,		
13	cherry, fig, sweet corn, mushroom, spinach		

Carbon dioxide emitters or scavengers are provided mostly in the form of sachets or labels. CO<sub>2</sub> absorbers are not only important for coffee but also for battered goods, cheese, fresh and dehydrated meat and poultry products. Most carbon dioxide scavengers just scavengeCO<sub>2</sub>, but there are also many dual action scavengers that will at the same time scavenge CO<sub>2</sub> and O<sub>2</sub>. The most common carbon dioxide scavengers are composed of calcium hydroxide, sodium hydroxide, potassium hydroxide, calcium oxide or silica gel. When CO<sub>2</sub> reacts with hydroxides, it produces carbonates. Polyethylene-lined coffee pouches with mixtures of calcium oxide and activated charcoal have been used as CO<sub>2</sub> scavengers but the more common systems in Japan and the USA are the dual-action scavengers [19-25]. These sachets and labels are commercially available for canned and foil pouched coffees [22]. Such systems will contain iron powder to scavenge O<sub>2</sub> and calcium hydroxide to scavenge CO<sub>2</sub> [3].

Active packaging systems involving carbon dioxide are a relatively small part of the AP market.

There is a growing interest in CO<sub>2</sub> scavengers and emitters, especially for dual action scavengers [5].

A list of commercially available single or dual action  $CO_2$  scavengers is given in table 2.9 [7].

Producer Market name Country Mechanism of action Mitsubishu Gas  $CO_2$  scavenging  $(Ca(OH)_2)/O_2$  scavenging (iron Chem. powder) Freshlock/Ageless E Japan Mitsubishu Gas Chem.  $CO_2$  generating (ascorbic acid)/ $O_2$  scavenging Ageless G Japan **Toppan** Printing Fertilizer CV  $CO_2$  s and  $O_2$  scavenging (non-ferrous metal) Со Japan Toppan Printing Со Fertilizer C and CW  $CO_2$  generating  $/O_2$  scavenging Japan  $CO_2$  generating  $/O_2$  scavenging Multisorbtechn. Freshpax M USA S.A.R.L. Codimer Verifrais France CO<sub>2</sub> generating Toagosei Chem. Ind. Co. Vitalon G  $CO_2$  generating  $/O_2$  scavenging Japan

Table 2.9. Commercial  $CO_2$  active packaging systems with possible  $O_2$  scavenging activity, adapted from [7].

## 2.4. Zeolites

Zeolites are microporous crystalline aluminosilicates of alkali and alkaline earth elements. We can differentiate naturally occurring and synthetic zeolites. They are characterized by unique threedimensional framework structures composed of tetrahedral SiO<sub>4</sub> and AlO<sub>4</sub>. Within zeolites, we can differentiate types based on the framework structure. Many zeolites are also modified by exchanging cations, in order to increase their specific activity[27-28].

Zeolites are composed of metal extraframework cations, framework ( $SiO_4$  and  $AlO_4$ ) and sorbed phase (H<sub>2</sub>O molecules). The extraframework metal cations are ion exchangeable. The framework can vary a lot in number of Al. The ratio between silicon and aluminum can be between 1 and infinity. Framework composition is controlled during synthesis for synthetic zeolites. With increasing Si/Al ratio, hydrothermal stability and hydrophobicity increases. During synthesis water will fill the internal voids of a zeolite. To remove water, thermal treatment is used which results in making the intracrystalline space available. Loss of water does not change the structural integrity. Having crystalline frameworks will result in uniform pore openings within a crystal. Substitution of Si by AI will result in negative charge density in the lattice of the zeolite. Neutralization of that charge is done by introduction of exchanged monovalent, divalent or trivalent cations in the structural sites of the zeolite. Metal cations occupy cavities in the channel walls and are coordinated with H<sub>2</sub>O molecules within the channel. If small cations are replaced by high molecular weight cations (e.g. cationic surfactants), exchange will occur at the external surface since the surfactants are too large to enter the zeolite pores. The most common applications of zeolites as molecular sieves and ion exchangers are due to different chemical, physical and structural properties within known zeolites. Using different concentrations of surfactants, such a modified zeolite can adsorb any of three major types of adsorbates, i.e. cations, anions and non-polar organics [11-12, 27-29].

Most natural zeolites are formed from volcanic glass. When saline ground water attacks the surface of the glass, it will leach soluble oxides and salts, which will leave zeolite crystals on the glass surface. Volcanic eruptions produce very reactive glasses, in the fly ash. To start nucleation of the crystals, relatively low heat is required so no excessive depth or volcanic activity is necessary for synthesis. Higher temperatures will result in production of quartz. Most natural zeolites will contain potassium since it is the most common cation in alkaline ground waters. About 40 natural zeolites are known. Most of them have lower Si/Al ratios than synthetic zeolites due to the absence of organic structure-directing agents. The two most commonly used natural zeolites are clinoptilolite and mordenite. They are extensively used for ion-exchange and sorption [27-28, 30].

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There are over 150 known synthetic zeolites. Most of them have no natural analogues. When compared to natural zeolites, they are characterized by high purity, uniform pore size and better ion-exchange abilities. Manufacture of synthetic zeolites requires specifically controlled temperature, pressure and time. In general, such a synthesis will be as follows: reactants (i.e. silica, alumina) will be mixed with the cation source (often in a high pH water-based medium), then the aqueous reaction mixture will be heated, usually above 100°C, in a sealed autoclave. During that time reactants will remain amorphous and after a specific time, crystalline zeolites will be present. At the end of the synthesis process, all amorphous material will be replaced by product crystals which will be recovered by filtration, washing and drying. Synthetic zeolites are also mostly applied in adsorption, ion exchange and catalysis [30-32].

Unique properties such as thermal stability, acidity, surface hydrophobicity or hydrophilicity, large ion-exchange capacity, low density, large void volume, uniform molecular sized channels, sorption of many different gases and vapors and catalytic properties make zeolites available for many applications. Although they are mostly used in catalysis, ion exchange and adsorption, they have become materials of interest also in other fields. For example, in environmental aspects they can be used for water purification, where they are capable of removing ammonia, heavy metals, radioactive species and organic substances. In industry, zeolites are applied in petroleum refining, petrochemical, coal and fine chemical industries. There is also a growing interest in using zeolites in more special application fields which can be as vast as process intensification, green chemistry, hybrid materials, medicine, animal food uses, optical and electrical based applications, multifunctional fabrics and nanotechnology [27-33].

Separation and purification of gas mixtures by selective adsorption is one of the most important and popular application of zeolites. It is utilized in the chemical, petrochemical, environmental, medical

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and electronic gas industries. A multitude of both natural and synthetic zeolites characterized by sorption capacities versus different gases are of growing interest also in other fields, like packaging. A variety of synthetic zeolites with high purities and the abundance of natural zeolites in some volcanic areas, together with their high sorption capacities, make them new and competitive alternatives to commercial sorption systems used nowadays [27-33].

Although not specifically for packaging applications, many zeolites have been proven to adsorb gases that play crucial roles in perishables and other products packaging. These studies included ethylene, carbon dioxide, ethane, propane, etc. Most of them were performed on zeolites themselves, not incorporated in any kind of material. ZSM-5 zeolite was proven to adsorb CO2 and C2H4, with increasing preference for those polar molecules with a decrease of the Si/Al ratio [33]. Engelhard titanosilicate (ETS-10) had isotherms measured for ethylene and ethane adsorption. When ETS-10 was exchanged with Na-, K- and Ag- cations, it was found that all of them had a strong absorption for both gases [34-35]. Large zeolite NaX crystals when dispersed with CuCl crystals demonstrated effective separation of ethylene and ethane mixtures through adsorption [36]. Adsorption kinetics and equilibria of carbon dioxide, ethylene and ethane were investigated for type 4A(CECA) commercial zeolite. There was decreasing adsorption affinity proven in the order  $CO_2>C_2H_4>C_2H_6$  which makes 4A zeolite capable of separating binary mixtures of the three gases [29]. Also 13X zeolite could be a good candidate for separation of ethylene from CO<sub>2</sub>, as it was reported to have ethylene adsorption properties [37]. G5 zeolite was investigated as a possible ethylene adsorbent. An automated apparatus recorded adsorption isotherms for methane, ethane and ethylene. It was discovered that G5 increases adsorption with increase in carbon number and amount of unsaturation (methane<ethane<ethylene) [38]. Comparison of natural clinoptilolite (CLN) and its modified forms showed the uptake of ethylene increasing in the following order Ca-CLN < Na-CLN < K-CLN < Natural CLN, which proved that natural CLN has a
considerable potential for ethylene removal [12]. Synthesized and modified with phenyl trimethyl ammonium bromide (PTAB), NaY zeolite demonstrated enhanced ethylene adsorption [11].

There is a relationship between the kinetic diameter of adsorbates and pore sizes in zeolites. A given zeolite cannot absorb gases of higher kinetic diameter than the pore size within the zeolite framework. Kinetic diameters of some gases and vapors are listed in table 2.10.

Gas	Kinetic diameter d <sub>k</sub> (Å)
H <sub>2</sub>	2.89
O <sub>2</sub>	3.46
N <sub>2</sub>	3.64
CO	3.76
CO <sub>2</sub>	3.3
$C_2H_4$	3.9
H <sub>2</sub> O	2.65

Table 2.10. Kinetic diameters of some gases, adapted from [74].

In porous solids, their surface and structural heterogeneity are sources of their adsorption capacity. Since zeolites have a regular structure, only defects in the framework, micropores or the crystal surface can result in heterogeneity. Channels and cavities in zeolites have molecular dimensions with their size and configuration being intrinsic properties of the given crystalline framework. Moreover, exchangeable cations will produce local electrostatic fields that will be very much responsible for any strong affinity for water and some polar molecules. Any zeolite crystal is well-defined and having a specific composition and structure will display adsorptive behavior. Changing the framework structure, the Si/Al ratio or cations within the zeolite gives a way to vary its adsorbent and ion exchange properties [27,82].



pressure

Figure 2.3. Types of sorption isotherms, adapted from [86].

Literature provides many classifications and types of isotherms [93]. The Brunauer classification of general types of sorption isotherms used for this discussion is shown in figure 2.3 [86]. The type II isotherm of the Brunauer classification is normal for microporous adsorbents that have pore size similar to their sorbate molecules' diameter. A visible saturation limit is due to the complete filling of the micropores. The liquid density and the packing density in micropores are not necessarily the same. Packing density could get slightly higher if the adsorbate molecules jam to cause higher uptake. It could also get decreased by 75% due to geometry restrictions. An isotherm of type IV is displayed when intermolecular attractions are large. The presence of two separate surface layers on a surface or in the pores will result in a type IV isotherm. Adsorbents with a wide range of pore sizes, for example natural zeolites, will be only ones to display type I and III isotherms. Then continuous progression from monolayer to multilayer adsorption will be observed due to increased loading and then finally capillary condensation. High relative pressures will cause an increase in adsorption capacity because of capillary condensation happening in pores of increased diameter due to the increase of pressure. Adsorption on external surfaces is characterized by low adsorption energy and a high adsorption rate as opposed to adsorption in cages and cavities. When adsorbate molecules are small enough to access micropores, type I isotherms will result. But to ensure that, proper activation is needed. In cases when adsorbate molecules are too large or access to the micropores is inhibited, the only choice for adsorption is to happen in extracrystalline pores. Then capillary condensation and surface adsorption will lead to isotherms of type III. This situation was determined for clinoptilolite and benzene when zeolite was water-saturated [27, 82-83].Adsorption of ethylene on natural and modified clinoptilolite was characterized by Erdogan et al, and it was found that all samples displayed type II isotherms. With an increase in temperature, the total sorption capacity was decreased. A comparison of natural to modified clinoptilolite showed higher ethylene sorption for the natural one, suggesting that ethylene can pass through the pore openings in clinoptilolite [12]. Chemisorption assumes that sorption takes place at specific sites, while physisorption is non-specific and has highly mobile adsorbed layers. There are many zeolite/adsorbent systems where each cage can only adsorb one specific molecule. Physisorption is usually characterized by multilayer adsorption. In some pores, a series of layers could built up. Capillary condensation happens when saturation vapor pressure in small pores is decreased by surface tension. As a result of capillary condensation, isotherms with a characteristic upward turn can be observed. It must be remembered that the capillary effect is only relevant in the case of small pores or relatively high partial pressures [82-84]. Often binary gas mixtures are investigated and their adsorption equilibrium is determined. Ethylene-carbon dioxide mixture sorption was characterized in ZSM5 zeolite by Jingu et al.

Based on the cation radius of molecules of interest it was the reason why carbon dioxide had higher adsorption capacity in zeolite than ethylene did. Larger cations in CO<sub>2</sub> have higher polarizability due to their larger ionic radius [85].

Based on the literature about zeolite sorption capacities and isotherms, commercial availability and applications as well as physical properties, two zeolites were chosen for study in development of an active packaging system with PLA as the polymer material: clinoptilolite as a natural zeolite and type 4A zeolite as a synthetic one. In table 2.11 some physical properties of these two compared to other commercial zeolites are listed [28, 81].

Zeolite	Crystal framework	Crystal structure	Frame-	Crystal density	Common ion- exchanged	Nominal pore	Pore Volume
	Si/Al ratio	symmetry	type	[g/cm <sup>3</sup> ]	forms	opening (Å)	[cm³/g]
					Na, K, Ag, Mg,		
А	0.7 - 1.2	Cubic	LTA	1.52	Са	3, 4, 5	0.508
Х	1.0 - 1.5	Cubic	FAU	1.47	Na, Li, Ca, Ba	7.5 - 10.0	0.506
Mordenite	4.5 - 5.0	Orthorhombic	MOR	1.83	Na, H, Ca	4	0.293
Chabazite	1.6 - 3.0	Trigonal	CHA	1.67	Na, Ca	4.9	0.434
Clinoptilolite	4.2 - 5.2	Monoclinic	HEU	1.85	K, Ca	3.5	0.279
ZSM-5	very high	Orthorhombic	MFI	1.79	none	5.3	0.242

Table 2.11. Physical properties of zeolites used commercially [28, 81].

#### 2.4.1. Clinoptilolite as the chosen natural zeolite

Clinoptilolite (CL) is one of the most commonly used natural zeolites due to commercial mining in the USA, Australia, Russia, Slovenia, Cuba, Indonesia, South Africa, Greece, Bulgaria, New Zealand, Turkey, China, Mexico, Hungary, Jordan and Outer Mongolia. CLs composition can be written as: Na<sub>5</sub>KCa<sub>25</sub>[(AlO<sub>2</sub>)<sub>7</sub>(SiO<sub>2</sub>)<sub>29</sub>]·24H<sub>2</sub>O.It has a monoclinic HEU framework type with a =17.718Å, b=17.879Å, c=7.428Å and  $\beta$ =116.42°, showed as HEU in [43]. The HEU is built using T9 (T = tetrahedral) units, where T9 stands for a double 4-ring (d4r) with additional bridging T atom(bold in figure 1 on page 156 in [44]. T9-units are connected into chains (as seen in figure 2 on page 156 in [44]). The two dimensional Periodic Building Unit (PerBU) connects neighboring chains through 4- and 5-rings (as in figure 3 on page 157 and figure 5 on page 158 in [44])[39-40, 43-44]. Neighboring PerBUs are connected through 8- and 10-rings [43].

#### 2.4.2. Type 4A zeolite as the chosen synthetic zeolite

Type 4A zeolite is one of the most commercially used synthetic zeolites. Its chemical formula is as follows:  $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$ . It has a cubic LTA framework with a = 11.9Å [43]. The LTA can be built from three different composite building units - d4r, sod, and Ita (as LTA in [43]). The Periodic Building Unit of the LTA - sodalite cage consists of 24T atoms (six 4-rings or four 6-rings). When PerBUs are linked through double 4-rings, a three dimensional LTA framework is formed (as in figure 2 on page 198 in [44]) [41-43]. An alternative PerBU can be obtained from d4rs. In cubic LTA channels are 8-ring ones [43].

### 2.5. Application of zeolites in active packaging

Although zeolites have been widely characterized based on their wide range of applications, there are limited reports of utilization in active packaging. Most studies have been done on zeolites not incorporated into any packaging materials or polymers.

A novel palladium-impregnated zeolite was tested at 20°C and approximately 100% RH. Ethylene concentrations were quantified by gas chromatography (GC FID) while zeolite samples were kept in closed jars. The new material was compared to that most commonly used in food packaging, potassium permanganate (KMNO<sub>4</sub>). It was determined that the zeolite material had significant adsorption capacity (4162  $\mu$ L/g) and was superior to KMNO<sub>4</sub>. Significant amounts of C<sub>2</sub>H<sub>4</sub> were removed within a few hours. Later experiments involved putting pieces of bananas and strawberries into similar jars. With actual produce, the Pd-promoted material was still very effective and decreased  $C_2H_4$  levels to sub-physiologically active levels only within the first 3 days of storage [87]. Further studies on palladiumpromoted zeolite material were carried by Rowsell et al [88]. The system and method were very similar as it involved zeolites, jars and micro GC equipped with TCD. Experiments were carried out at low temperature (5°C) and 0% or 100% RH. It was found that the material is not only an effective ethylene scavenger when green bananas and green avocado fruits are placed in jars but also reduced production of CO<sub>2</sub> was observed in such systems [88].

Studies of ethylene-moisture absorbent sachets placed in polyvinyl chloride-polyethylene trays heat sealed with polyethylene terephthalate/adhesive/cast polypropylene combination lid films and filled with fresh strawberries involved also chlorine dioxide (ClO<sub>2</sub>)treatment as a sanitizing agent. Measurements took 3 weeks and were done at 4°C. It was found that in the presence of the sachets ethylene production was inhibited for 7 days. After that time the sachets reached saturation. Minimum CO<sub>2</sub> levels were present in the packages due to the ClO<sub>2</sub> treatment [89].

Actual polymer materials containing zeolites and described as ethylene scavengers that have been evaluated in literature are polyethylene-based. Chilean natural zeolite (NZ-Ch) has been incorporated into LDPE film by extrusion of a masterbatch. Produced films were varied by different wt% of NZ-Ch (2.5, 5.0, 7.5 and 10.0 wt%). Ethylene adsorption in active films was evaluated by GC while film samples were kept in adsorption cells at 25°C. Results showed that in the first 50 hours ethylene concentration is reduced quickly while after that time  $C_2H_4$  removal is much slower. After a total time of 100 h, 37% of the ethylene content was scavenged [10]. Experiments involving an LDPE/zeolite system and applied to broccoli were designed to resemble real life situations. Broccoli was packed in LDPE bags that had 8 wt% zeolites incorporated into the material. The production method was blown film extrusion from a masterbatch of LDPE and Tazetut zeolite. Analysis of CO<sub>2</sub> concentration (%) and  $C_2H_4$  content (ppm)was done by gas analyzers. Packages were kept for 20 days at 25°C and RH inside the packages was 90%. It was determined that throughout the whole experiment the concentration of  $C_2H_4$  in the zeolite based bags was 0.33 ppm. Carbon dioxide concentrations were about 9% during the storage time. New LDPE/zeolite packaging materials were able to prevent changes in physicochemical characteristics of broccoli and extend their shelf life from 5 to 20 days when compared to produce packed in normal LDPE bags [26].

No literature about ethylene scavenging or active packaging materials composed of PLA and zeolites was found.

#### 2.6. Polymer/zeolite systems

For packaging purposes, zeolites are often incorporated into polymers to form a polymer/zeolite film with no need of using sachets or any other non-incorporated parts of active packaging systems. Several ways to successfully incorporate zeolites into different polymers have been developed.

One of the common technologies for mixing polymers with additives is production of a masterbatch followed by extrusion. A composite material containing low density polyethylene (LDPE) and Chilean natural zeolite was prepared by masterbatch production in a co-rotating twin-extruder, followed by pelletization and dilution of the masterbatch by addition of LDPE pellets in a co-rotating twin-extruder, with extruded film collected on a chill roll. No compatibilizer was used and the resulting film was proven to work as an active packaging system for ethylene scavenging [10]. A similar process was utilized for production of PLA/zeolite composite film where two zeolites, synthetic type 4A and natural chabazite, were used. First PLA and zeolites were placed in a micro extruder with co-rotating twin-screws; the extrudate was transferred to a mini-injection molder and discs were formed. To produce a thin film, discs were compressed. Again no compatibilizer was needed [51-52].

Production of polyethylene (PE) film with zeolites was attempted with six different manufacturing methods: hot pressing, addition of zeolite to molten PE and dissolved PE solution, coating PE beads with zeolite in a revolving heating pan, extrusion of PE beads with zeolite and finally hot pressing of the extruded mix film. In hot pressing there were two alternative procedures. The first was to embed zeolite onto the surface of PE film confined between two plates. The second was to spread large zeolite particles on polyethylene film. In both cases the resulting films did not have uniform spreading of the zeolites. When adding zeolite to melted or dissolved solutions of polyethylene there were also two procedures tested. The first was to melt polyethylene and add zeolite to the melt. But the mixture was not perfectly homogeneous. Next film was produced by spreading the mixture using an automatic spreading machine. The second option was to dissolve PE in solution and then add zeolite to it. After obtaining a homogeneous mixture, it was poured as a thin film in a petri dish and dried in a vacuum oven to evaporate the solvent. The sizes of the zeolite particles had a big influence on the process; too large particles yielded a very heterogeneous appearance of the final film, while too small particles required greater amounts to be used and increased the density of the film. Also the spreading of the hot mixture caused trouble. The solution was too hot and too viscous to use in the automatic spreading machine. Manual spreading produced thickness that was not uniform. In both cases, the mixture was cooling too fast and sticking to the spreader blade. When using solvent, the mixture of the dissolved PE and zeolite was like a jelly, which did not help with uniform spreading. Evaporation of the solvent gave relatively thick films which were then hot pressed to thin films. When compared to hot pressing, using solutions of PE was relatively more successful, resulting in more uniform distribution of zeolite, a more flexible and clear film and control over thickness. But they also had too many drawbacks to be applied in industry, which made it too expensive, i.e. toxic solvent (xylene), took a long time to remove, additional equipment and good ventilation was required for evaporation. The last group of methods involved coating of PE beads with zeolite. A rotating stainless steel heated pan was used. For extrusion, the PE beads were mixed with zeolites and heated only enough for the zeolites to attach to the partially melted beads. Next they were hot extruded. Such films had large amounts of zeolites but also low flexibility and many surface defects like holes. The curing process applied was again hot pressing. Coating followed by extrusion had in general a very low production rate. Attaching zeolites to beads was also very difficult. During extrusion, heavy aggregates of zeolites sedimented on the bottom of the films. In general this last method resulted in non-uniform films and a lot of material was lost in the process [52].

Blown film extrusion is another manufacturing process applied for zeolite filled polymeric film production. Zeolite beta (BEA) and ZSM-5 were first mixed with LDPE in a mixer with a roller rotor and then ground into small pieces and finally blown film was extruded using a single screw extruder. Using modified zeolites, enhanced ethylene permeability and ethylene/ $O_2$  selectivity were observed [53].

Solution casting/solvent evaporation and melt mixing/compression molding have been proven as successful methods of producing PLA/silver zeolite composite films. Using dichloromethane as a solvent, PLA/silver zeolite mixtures were cast on petri dishes, dried overnight and desorbed in a vacuum oven in the first method. The second method involved PLA/silver zeolites melt mixed in a twin screw mixer, cooled down to room temperature and turned into sheets by compression molding in a hot-plate hydraulic press. It was determined that films produced by the first method were characterized by better Ag+ migration and antimicrobial activity [54].

Chloroform solution casting followed by thermoforming was the production process of choice for poly(lactic acid) film composites filled with mica, zeolite and vansil [55].

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# 2.7. Poly(lactic acid) (PLA)

Poly(lactic acid) is a biobased polymer that is certified to be compostable in industrial compost systems. PLA can be obtained from renewable resources like corn, potato or sugar beets. PLA is produced from lactic acid (2-hydroxy propionic acid) by two different polymerization methods, polycondensation or ring-opening polymerization (ROP). Lactic acid (LA) can be obtained by carbohydrate fermentation or chemical synthesis. Most of the lactic acid in the market is produced by fermentation. During this process, conversion of sugars to lactic acid is done by microorganisms in anaerobic conditions. Most of these microorganisms will be inactive with oxygen present. Since lactic acid is a hydroxyl acid with an asymmetric carbon atom, there are two optically active configurations, the L(+) and D(-) isomers. ROP of the ring formed dimer, dilactide, will produce high molecular weight poly(lactic acid), while polycondensation of lactic acid will give PLA with low molecular weight and poor mechanical properties, which makes it undesired for many applications [57, 59-61]. Structure of PLA is shown in figure 2.4.



Figure 2.4. Poly(lactic acid).

Poly(L-lactic acid) (PLLA) is most commercially produced PLA polymer. Substrate L-lactide (LLA) is prepared by corn starch fermentation. PLLA is characterized by semicrystallinity, high melting and glass transition temperatures (T<sub>g</sub>), excellent mechanical properties, good biocompatibility, low toxicity and versatility. Disadvantages that limit its wide application are relatively high brittleness and hardness combined with very low elongation at break, hydrophobicity and a long degradation process [59-61, 90].

Poly(lactic acid) available in the market is a blend of PLLA and PDLA or a copolymer PDLLA (the result of LLA polymerization with DLLA). The ratio of D-/L-enantiomers and their sequence of arrangement can determine many properties of polymers. When PLLA is>90% then PLA will be crystalline while a decrease in PLLA content will result in more amorphous polymers, but also lower melting and glass transition temperatures [59-61, 91].

PLAs high cost of production used to limit its application as a packaging material in general. But as the cost has continued to decrease, PLA is more and more used. As it can be used in different manufacturing processes (extrusion molding, injection molding, blow molding, extrusion foaming, etc) its potential applications in the packaging industry are vast. Nowadays it is commercially used as a retail package for fresh food in the form of clamshell containers, thermoformed foam trays or pouches made of film, but also as beverage bottles or blister packages. With growing public concern about eliminating petrochemical based polymers from the food industry, PLA has become a material of interest [56-60].

Barrier properties of packaging materials are crucial when decisions are made about products. In the fresh produce industry concentrations of headspace gases (carbon dioxide, oxygen, nitrogen, ethylene) and moisture content inside the package will determine how fresh and safe, and for how long, perishables will be. Barrier properties of commercially available polymers used in the packaging industry have been measured at many different conditions. Permeabilities of several common gases in polymers are presented in the tables 2.13 - 2.17.

PLA has lower  $CO_2$  permeability coefficients than many petroleum-based polymers, which makes it a better carbon dioxide barrier (table 2.12) [92].

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	CO <sub>2</sub> Permeability (10 <sup>-17</sup> kg m	ı/m² s Pa)
Polymer	23°C	30°C
Poly(lactic acid)	-	1.52
High-density polyethylene	4.44 - 6.31	5.25
Low-density polyethylene	6.31 - 13.5	52.82
Poly(ethylene terephthalate)	0.18 - 0.44	0.02
Polypropylene	9.0 - 18.0	13.8
Polystyrene	-	13.2

Table 2.12. CO<sub>2</sub> permeability coefficients at 23°C and 30°C, adapted from [92].

Oxygen permeability values show that barrier properties of PLA and many petroleum-based

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polymers are similar (table 2.13). PLA, polyolefins and polystyrene are poor oxygen barriers [92].

	O <sub>2</sub> Permeability (10 <sup>-17</sup> kg m	ı/m² s Pa)
Polymer	23ºC	30°C
Cellophane	0.0013	-
Poly(vinyl alcohol)	0.0001	-
Poly(ethylene terephthalate)	0.0540	0.0333
Poly(lactic acid)	-	0.4948
High-density polyethylene	-	1.5924
Low-density polyethylene	4.3183	8.2498
Polypropylene	1.3490	3.4540
Polystyrene	3.7780	1.6464

Table 2.13. O<sub>2</sub> permeability coefficients 23°C and 30°C, adapted from [92].

Values for nitrogen permeability coefficients at 30°C are listed in table 2.14. The PLA value is

much larger than for PET , but very similar to N<sub>2</sub> permeability coefficients of PS and LDPE [63].

	N <sub>2</sub> Permeability (10 <sup>-14</sup> kg m/m <sup>2</sup> s Pa)
Polymer	30°C
Poly(lactic acid)	1.93
Poly(ethylene terephthalate)	0.0119
Polystyrene	3.27
Low-density polyethylene	2.82

# Table 2.14. N<sub>2</sub> permeability coefficients at 30°C [63].

Table 2.15lists water vapor permeabilities. High values for PLA show that it is a poor barrier to  $H_2O$  [92].

H <sub>2</sub> O vapor Permeability (10 <sup>-13</sup> kg m/m <sup>2</sup> s Pa)		
Polymer		23°C
Poly(lactic acid)		80 - 360
Cellulose nitrate		472
Poly(ethylene terephthalate)		110
Polystyrene		670
High-density polyethylene		225
Polypropylene		225
Low-density polyethylene		670

Table 2.15.  $H_2O$  vapor permeability coefficients at 23°C, adapted from [92].

Ethylene permeability of amorphous PLA and couple of conventional polymers are listed in table 2.16. A decrease in ethylene permeability was associated with increasing crystallinity of PLA. All three materials are good barriers for ethylene, which makes it undesired for fresh produce packaging since accumulation of  $C_2H_4$  inside the package will occur resulting in senescence, ripening and decrease of shelf life [61].

Table 2.16. C<sub>2</sub>H<sub>4</sub> permeability coefficients [61].

Polymer	$C_2H_4$ Permeability (10 <sup>-18</sup> m <sup>3</sup> m/m <sup>2</sup> s Pa)
Poly(lactic acid)	6.8
Poly(ethylene terephthalate)	0.03
Low-density polyethylene	22

Based on the barrier properties discussed above, but also its low thermal stability and impact resistance, PLA in order to be used as a competitive material against conventional polymers in thermoplastic applications has to be modified. Obtaining desired properties of poly(lactic acid) packaging materials can be achieved by producing copolymers, PLA blends, composites and nanocomposites or by laminating or coating the PLA surface. Blending PLA with other polymers is the easiest method of improving desired properties. PLA has been successfully blended with polymers from renewable resources like chitosan or starch, but also with petrochemical-based ones (PVA, PCL or PEG) [75-76]. Also blending with cyclodextrins (CDs) resulted in changes in polymer barrier and mechanical properties. Permeability was increased while tensile strength and elongation at break were decreased [77-78].

Degradation of PLA may occur through hydrolytic degradation, enzymatic degradation, thermal degradation, photodegradation and radiative degradation or biodegradation. Hydrolytic degradation is a primary degradation process for poly(lactic acid) which happens in two steps. The first step involves random non-enzymatic chain scission of the ester groups, which as a result reduces molecular weight. In the second step, low molecular weight PLA will diffuse from the bulk and microorganisms can metabolize it and produce CO<sub>2</sub>, H<sub>2</sub>O and humus [59].

# 2.8. Measurements of ethylene

The importance of achieving a proper concentration of ethylene inside the package has been explained already. For optimal freshness, safety and shelf life, the amounts of ethylene need to be controlled at levels of ppm and ppb, so a properly sensitive and reliable analytical method of monitoring and quantification is required.

Attempts at measuring ethylene go back to 1934 and include techniques like bioassays, gravimetric analyses, manometric techniques after mercury complexation/decomposition and physicochemical colorimetric assays. Although detection limits were down to 10ppb, none of these methods were easily automated [64-65].

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Currently, many methods are more or less successfully utilized. The variety of methods may be due to the vastness of ethylene sources (i.e. plants, fruits or cylinders), sampling systems (i.e. separate systems for keeping samples vs. those incorporated into analytical instruments) and what is exactly to be determined (i.e. adsorption, permeability, etc.). Each of these methods will have its advantages and limitations which makes it very difficult but also important to match exactly to a specific research project.

Nowadays, the most commonly used method for separation and analysis of volatile compounds is gas chromatography. This detection technique can separate, analyze and quantify individual components from complex mixtures by using appropriate columns and detectors. Thermal conductivity detectors (TCD) were first used in GC systems for ethylene detection, but due to poor detection limits (10-100 µL/L) it was not a very effective method. Development of flame ionization detection (FID) and later photoionization detection (PID) significantly improved detection limits for ethylene to tens of nL/L for FID and sub-nL/L for PID. Besides good detection limits, GCs offer more advantages over other techniques, like small sample requirements, high selectivity, fast analysis with minute time scales and relatively easy operation. The main disadvantages are high costs and limited sensitivity [10,18, 64-71].

Recent advances in electrochemical sensor technology have allowed these techniques to be applied to an even wider range of compounds, including ethylene. In general, such a sensor will transform a gas concentration into a detectable physical signal. Classification of electrochemical sensors is based on the physical change measured. Amperometric sensors will measure current (A), chemoresistive sensors resistance ( $\Omega$ ) and capacitive sensors will deal with capacitance (C). Advantages of these sensors are as follows: ethylene detection limits between  $\mu$ L/L and tens of nL/L, good repeatability and accuracy, response time below 1 min, low power consumption, and low cost. Disadvantages include: sensitivity to interfering gases and to temperature and humidity changes, limited

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temperature range and lifetime dramatically reduced when exposed to higher ethylene concentrations [65].

Interaction between ethylene molecules and light can result in its absorption, emission or scattering. This interaction allows for optical sensors to be used for ethylene measurements. The strongest absorption characteristics of C<sub>2</sub>H<sub>4</sub> are in the mid-infrared (IR) region (2-12 µm). Quantification of ethylene concentration can be achieved by knowing the absorption strength of ethylene at a specific IR light frequency. In non-dispersive infrared (NDIR) instruments all wavelengths from a broadband source will not be separated but considered at the same time and the resulting spectrum will not be resolved. This is why band-pass filters are very important in NDIR sensors. Using filters will increase sensitivity for ethylene which is relatively little without filters and attenuate undesired absorbents. Being simple and robust instruments does not overcome their limited sensitivity and lack of selectivity [65, 67].

A novel approach in ethylene detection is the use of laser-based detectors. They utilize laser photothermal deflection or laser-driven intracavityphotoacoustic spectroscopy. Laser-based sensors have the highest sensitivities (below nL/L) and selectivities for ethylene with detection limits of 0.5ppb for laser photothermal deflection and 10ppt for laser-driven intracavityphotoacoustic spectroscopy. Laser response time is within seconds, which makes them applicable in real-time monitoring, and measurements can be made directly and almost continuously. In spite of all the advantages, the disadvantages are difficult to overcome: lasers are very expensive and provide only single gas detection [64-65].

For the purpose of surface area and pore size characterization, volumetric sorption analyzers have been developed. They are called quantasorb sorption analyzers, or in short quantachromes. Their principle of operation is based on a volumetric method. A gas is added in controlled increments to a sample and pressure is allowed to equilibrate in the system. From the known volume of the container the adsorbed mass can be calculated. These instruments have also been utilized for ethylene adsorption analysis [11-12, 72-73].

REFERENCES

# REFERENCES

- 1. Ozdemir M., Floros J. D. Active Food Packaging Technologies Critical Reviews in Food Science and Nutrition, 2004 (44) 185-193
- 2. Scully A. D., Horsham M. A. Active packaging for fruits and vegetables in Wilson C. L. (ed.)Intelligent and Active Packaging for Fruits and Vegetables (57-71) CRC Press 2007
- 3. Zagory D. Ethylene-removing packaging in Rooney M.L. (ed.) Active Food Packaging (38-54) Chapman & Hall 1995
- 4. Day B. Active Packaging of Food in Kerry J., Butler J. (ed.) Smart packaging technologies for fast moving consumer goods (1-18) John Wiley & Sons 2008
- Coles R. Introduction in Coles R., Kirwan M. (ed.) Food and beverage packaging technology (1-29) Blackwell Publishing 2011
- 6. Arvanitoyannis I. Principles of MAP and Definitions of MAP, CA and AP in Arvanitoyannis I. (ed.) Modified Atmosphere and Active Packaging Technologies (3-7) CRC Press 2012
- 7. Vermeiren L., Devlieghere F., van Beest M., de Kruijf N., Debevere J. Developments in active packaging for foods, Trends in Food Science & Technology 1999 (10) 77-86
- Soares N., Pires A., Camilloto G., Santiago-Silva P., Espitia P. J., Silva W. A. Recent Patents on Active Packaging for Food Application, Recent Patents on Food, Nutrition & Agriculture2009(1)171-178
- 9. 2012 Production guide for Storage of Organic Fruits and Vegetables NYS IPM Publication no.10
- Coloma A., Rodriguez F.J., Bruna J.E., Guarda A., Galotto M.J. Development of an Active Film with Natural Zeolite as Ethylene Scavenger, Journal of the Chilean Chemical Society 2014 (49) 2409-2414
- Patdhanagul N., Srithanratana T., Rangsriwatananon K., Hengrasmee S. Ethylene adsorption on cationic surfactant modified zeolite NaY, Microporous and Microporous Materials 2010 (131) 97-102
- 12. Erdogan B., Sakizci M., Yorukogullari E. Characterization and ethylene adsorption of natural and modified clinoptilolites, Applied Surface Science 2008 (254) 2450-2457
- Kader A.A. Postharvest Biology and Technology: An Overview in Kader A. A. (ed.) Postharvest technology of horticultural crops (39-48) University of California Agriculture and Natural Resources Publication 3311 2002
- Martínez-Romero D. Tools to Maintain Postharvest Fruit and Vegetable Quality through the Inhibition of Ethylene Action: A Review, Critical Reviews in Food Science and Nutrition2007 (47) 543–560

- 15. Saltveit, M.E. The future of CA & MA recommendations Seventh International Controlled Atmosphere Research Conference1997 (18) 2-7
- 16. Abe K., Watada A.E. Ethylene absorbent to maintain quality of lightly processed fruits and vegetables, Journal of Food Science 1991 (56) 1589-1592
- 17. Faubion D., Kader A. Evaluation of two new products with claimed ethylene removal capacity, Perishables Handling Newsletter 1996 (86) 27-28
- Suslow T. Performance of zeolite based products in ethylene removal, Perishables Handling Quarterly 1997 (92) 32-33
- Potter, L., Campbell, A.J. and Cava, D. Active and Intelligent Packaging a Review. Review No. 62 Campden BRI 2008
- 20. Garrett E. H. Fresh-cut produce in Blakistone, B.A. (ed.) Principles and Application of Modified Atmosphere Packaging of Foods (125-134) Blackie Academic& Professional 1998
- van Dongen J. T., Gupta K. J., Ramirez-Aguilar S. J., Araujo W. L., Nunes-Nesi A., Fernie A. R. Regulation of respiration in plants: a role for alternative metabolic pathways, Journal of Plant Physiology 2011(12)1434-1443
- 22. Aday M. S, Caner C., Rahvalı F. Effect of oxygen and carbon dioxide absorbers on strawberry quality, Postharvest Biology and Technology 2011 (62) 179–187
- Charles, F., Anchez, J.S., Gontard, N. Modeling of active modified atmosphere packaging of endives exposed to several postharvest temperatures, Journal of Food Science2005 (70) 443– 449
- Lee, J.W., Cha, D.S., Hwang, K.T., Park, H.J. Effects of CO<sub>2</sub> absorbent and high pressure treatment on the shelf-life of packaged Kimchi products International, Journal of Food Science and Technology2003 (38) 519–524
- 25. Jayathunge, L., Illeperuma, C. Extension of postharvest life of oyster mushroom by modified atmosphere packaging technique, Journal of Food Science 2005 (70) 573–578
- Esturk O., Ayhan Z., Gokkurt T. Production and Application of Active Packaging Film with Ethylene Adsorber to Increase the Shelf Life of Broccoli (*Brassica oleracea* L. var. Italica), Packaging Technology and Science 2013 (27) 179-191
- 27. Elaiopoulos K. Operations involving organic gases and vapors in Inglezakis V. J., Zorpas A. A.(ed.) Handbook of Natural Zeolites(246-252) Bentham Science Publishers 2012
- 28. Sircar S., Myers A. L. Gas Separation by Zeolites in Auerbach S. M., Carrado K. A., Dutta P. K.(ed.) Handbook of Zeolite Science & Technology (1354-1406) Dekker2003
- 29. Romero-Perez A., Aguilar-Armenta G. Adsorption kinetics and equilibria of carbon dioxide, ethylene and ethane on 4A(CECA) zeolite, Journal of Chemical and Engineering Data 2010 (55) 3625–3630

- 30. Chen N. Y., Degnan T. F., Smith C. M. Molecular Transport and Reaction in Zeolites: Design and Application of Shape Selective Catalysis John Wiley & Sons 1994
- Di Renzo F., Fajula F. Introduction to molecular sieves: trends of evolution of the zeolite community in Cejka J. (ed.) Zeolites and Ordered Mesoporous Materials: Progress and Prospects (1-12) Elsevier Science & Technology 2005
- 32. Bogdanov B., Georgiev D., Angelova K., Hristov Y. Synthetic zeolites and their industrial and environmental applications, Review International Science conference Economics and Society development on the Base of Knowledge 2005
- Calleja G., Pau J., Calles J. A. Pure and Multicomponent Adsorption Equilibrium of Carbon Dioxide, Ethylene, and Propane on ZSM-5 Zeolites with Different Si/Al Ratios, Journal of Chemical and Engineering Data 1998 (43) 994–1003
- Al-Baghli N. A., Loughlin K. F. Adsorption of Methane, Ethane, and Ethylene on TitanosilicateETS-10 Zeolite, Journal of Chemical and Engineering Data 2005 (50) 843-848
- 35. Anson A., Wang Y., Lin C. C. H., Kuznicki T. M., Kuznicki S. M. Adsorption of ethane and ethylene on modified ETS-10, Chemical Engineering Science 2008 (63) 4171–4175
- 36. van Miltenburg, A., Zhu, W., Kapteijn, F., Moulijn, J. A. Adsorptive Separation of Light Olefin Paraffin Mixtures, Chemical Engineering Research and Design 2006 (84) 350–354
- E. Costa, G. Calleja, A. Jimenez, J. Pau, Adsorption equilibrium of ethylene, propane, propylene, carbon dioxide, and their mixtures on 13X zeolite, Journal of Chemical and Engineering Data 1991 (36) 218-224
- 38. K. Berlier, M.G. Olivier, R. Jadot Adsorption of methane, ethane and ethylene on zeolite, Journal of Chemical and Engineering Data 1995 (40) 1206–1208
- 39. Alberti, A.On the Crystal Structure of the Zeolite Heulandite, Tschermaksmineralogische und petrographische, Mitteilungen 1972 (18) 129-146
- 40. Merkle A. B., Slaughter M. The crystal structure of heulandite (Ca,Na<sub>2</sub>)[Al<sub>2</sub>Si<sub>7</sub>O<sub>18</sub>]·6H<sub>2</sub>O, American Mineralogist 1967 (52) 273-276
- 41. Gramlich V., Meier W. M. The crystal structure of hydrated NaA: A detailed refinement of a pseudosymmetric zeolite structure, Zeitschrift für Kristallographie 1971 (133) 134-149
- 42. Reed T.B., Breck D.W.Crystalline zeolites. II. Crystal structures of synthetic zeolite, type A, Journal of American Chemical Society 1956 (78) 5972-5977
- 43. http://izasc.ethz.ch/
- 44. van Koningsveld H. Compendium of zeolite framework types building schemes and type characteristics, Elsevier 2007
- 45. Faux D. A., Smith W., Forester T. R. Molecular Dynamics Studies of Hydrated and Dehydrated Na+-Zeolite-4A, Journal of Physical Chemistry B 1997 (101) 1762–1768

- 46. Breck D. W. Crystalline Molecular Sieves, Journal of Chemical Education 1964 (41) 678-689
- 47. Ugal J. R., Hassan K. H., Ali I. H. Preparation of type 4A zeolite from Iraqi kaolin: Characterization and properties measurements, Journal of the Association of Arab Universities for Basic and Applied Sciences 2010 (9) 2–5
- Breck D. W., W. G. Eversole W. G., Milton R. M., T. B. Reed T. B., Thom T. L. Crystalline Zeolites. I. The Properties of a New Synthetic Zeolite, Type A, Journal of the American Chemical Society 1956 (78) 5963–5972
- 49. Reed T. B., Breck D. W. Crystalline Zeolites. II. Crystal Structure of Synthetic Zeolite, Type A, Journal of the American Chemical Society 1956 (78) 5972–5977
- Yuzay I. E., Auras R., Selke S. Poly(lactic acid) and Zeolite Composites Prepared by Melt Processing: Morphological and Physical–Mechanical Properties, Journal of Applied Polymer Science 2009 (115) 2262–2270
- Yuzay, I. E., Auras R., Soto-Valdez H., Selke S. Effects of synthetic and natural zeolites on morphology and thermal degradation of poly(lactic acid) composites, Polymer Degradation and Stability 2010 (95) 1769–1777
- 52. Dirim S. N., Esin A., Bayindirli A. A New Protective Polyethylene Based Film Containing Zeolites for the Packaging of Fruits and Vegetables: Film Preparation Turkish, Journal of Engineering and Environmental Sciences 2003 (27) 1 – 9
- 53. Fuongfuchat A., Sirikittikul D., Booncharoen W., Raksa P., Ritvirulh C., Sooknoi T. Hydrophobic Zeolite-Filled Polymeric Films with High Ethylene Permselectivity for Fresh Produce Packaging Applications, Packaging Technology and Science 2014 (27) 763–773
- 54. Fernandez A., Soriano E., Hernandez P., Gavara R. Migration of Antimicrobial Silver from Composites of Polylactide with Silver Zeolites Journal of Food Science2010 (75) E186-E193
- 55. Gregorova A., Machovsky M., WimmerR. Viscoelastic Properties of mineral-filled poly(lactic acid) composites, International Journal of Polymer Science 2012 (12) 1-6
- 56. Esturk O., Ayhan Z., Gokkurt T. Production and application of active packaging film with ethylene adsorber to increase the shelf life of broccoli (*Brassica oleracea* L. var. Italica), Packaging Technology and Science 2014 (27) 179-191
- 57. Sodergard A., Stolt M. Industrial production of high molecular weight poly(lactic acid) in Auras R., Lim L.-T., Selke S., Tsuji H. (ed.) Poly(lactic acid) Synthesis, Structures, Properties, Processing and Applications (27-41) John Willey and Sons 2010
- 58. Gonzales-Buesa J., Page N., Kaminski C., Ryser E.T., Beaudry R., Almenar E. Effect of nonconventional atmospheres and bio-based packaging on the quality and safety of *Listeria monocytogenes*-inoculated fresh-cut celery (*Apiumgraveolens L.*)during storage, Postharvest Biology and Technology 2014 (93) 29-37
- 59. Auras R., Harte B., Selke S. An overview of Polylactides as Packaging Materials, Macromolecular Bioscience 2004 (4) 835–864

- 60. Galotta D.A Literature Review of Poly(Lactic Acid), Journal of Polymers and the Environment 2001 (9) 63-84
- Domenek S., Courgneau C., Ducruet V. Characteristics and Applications of PLA in Kalia S., Averous L. (ed.) Biopolymers: Biomedical and Environmental Applications(183-223) Wiley-Scrivener 2011
- 62. Sodergard A., Inkinen S. Production, Chemistry and properties of Polylactides in Plackett D. (ed.) Biopolymers - New Materials for Sustainable Films and Coatings (43-63) Wiley 2011
- 63. Lehermeier H. J., Dorgan J. R., Way J. D.Gas permeation properties of poly(lactic acid)2001 (190) 243-251
- 64. Pham-Tuan H., Vercammen J., Devos C., Sandra P. Automated capillary gas chromatographic system to monitor ethylene emitted from biological materials, Journal of Chromatography A 2000 (868)249-59
- 65. Cristescu S. M., Mandon J., Arslanov D., De Pessemier J., Hermans C., Harren F. J. Current methods for detecting ethylene in plants, Annals of Botany 2013 (111)347-360
- 66. Meigh D. F. Use of gas chromatography in measuring the ethylene production of stored apples, Journal of the Science of Food and Agriculture 2006 (11) 381-385
- 67. Sklorz A., Miyashita N., Schäfer A., Lang W. Low Level Ethylene Detection Using Preconcentrator/Sensor Combinations IEEE SENSORS 2010 Conference 2494- 2499
- 68. De Greef J., De Proft M., De Winter F. Gas chromatographic determination of ethylene in large air volumes at fractional parts-per-billion level, Analytical Chemistry 1976 (48) 38–41
- 69. Sharma S., Sharma R. R., Pal R. K., Jhalegar M. J., Singh J., Srivastav M., Dhiman M. R. Ethylene absorbents influence fruit firmness and activity of enzymes involved in fruit softening of Japanese plum (Prunussalicina Lindell), Santa Rosa Fruits 2012 (67) 257–266
- 70. Peiser G., Suslow T. V. Factors Affecting Ethylene Adsorption by Zeolite: The Last Word (from us), Perishables Handling Quarterly 1998 (95) 17-19
- 71. Piergiovanni L., Scolaro M., Fava P. Measurement of ethylene permeability of plastic films, Packaging Technology and Science 1992 (5) 189-196
- 72. Berlier K., Olivier M. G., Jadot R. Adsorption of Methane, Ethane and ethylene on zeolite, Journal of Chemical and Engineering Data1995 (40) 1206–1208
- Ouoba S., Cherblanc F., Cousin B., Benet J. C. A new experimental method to determine the sorption isotherm of a liquid in a porous medium, Environmental Science and Technology 2010 (44) 5914-5919
- 74. Matteucci S., Yampolskii Y., Freeman B. D. Pinnaul. Transport of Gases and Vapors in Glassy and Rubbery Polymers Wiley 2006

- 75. Yu L., Dean K., Li L. Polymer blends and composites from renewable resources, Progress in Polymer Science 2006 (31) 576-602
- 76. Ke T., Sun X. S. Effects of moisture content and heat treatment on the physical properties of starch and poly(lactic acid) blends, Journal of Applied Polymer Science 2001 (81) 3069-3082
- Joo M. J., Merkel C., Auras R., Almenar E. Development and characterization of antimicrobial poly(I-lactic acid) containing trans-2-hexenal trapped in cyclodetrins, International Journal of Food Microbiology 2012 (153) 297-305
- 78. Joo M. J., Auras R., Almenar E. Preparation and characterization of blends made of poly(L-lactic acid) and β-cyclodextrin: Improvement of the blend properties by using a masterbatch, Carbohydrate Polymers 2011 (86) 1022-1030
- 79. Mehio N., Dai S., Jiang D. Quantum Mechanical Basis for Kinetic Diameters of Small Gaseous, Molecules Journal of Physical Chemistry A 2014 (118) 1150–1154
- Koyama T., Hayashi Y., Horie H., Kawauchi S., Matsumoto A., Iwase Y., Sakamoto Y., Miyaji A., Motokuraa K., Baba T. Key role of the pore volume of zeolite for selective productionof propylene from olefins, Physical Chemistry Chemical Physics 2010 (12) 2541–2554
- 81. http://helios.princeton.edu/zeomics/
- 82. Rouquerol F., Rouquerol J., SingK. Adsorption by Powders and Porous Solids. Principles, Methodology and Applications Academic Press 2014
- 83. Breus I., Denisova A., Nekljudov S., Breus V. Adsorption of volatile hydrocarbons on natural zeolite-clay material, Adsorption 2008 (14) 509-523
- 84. Jinqu W., Yongchun Z. Adsorption equilibrium of ethylene-carbon dioxide mixture on zeolite ZSM5 and its correlation, Journal of Chemical Industry and Engineering (China) 1992 (7) 208-215
- Aguilar-Armenta G., Hernandez-Ramirez G., Flores-Loyola E., Ugarte-Castaneda A., Silva-Gonzalez R., Tabares-Munoz C., Jimenez-Lopez A., Rodriguez-Castellon E. Adsorption Kinetics of CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> in Cation-Exchanged Clinoptilolite, Journal of Physical Chemistry B 2001 (105) 1313-1319
- 86. Rogers C. E. Permeation of Gases and Vapours in Polymers in Comyn J. (ed) Polymer permeability(11-73) Chapman & Hall 1985
- 87. Terry L. A., Ilkenhans T., Poulston S., Rowsell L., Smith A. W. J. Development of new palladiumpromoted ethylene scavenger, Postharvest Biology and Technology 2007 (45) 214-220
- Smith A. W. J., Poulston S., Rowsell L., Terry L. A., Anderson J. A. A New Palladium-Based Ethylene Scavenger to Control Ethylene-Induced Ripening of Climacteric Fruit, Platinum Metals Review 2009 (53) 112-122
- Imran Muhammad, Revol-Junelles A.-M., Martyn A., Tehrany E. A., Jacquot M., Linder M., Desobry S. Active Food Packaging Evolution: Transformation from Micro- to Nanotechnology, Critical Reviews in Food Science and Nutrition 2010 (50) 799-821

- Albertsson A.-C., Varma I. K., Lochab B., Finne-Wistrand A., Kumar K. Design and synthesis of different types of poly(lactic acid) in Auras R., Lim L.-T., Selke S., Tsuji H. (ed.) Poly(lactic acid) Synthesis, Structures, Properties, Processing and Applications (43-65) John Willey and Sons 2010
- 91. Jiang X., Luo Y., Tian X., Huang D., Reddy N., Yang Y. Chemical structure of poly(lactic acid) in Auras R., Lim L.-T., Selke S., Tsuji H. (ed.) Poly(lactic acid) Synthesis, Structures, Properties, Processing and Applications (69-95) John Willey and Sons 2010
- 92. Almenar E., Auras R. Permeation, sorption, and diffusion in poly(lactic acid) in Auras R., Lim L.-T., Selke S., Tsuji H. (ed.) Poly(lactic acid) Synthesis, Structures, Properties, Processing and Applications (155-179) John Willey and Sons 2010
- 93. Carmody O., Frost R., Xi Y., Kokot S. Surface characterization of selected sorbent materials for common hydrocarbon fuels, Surface Science 2007 (601) 2066-2076

#### CHAPTER 3

# Ethylene and carbon dioxide sorption of natural and synthetic zeolites as affected by fresh produce conditions

#### 3.1. Introduction

Ethylene ( $C_2H_4$ ) is a plant hormone that accelerates ripening and senescence of climacteric fruits and vegetables by increasing their respiration rate. It is a colorless gas that is produced by plants as they ripen. Too high levels of  $C_2H_4$  during storage can shorten shelf life and also produce physiological defects of the harvest (textural and color changes or even tissue degradation, for example russet spotting on lettuce and scald on apples).  $C_2H_4$ ,by increasing the respiration rate, causes early maturity and softening of climacteric fruits and vegetables. It can also induce yellowing of green vegetables. Even very low concentrations of  $C_2H_4$ , at the level of parts per billion (ppb) and parts per million (ppm), can be critical. Commodities can be grouped based on their  $C_2H_4$  production rates, which usually range between 0.1 -100  $\mu$   $C_2H_4/kg$  h at 20°C.  $C_2H_4$  sensitivity of these groups might or might not be proportional to their production rates, and has been determined to be significant at levels as small as 0.01 and as large as 0.4 ppm [1-13, 17].

During respiration, a metabolic process, organic substrates (carbohydrates, lipids and organic acids) are oxidized and carbon dioxide ( $CO_2$ ) and water are produced. Although high levels of  $CO_2$  in the fresh produce package headspace might be beneficial in many cases (slow down respiration and lipid oxidation, reduce color change, inhibit growth of molds, yeasts and bacteria), excessive concentrations of  $CO_2$  inside the package might reduce the pH of the product, which will result in development of an acid taste or cause flavor tainting and drip loss. Also if the wrong packaging material is used, especially with high respiration classes of perishables, there is a danger of blowing up the package by excessive

package expansion. Depending on the fresh produce group, respiration rates between 5 - 60 mg  $CO_2/kg$  hat 5°C can be observed, while the maximum  $CO_2$  tolerance can vary between 5 - 15 %. This means many commodities produce more carbon dioxide than they can tolerate [14-17].

Zeolites are crystalline aluminosilicates of alkali and alkaline earth elements that are characterized by unique three-dimensional framework structures composed of  $SiO_4$  and  $AlO_4$ . Zeolites can be grouped into different types based on their framework structure. Since zeolites can be applied in many disciplines, for example gas adsorption and separation, and removal of odors, they are often modified by exchanging cations so that their activity toward specific molecules increases [3-4]. There are few reported cases when zeolites have been used as  $C_2H_4$  and  $CO_2$  scavengers [2,19-20].

The purpose of this study was to investigate C<sub>2</sub>H<sub>4</sub>and CO<sub>2</sub>sorption characteristics (capacities, time) of two types of zeolites - natural clinoptilolite and synthetic - type 4A at conditions relevant to fresh produce. These include two different conditions of temperature, relative humidity and a few combinations of headspace gases in the sampling systems. Similar studies of sorption capacities for zeolites have been done but not in a closed system and with so many variations of conditions inside the system. Results obtained in this study were treated as preliminary data for further studies that involved production of polymer/zeolite composite films that could be new alternatives to current active packaging systems available in the market.

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# 3.2. Experimental section

# 3.2.1. Materials

# 3.2.1.1. Zeolites

Zeolites in form of fine powders have been purchased from following companies, clinoptilolite (the Liquid Zeolite Company Inc., Cedar Grove, NJ, US) and type 4A zeolite (UOP LLC, A Honeywell Company (Des Plaines, IL, US). Prior to using, both zeolites were activated by drying in vacuum oven (4h at 110°C followed by 4h at 200°C) and afterwards placed into a desiccator. Figure 3.1 shows the physical appearance of both zeolites. CL is beige and 4A is white.



Figure 3.1. Images of natural clinoptilolite (on left) and synthetic type 4A (on right) zeolites.

# 3.2.1.2. Gases

Adsorbent gases were provided by Airgas (Radnor, PA, US) as size 200 certified cylinders. Three cylinders used were as follows: 500ppm of  $C_2H_4$  balanced in  $N_2$ , 100%  $CO_2$  and a mixture of headspace gases (5%  $O_2$ , 15%  $CO_2$  and 80%  $N_2$ ).

#### 3.2.2. Methods

All gases were detected by gas chromatography.

#### 3.2.2.1. Gas Chromatography with Flame Ionization Detector (GC FID)

For  $C_2H_4$  Flame Ionization Detector (FID) was chosen(Hewlett Packard GC 6890, Agilent Technologies, Santa Clara, CA, US) and oven temperature was kept constant through the 13 min measurement (150°C) with 220°C for inlet and detector. Ethylene peaks were detected at 11 min.

# 3.2.2.2. Gas Chromatography with Thermal Conductivity Detector (GC TCD)

While for  $CO_2$ ,  $O_2$  and  $N_2$  Thermal Conductivity Detector (TCD) was utilized (ThermoScientific Trace GC Ultra GC with FID/TCD, Waltham, MA, US). The initial temperature of 45°C was held for 4 min and then a ramp of 60°C/min was used to reach 190°C where it was held for 1.3 min. A second ramp of 120°C/min continued to 230°C and was held for 1 min to clean the column. The inlet was kept at 200°C and the detector at 250°C. During the total run time of 9 min the following retention times were recorded: 3.4 min for  $O_2$ , 3.6 min for  $N_2$  and 7.2 min for  $CO_2$ .

For all gases the same columns were appropriate, SupelcoCarboxen 1010 PLOT, L x I.D. 30m x 0.53 mm, packed with fused silica.

Calibration curves for all gases can be found in appendix below.

# 3.2.3. Sampling system and measuring conditions

One g of each zeolite was placed into 250 mL glass jars with aluminum closures. Each jar had a small hole drilled in the closure to allow flushing with the chosen gases directly from the cylinder and

also for further withdrawal of sample gas. The hole was closed with a gray butyl rubber septum. A 100µL gas tight syringe with needle valve (Supelco SGE, Australia) was used to withdraw 50 µL gas from jars. Depending on what gases were present in the system, samples were injected into the GC TCD or the GC FID for single gas detection or simultaneously into both instruments if both gases of interest were present. To provide the different temperatures the jars were kept in a controlled condition room or in an environmental chamber. Two temperatures were chosen - room temperature ( $23 \pm 3^{\circ}$ C in a room) and low temperature ( $7 \pm 1^{\circ}$ C in a chamber) to mimic the two temperatures at which produce would likely be kept. To reach 100% relative humidity in the jar, a small vial with deionized water was placed inside. When the jars were closed without water, it was assumed to be 0% RH. Since dry gases were used to fill the jars and experiments with desiccant placed inside the jars gave similar results to those without desiccant, the assumption of 0% RH was reasonable. Variations of headspace gases included: 500 ppm C<sub>2</sub>H<sub>4</sub>, 100% CO<sub>2</sub>, 250 ppm ethylene and 50% CO<sub>2</sub> together, and 15% CO<sub>2</sub> with 5% O<sub>2</sub>. In all cases, when the investigated gases were not pure, they were balanced with N<sub>2</sub>.

### 3.2.4. Adsorption measurements

Depending on the rate of adsorption, samples were tested every 2.5 hours in the beginning of the experiments for  $CO_2$  and  $C_2H_4$ , for up to 18 hours; every 24 hours after initial measurements were done for  $CO_2$  and  $C_2H_4$ , or weekly for  $C_2H_4$ after sorption of  $CO_2$  was complete. Sampling was stopped when the maximum sorption was reached or there was a suspicion of leakage based on results from control jars with no zeolite but all the gases inside. Each sample type had three replicates. Ethylene adsorption is presented in three ways, in concentration units of ppm and % and volume units of  $\mu$ L and nL. Concentration in ppm and volume in nL for  $C_2H_4$  and volume in mL for  $CO_2$  is intended to show the exact amount of adsorbed gas, while concentration in % for  $CO_2$  and  $C_2H_4$  is provided to show the change in total concentration due to gas adsorption. All % results were normalized to mass as in equation 3. 1.

$$\frac{\text{initial gas concentration-final gas concentration}}{\text{initial gas concentration}} \cdot \frac{1}{g \text{ zeolite}} \cdot 100\%$$
(3.1)

For ppm results, they were normalized as in equation 3.2.

Volume results (nL, mL) were normalized according to equation 3.3.

To compare all data sets measured at different conditions of temperature, relative humidity and composition of headspace gases, specific times were chosen. For C<sub>2</sub>H<sub>4</sub> there were three times of comparison: 2 days when the largest and fastest sorption occurred, 5 days when some of the sets had reached equilibrium, and total time which was treated as the highest measured sorption (based on the control samples). When the control samples were suspected of leakage, measurements ended. For CO<sub>2</sub> two times were chosen: 5 hours when rapid sorption happened, and total time when all sets reached maximum sorption.

## 3.2.5. Characterization of zeolites

#### 3.2.5.1. Automated Gas Sorption Analyzer (Quantachrome)

A Quantachrome Autosorb iQ2 (Quantachrome Instruments, Boynton Beach, FL, USA) was used to determine zeolite surface areas and pore characteristics. Forty mg of each sample was degassed to 1 torr prior to measurements to remove  $H_2O$ ; zeolites were kept for 16 hours at 110°C and 4 hours at 200°C. Analysis was done in 9 mm cells with rods. Surface areas were obtained by applying BrunauerEmmet-Teller and Langmuir sorption isotherm equations to measure adsorption of  $N_2$  at standard temperature and pressure.

## 3.2.5.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) (Carl Zeiss Variable Pressure SEM EVO LS25, Germany) was used to determine the particle size and shape of the zeolites. Samples were coated with tungsten. Images were acquired with an accelerating voltage of 20 kV and a working distance of 10mm at 6k and 11k x magnification.

# 3.2.6. Statistical methods

Analysis of variance (ANOVA) was performed in the analytical software SPSS version 22 (SPSS Inc., Chicago, IL, US). Means were separated using the Tukey honestly significant difference (HSD) test (p < 0.05).

### 3.3. Results and discussion

# 3.3.1. Surface characteristics

Both zeolites were characterized by Quantachrome to determine their external and internal surface characteristics. Results are listed in table 3.1.

sample	[m²/g]	[m²/g]	radius [Å]	volume [cm³/g]
CL	31.4 ± 5.4 a*	169.8 ± 17.8 a	5.5 ±0.8 a	0.85 ± 0.08 a
4A	48.0 ± 26.0 a	171.3 ± 79.4 a	2.3 ± 0.7 b	0.41 ± 0.28 b

Tahla 3 1	Surface	characteristics	of investigated	zaalitas
Table 3.1.	Surrace	characteristics	of investigated	zeomes.

\* means followed by the same lower case letter in column are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Recorder results have larger standard deviations for 4A than for CL due to the framework structure of the zeolites. The cubic LTA in 4A can result in more possible combinations than those of HEU in natural zeolite (CL). Average pore radius and total pore volumes are larger for CL than 4A which might suggest that physisorption on the external surface will be more probable for 4A and inside cages and cavities for CL. Comparing recorded results to values in the literature, it can be seen that CL had a pore radius larger than reported (5.5 ± 0.8 Å vs. 3.5 Å), while 4A had a smaller one (2.3 ± 0.7 Å vs. 4 Å) [24, 26]. A similar situation can be observed for pore volumes. The measured volume of CL,  $0.85 \pm 0.01$ cm<sup>3</sup>/g is larger than in the literature, 0.279 cm<sup>3</sup>/g, while for 4A the measured value of 0.41 ± 0.28 cm<sup>3</sup>/g is smaller than the literature value of 0.508 cm<sup>3</sup>/g [24. 26]. BET surface areas for both investigated zeolites  $(31.4 \pm 5.4 \text{ m}^2/\text{g} \text{ for CL} \text{ and } 48.0 \pm 26.0 \text{ m}^2/\text{g} \text{ for 4A})$  are within the range found in literature, 28 -60 m<sup>2</sup>/g [4]. Differences between zeolites are due to frameworks, cavities and cages. CL is composed of a single building block and has both 10- and 8-ring channels, while type 4A zeolite is composed of three different building blocks of varying sizes and dimensions. Also both the 4- and 8-ring channels are smaller. BET and Langmuir surface areas are comparable for both zeolites (p > 0.05), while there are significant differences for pore radius and pore volume (p < 0.05). Data listed in table 3.1 are based on sorption isotherms determined by Quantachrome. Figures 3.2 and 3.3 present N<sub>2</sub> sorption isotherms for CL and 4A zeolites. Both sorption isotherms resemble type IV isotherms with visible presence of two separate surface layers on a surface or in the pores. . A Type IV isotherm is displayed when intermolecular attractions are large.  $N_2$  has a kinetic diameter of 3.64 Å [24], which is larger than the pore openings in 4A (2.3± 0.7 Å) but smaller than in CL (5.5 ± 0.8 Å), so there is a possibility for adsorbent molecules to enter pores in CL, but not in 4A.



Figure 3.2. Nitrogen sorption isotherm for clinoptilolite.



Figure 3.3. Nitrogen sorption isotherm for type 4A zeolite.

To understand more if there is any effect of surface characteristics on adsorption taking place in both zeolites of interest, SEM images of CL and 4A were taken (figure 3.4). It can be seen that the synthetic particles are very symmetrical in their shape, and the size distribution is much smaller when compared to the natural zeolite. In clinoptilolite, we can see non-regular molecules with relatively broad size distribution. For 4A the particle size range was between 0.971  $\mu$ m and 3.5  $\mu$ m, while for clinoptilolite it was between 0.219  $\mu$ m and 4.8  $\mu$ m.



Figure 3.4. SEM images of clinoptilolite (on left) and type 4A zeolite (on right).

Supporting data for this chapter can be found in appendix below.

# 3.3.2. Adsorption measurements

Tables 3.2 and 3.3 list total times for all measurements carried out. It can be seen that depending on conditions (temperature, relative humidity and headspace gases) inside the jars, the end times for measurements could change from 5 to 18 days for  $C_2H_4$  and from 7.5 to 48 hours for  $CO_2$ . Longer times for  $C_2H_4$  and  $CO_2$ were observed in the presence of both gases in the systems. Reasons for increases in adsorption times might be due to competition between  $C_2H_4$  and  $CO_2$  for adsorption sites and inhibiting sites for the other gas in the process.

system	total time [h/d]
C <sub>2</sub> H <sub>4</sub> (23 <sup>o</sup> C)	96/5
C <sub>2</sub> H <sub>4</sub> + CO <sub>2</sub> (23°C)	288/13
C <sub>2</sub> H <sub>4</sub> (23°C, H <sub>2</sub> O)	96/5
$C_2H_4 + CO_2$ (7°C)	432/18
C <sub>2</sub> H <sub>4</sub> (7°C, H <sub>2</sub> O)	96/5

Table 3.2. Total times for ethylene adsorption measurements.

Table 3.3. Total times for carbon dioxide adsorption measurements.

system	total time [h]
CO <sub>2</sub> (23°C)	10
$CO_2 + C_2H_4$ (23°C)	48
CO <sub>2</sub> + O <sub>2</sub> (23°C)	15
CO <sub>2</sub> (23°C, H <sub>2</sub> O)	7.5
$CO_2 + C_2H_4$ (7°C)	48
CO <sub>2</sub> (7°C, H <sub>2</sub> O)	12.5

Data shown in figures 3.5 - 3.19 indicates superior performance of the synthetic zeolite - type 4A when compared to the natural one - clinoptilolite (CL), in all studied cases. Differences in amount of  $C_2H_4$  adsorbed were as low as 20% for  $C_2H_4$  (23°C, 0% RH) and up to 100% for  $C_2H_4$  (7°C, 100% RH). For  $CO_2$  adsorption the differences were smaller, but still relatively important, 20% for  $CO_2 + O_2$  (7°C, 0% RH) and a maximum of 50% for  $CO_2 + O_2$  (23°C, 0% RH).

Focusing first on  $C_2H_4$  adsorption, figures 3.5 - 3.13 are relevant. No matter which units of adsorbed $C_2H_4$  are presented (ppm, % or nL), all show the same trends. The presence of  $CO_2$  in the headspace had an inhibiting effect on  $C_2H_4$  sorption for CL (p <0.05), while it did not influence 4A performance. Selectivities towards gases,  $CO_2$  or  $C_2H_4$  in our case, are due to predominant interaction energies, which are dependent on physical properties of the gases (i.e. quadrupole moment, polarizabilities, etc.). In 4A zeolite,  $CO_2$  and  $C_2H_4$  have to compete for adsorption sites. Molecules with
bigger quadrupole moment (CO<sub>2</sub> - 0.64 Å, C<sub>2</sub>H<sub>4</sub> - 0.48 Å) will have stronger interaction [24]. Also a decrease in temperature and increase of relative humidity significantly decreased the adsorption capacity of CL (p < 0.05). In sets where high humidity was applied, the initial high sorption data for 4A decreased over time (p < 0.05). It is suspected that water was replacing C<sub>2</sub>H<sub>4</sub> in the zeolite matrix and C<sub>2</sub>H<sub>4</sub> was released back to the headspace after 5 days. Low temperature tended to have a smaller effect on C<sub>2</sub>H<sub>4</sub> sorption of 4A than CL.

Looking at total measurement times (figures 3.5 - 3.13), showed that the presence of  $CO_2$  in the headspace increased sorption time about 3 fold when compared to sets with just  $C_2H_4$  in the jar for 4A. High humidity had the opposite effect; it decreased the total time over which zeolites adsorbed. Lowering the temperature did not seem to have any critical effect on time in both zeolites.



Figure 3.5. Amount of ethylene (ppm) adsorbed by zeolites after 2 days.



Figure 3.6. Amount of ethylene (%) adsorbed by zeolites after 2 days.



Figure 3.7. Amount of ethylene (nL) adsorbed by zeolites after 2 days.



Figure 3.8. Amount of ethylene (ppm) adsorbed by zeolites after 5 days.



Figure 3.9. Amount of ethylene (%) adsorbed by zeolites after 5 days.



Figure 3.10. Amount of ethylene (nL) adsorbed by zeolites after 5 days.



Figure 3.11. Amount of ethylene (ppm) adsorbed by zeolites after total measurement time.



Figure 3.12. Amount of ethylene (%) adsorbed by zeolites after total measurement time.



Figure 3.13. Amount of ethylene (nL) adsorbed by zeolites after total time.

Figures 3.14 - 3.17 present  $CO_2$  adsorption results for both zeolites at different conditions (°C, %RH, gases in jars) and two times (5h and total).

Adsorption of  $CO_2$  was much faster than sorption of  $C_2H_4$  in all cases. Based on the Quantachrome results, it is more probable for  $CO_2$  to adsorb on the external surfaces, especially for 4A, than for  $C_2H_4$  to get into the cavities and cages, especially in CL. Equilibrium for all  $CO_2$  adsorption studies

was reached after a maximum of 2 days while adsorption of  $C_2H_4$  continued sometimes until 18 days. This suggests that there are different parts of the zeolites within their structure/framework that are responsible for sorption of these two gases,  $CO_2$  and  $C_2H_4$ . This difference might be due to an increase in ionic radius, which is associated with higher polarizability of the larger ionic radius.

Also, type 4A zeolites for both  $CO_2$  and  $C_2H_4$ , showed superior performance when compared to CL, although CL showed much more adsorption capacity for  $CO_2$  than for  $C_2H_4$ . The presence of additional gases in the headspace increased sorption potential of both zeolites (p < 0.05). More  $CO_2$  was adsorbed when  $C_2H_4$  was present, but also when  $O_2$  was present in the absence of  $C_2H_4$ .

High humidity had an effect on both gases. As shown above in figures 3.5 - 3.17 for  $C_2H_4$  and also for  $CO_2$  it decreased the sorption (p < 0.05). After initial  $C_2H_4$  sorption, water replaced  $C_2H_4$  in both zeolites and sorption was reversed in 4A. For CL (figures 3.5 - 3.13), at both temperatures in the presence of water, there was no sorption of  $C_2H_4$  (p < 0.05). A decrease in temperature did not affect the sorption as much as high humidity, although it decreased adsorption of  $C_2H_4$  in both zeolites and increased  $CO_2$  adsorption in CL, but decreased it in 4A.This might be explained by the endothermic character of  $C_2H_4$ adsorptionin both zeolites and  $CO_2$  adsorption in 4A, and the exothermic character of  $CO_2$  adsorption in CL.



Figure 3.14. Amount of carbon dioxide (%) adsorbed by zeolites after 5 hours.



Figure 3.15. Amount of carbon dioxide (mL) adsorbed by zeolites after 5 hours.



Figure 3.16. Amount of carbon dioxide (%) adsorbed by zeolites after total measurement time.



Figure 3.17. Amount of carbon dioxide (mL) adsorbed by zeolites after total measurement time.

Although not determined in this research but based on literature, it is known that adsorption isotherms for  $C_2H_4$  and  $CO_2$  in clinoptilolite have a classic isotherm form (Langmuir). These isotherms are

often observed in the case of adsorbents with a wide range of pore sizes, like natural zeolites. Type II isotherms are observed when adsorbate molecules are small enough to enter zeolite micropore systems. The kinetic diameters of CO<sub>2</sub> (3.3 Å) and C<sub>2</sub>H<sub>4</sub> (3.9 Å) are both smaller than the measured average pore radius in clinoptilolite (5.5 ± 0.8 Å), which was actually larger than the literature value (3.5 Å) [24-25]. This suggests that both gases could get inside the cages and cavities in the zeolite framework. Since physisorption was happening not only on external but also on internal surfaces, it was characterized by a higher adsorption energy but allow adsorption rate [3-4, 20]. For type 4A zeolite it was found that the adsorption isotherm for  $CO_2$  also had a characteristic type II shape while the one for  $C_2H_4$  had a type I shape and followed Henry's law [21-22]. Type I isotherms are normal for microporous adsorbents that have pore sizes similar to the diameter of the molecules that will be sorbed. Adsorbents with a wide range of pore sizes, like in this case the 4A zeolite, will display type I isotherms, which are often associated with continuous progression from monolayer to multilayer adsorption [21-22]. Again comparing pore openings in 4A measured by Quantachrome (2.3 ± 0.7 Å) to those found in the literature (4 Å) shows that the actual pore radius is much smaller, probably due to different cations occupying the corner sites in cavities and cages and therefore reducing the channel. This might suggest that all physisorption took place on the external surface of the zeolite (mesopores or larger) and was characterized by low adsorption energy and high adsorption rate [21-22]. Adsorption of both gases in all cases in the type 4A zeolite was much faster and adsorption capacities were higher than in clinoptilolite. As for water (2.65 Å) when compared to the pores in both zeolites, again it is possible for  $H_2O$  to enter the pores in clinoptilolite and block adsorption sites for  $C_2H_4$  and  $CO_2$ , while it is often too large for 4A zeolite pores and this is why the effect of water was not as critical to sorption as in the case of the natural zeolite. Increased sorption of  $CO_2$  when compared to  $C_2H_4$  could be due to higher polarizability associated with the larger ionic radius [23, 25]. All of the above shows a potential for all three molecules to pass through natural zeolite pore openings and all except  $H_2O$  to not be able to go inside the cages

and cavities inside the synthetic zeolite. For all three molecules,  $CO_2$ ,  $C_2H_4$ ,  $H_2O$ , physisorption in both zeolites can occur on the surface (adsorption) while for CL having larger pore sizes there is also a possibility for all molecules to have absorption occur inside the zeolite framework.

Figures 3.18 - 3.33 show the sorption for both gases as they were measured during the experiments. For  $C_2H_4$  all data are shown in ppm, % and nL, while for  $CO_2$  only % and mL are presented. In all cases the greatest increase in sorption occurred in the beginning and the rate of increase slowed as the experiment continued.



Figure 3.18. Amount of ethylene sorption (ppm) at room temperature and 0% RH.



Figure 3.19. Amount of ethylene sorption (%) at room temperature and 0% RH.

Comparing figures 3.18 - 3.21 we can observe the effect of the second gas present in the headspace. In the first case, with just  $C_2H_4$  present, the whole process reached equilibrium within 100 hours, while in the presence of  $CO_2$ , the time for equilibrium was extended to roughly 300 hours, while the percent of total sorption increased by 15% in presence of  $CO_2$ . But after 20h, more  $C_2H_4$  was adsorbed in the presence of  $CO_2$ .



Figure 3.20. Amount of ethylene sorption (ppm) at room temperature and 0% RH with carbon dioxide present.



Figure 3.21. Amount of ethylene sorption (%) at room temperature and 0% RH with carbon dioxide present.

Decreasing the temperature (figures 3.20 - 3.23) extended the adsorption from about 100h to over 400h and significantly affected the total percent of adsorption in CL. Lower temperature increased it significantly by more than 50% (p < 0.05).



Figure 3.22. Amount of ethylene sorption (ppm) at 7°C and 0% RH with carbon dioxide present.



Figure 3.23. Amount of ethylene sorption (%) at 7°C and 0% RH with carbon dioxide present.

The presence of water in the system (100% RH) significantly decreased the total time of adsorption (p < 0.05) (figures 3.24 and 3.25). For CL there was no significant adsorption of C<sub>2</sub>H<sub>4</sub> during the whole experimental time (p < 0.05), while for 4A type zeolite the initial high adsorption decreased over time. All of this suggests that H<sub>2</sub>O acted as a competitive molecule to C<sub>2</sub>H<sub>4</sub> and blocked the sorption sites in both zeolites. In clinoptilolite, it was more prone to do so from the very beginning while in 4A, it appeared to reverse the initial sorption of C<sub>2</sub>H<sub>4</sub> after about 48 hours.



Figure 3.24. Amount of ethylene sorption (ppm) at room temperature and 100% RH.



Figure 3.25. Amount of ethylene sorption (%) at room temperature and 100% RH.

Lowering the temperature in the presence of water in the system (figures 3.26 - 3.27) caused desorption of  $C_2H_4$  to continue over time in the synthetic zeolite. At room temperature the initial drop was stopped, while at 7°C  $C_2H_4$  continued to be desorbed until the end of the experiment.



Figure 3.26. Amount of ethylene sorption (ppm) at 7°C and 100% RH.



Figure 3.27. Amount ethylene sorption (%) at 7°C and 100% RH.

As for CO<sub>2</sub>adsorption (figures 3.28 - 3.33), in general, the final adsorption capacities were reached much faster than for any C<sub>2</sub>H<sub>4</sub> case. Again the synthetic type 4A zeolite was superior in all cases (p < 0.05).



Figure 3.28. Amount of carbon dioxide sorption (%) at room temperature and 0% RH.

The same situation as with  $C_2H_4$  can be observed; the presence of a second gas in the headspace slowed down the adsorption process (p < 0.05) (figures 3.28 and 3.29). A few percent decrease in sorption for the 4A zeolite was observed, while in the natural zeolite there was no significant difference (p < 0.05).



Figure 3.29. Amount of carbon dioxide sorption (%) at room temperature and 0% RH in presence of ethylene.

Decreasing the concentration of CO<sub>2</sub>from 35% (figure 3.29) to 15% and the presence of 5% O<sub>2</sub>did not result insignificant differences when compared to the other cases (p > 0.05) (figure 3.30). CL immediately reached its maximum sorption capacity and maintained it on the same level to the end of the measurements. In the case of the synthetic zeolite, the behavior was similar to many other cases, sorption increased for a long time and reached equilibrium after 12.5h. The adsorption was still relatively fast and the maximum capacities were reached much faster than in any case involving  $C_2H_4$ adsorption.



Figure 3.30. Amount of carbon dioxide sorption (%) at room temperature and 0% RH in presence of oxygen.

The presence of water at either temperature ( $23^{\circ}C$  or  $7^{\circ}C$ ) (figures 3.31 and 3.33) did not affect adsorption of CO<sub>2</sub>. No significant desorption was observed and the maximum sorption capacity was reached quite quickly (between 8h and 12h) (p <0.05).



Figure 3.31. Amount of carbon dioxide sorption (%) at room temperature and 100%RH.

Both decreasing temperature and the presence of  $C_2H_4$  in the headspace as well as absence of  $H_2O$  increased adsorption time but also significantly increased adsorption of  $CO_2$  for both zeolites (p < 0.05) (figures 3.31 and 3.32). As was discussed, lower temperature resulting in increased adsorption suggests that this process is exothermic in nature. Also the absence of water means absence of competitive molecules that can block available adsorption sites for the other two gases,  $CO_2$  and  $C_2H_4$ .



Figure 3.32. Amount of carbon dioxide sorption (%) at 7°C and 0% RH in presence of ethylene.

The presence of water significantly decreased the sorption time and sorption capacity (figure 3.33), suggesting again that  $H_2O$  acts as a competitive molecule to  $CO_2$ .



Figure 3.33. Amount of carbon dioxide sorption (%) at 7°C and 100% RH.

## 3.4. Conclusions

All of the investigated cases with changing headspace gases, temperatures and humidities showed promising sorption capacities for zeolites that can be applied to packaging of perishables. Even though the most relevant conditions of storage of fresh produce (7°C and 100% RH) showed the smallest sorption capacities for both zeolites, it must be remembered that fruits and vegetables produce small concentrations of these gases and are only going to be stored for a few days. Lowering temperature from 23°C to 7°C increased sorption of CO<sub>2</sub> in CL but decreased it in 4A, which means that we have exothermic and endothermic adsorptions, respectively. In case of ethylene adsorption the same situation happened for both zeolites, adsorption was decreased due to the endothermic character of this process. Presence of H<sub>2</sub>O had an effect on both zeolites. Due to the hydrophilicity of CL it inhibited its adsorption ofCO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, while for 4A the initial high adsorption of C<sub>2</sub>H<sub>4</sub> was reversed and H<sub>2</sub>O molecules were exchanged with C<sub>2</sub>H<sub>4</sub> on the adsorption sites, showing that H<sub>2</sub>O is a competitive molecule to the other two gases. Adsorption of CO<sub>2</sub> was not affected in 4A, which is in accord with the zeolite's hydrophobic character. The presence of additional gases as compared to pure single component systems showed increased adsorption capacities. Higher polarizabilities and quadrupole moments of ions with larger radii cause them to adsorb first.

After the sorption capacities of the two zeolites in the form of powder were determined in conditions relevant to fresh produce, the next step was to produce a polymer film with zeolites incorporated in it, which could work as a new active packaging material for fresh produce. This will be reported in the next chapter.

APPENDIX



Figure A3.1. Ethylene calibration curve for GC FID.

area [µV*s]	ethylene [µL]
1198424	0.05
1208126	0.05
1179961	0.05
1240137	0.05
1205877	0.05
989736	0.04
971170	0.04
971578	0.04
964135	0.04
964614	0.04
616687	0.025
616902	0.025
618923	0.025
622984	0.025
624110	0.025
231309	0.01
238529	0.01
234532	0.01
225987	0.01
223184	0.01
0	0

Table A3.1. Ethylene calibration data for GC FID.



Figure A3.2. Oxygen calibration curve for GC TCD.



Figure A3.3. Nitrogen calibration curve for GC TCD.



Figure A3.4. Carbon dioxide calibration curve for GC TCD.

	oxygen [%]	area [counts]
(nitrogen)	0	0
(nitrogen)	0	0
(nitrogen)	0	0
(carb. diox.)	0	0
(carb. diox.)	0	0
(carb. diox.)	0	0
(mix)	5	0
(mix)	5	0
(mix)	5	0
(air)	20.9476	0
(air)	20.9476	0
(air)	20.9476	0
(oxygen)	100	0
(oxygen)	100	0
(oxygen)	100	0

Table A3.2. Oxygen calibration data for GC TCD.

Table A3.3. Nitrogen calibration data for GC TCD.

	nitrogen [%]	area [counts]
(carb. diox.)	0	0
(carb. diox.)	0	0
(carb. diox.)	0	0
(oxygen)	0	0
(oxygen)	0	0
(oxygen)	0	0
(air)	78.084	8493546
(air)	78.084	8512040
(air)	78.084	8555943
(mix)	80	8809718
(mix)	80	8917720
(mix)	80	8917346
(nitrogen)	100	11048430
(nitrogen)	100	11006169
(nitrogen)	100	11246913

	carbon dioxide [%]	area [counts]
(oxygen)	0	0
(oxygen)	0	0
(oxygen)	0	0
(nitrogen)	0	0
(nitrogen)	0	0
(nitrogen)	0	0
(air)	0	0
(air)	0	0
(air)	0	0
(mix)	15	2802832
(mix)	15	2832167
(mix)	15	2858897
(carb. diox.)	100	20462952
(carb. diox.)	100	20508062
(carb. diox.)	100	20922885

Table A3.4. Carbon dioxide calibration data for GC TCD.

Table A3.5. Summary of ethylene (ppm) measurements taken for powder zeolites in chapter 3.

conditions	sample	2 days ∆ ppm	5 days ∆ ppm	total ∆ ppm
	CO	3.3 ± 0.8 aA*	6.6 ± 1.7 aA	6.6 ± 1.7 aA
C <sub>2</sub> H <sub>4</sub> (23°C)	CL	221.3 ± 21.0 dA	267.7 ± 24.9 eB	267.7 ± 24.9 eB
	4A	342.7 ± 43.0 eA	357.8 ± 34.6 fA	357.8 ± 34.6 fA
	CO	2.2 ± 0.7 aA	4.4 ± 0.3 aB	7.7 ± 7.5 aC
C <sub>2</sub> H <sub>4</sub> + CO <sub>2</sub> (23°C)	CL	15.4 ± 5.2 aA	22.3 ± 7.8 aAB	37.0 ± 9.8 aB
	4A	113.3 ± 12.9 cA	122.9 ± 14.9 cA	130.2 ± 14.4 cA
	CO	1.3 ± 1.6 aA	2.4 ± 3.4 aA	2.4 ± 3.4 aA
$C_2H_4$ (23°C + $H_2O$ )	CL	9.9 ± 9.3 aA	9.5 ± 13.8 aA	9.5 ± 13.8 aA
	4A	127.6 ± 1.9 cA	116.0 ± 13.2 bcA	116.0 ± 13.2 cA
	CO	2.5 ± 4.3 aA	2.2 ± 1.7 aA	22.7 ± 38.3 aB
$C_2H_4 + CO_2 (7^{\circ}C)$	CL	33.7 ± 13.0 abA	24.2 ± 7.2 aA	46.6 ± 9.0 aA
	4A	64.6 ± 9.5 bA	90.1 ± 4.9 bB	131.1 ± 6.8 cC
	CO	3.9 ± 2.4 aA	6.8 ± 5.7 aA	6.8 ± 5.7 aA
$C_2H_4$ (7°C + $H_2O$ )	CL	10.1 ± 0.9 aA	6.9 ± 1.7 aA	6.9 ± 1.7 aA
	4A	433.6 ± 8.9 fA	220.2 ± 15.7 dB	220.2 ± 15.7 dB

conditions	sample	normalized 2 days $\Delta$ %	normalized 5 days $\Delta$ %	normalized total $\Delta$ %
	CO	0.6 ± 0.2 aA*	1.2 ± 0.3 aA	1.2 ± 0.3 aA
C <sub>2</sub> H <sub>4</sub> (23°C)	CL	42.1 ± 3.9 dA	50.9 ± 4.6 eB	50.9 ± 4.6 deB
	4A	66.5 ± 8.5 Ea	69.4 ± 6.9 Fa	69.4 ± 6.9 Fa
	CO	0.9 ± 0.3 aA	1.8 ± 0.6 abA	3.2 ± 3.2 aB
C <sub>2</sub> H <sub>4</sub> + CO <sub>2</sub> (23 <sup>o</sup> C)	CL	6.2 ± 1.3 abA	8.9 ± 1.9 abA	14.9 ± 2.1 bB
	4A	69.4 ± 1.4 eA	75.3 ± 1.9 gB	79.8 ± 1.9 gC
	CO	0.3 ± 0.4aA	0.5 ± 0.7 aA	0.5 ± 0.7 aA
C <sub>2</sub> H <sub>4</sub> (23°C + H <sub>2</sub> O)	CL	2.2 ± 2.0 aA	2.1 ± 3.0 abA	2.1 ± 3.0 aA
	4A	96.1 ± 1.0 fA	25.3 ± 3.0 cB	25.3 ± 3.0 cB
	CO	1.1 ± 1.8aA	1.0 ± 0.7 aA	4.4 ± 1.8 aB
$C_2H_4 + CO_2 (7^{o}C)$	CL	13.6 ± 4.5 bA	9.8 ± 2.4 bA	19.3 ± 5.4 bcA
	4A	28.8 ± 3.6cA	40.2 ± 1.5 dB	58.5 ± 1.4 eC
	CO	1.0 ± 0.4 aA	1.7 ± 1.2 abA	1.7 ± 1.2 aA
$C_2H_4$ (7°C + H <sub>2</sub> O)	CL	2.2 ± 0.2 aA	1.5 ± 0.4 abA	1.5 ± 0.4 aA
	4A	95.3 ± 1.2 fA	48.4 ± 3.8 deB	48.4 ± 3.8 dB

Table A3.6. Summary of ethylene (%) measurements taken for powder zeolites in chapter 3.

conditions	sample	2 days ∆ nL	5 days ∆ nL	total Δ nL
	СО	0.3 ± 0.1 aA*	0.3 ± 0.0 aA	0.3 ± 0.0 aA
C <sub>2</sub> H <sub>4</sub> (23°C)	CL	11.1 ± 1.0 dA	13.4 ± 1.2 eB	13.4 ± 1.2 eB
	4A	17.1 ± 2.1 eA	17.9 ± 1.7 fA	17.9 ± 1.7 fA
	СО	0.0 ± 0.1 aA	0.2 ± 0.1 aB	0.4 ± 0.4 aC
C <sub>2</sub> H <sub>4</sub> + CO <sub>2</sub> (23°C)	CL	0.8 ± 0.3 aA	1.1 ± 0.4 aAB	1.8 ± 0.5 aB
	4A	5.7 ± 0.6 cA	6.1 ± 0.7 cA	6.5 ± 0.7 cA
	СО	0.1 ± 0.1 aA	0.1 ± 0.1 aA	0.1±0.1 aA
C <sub>2</sub> H <sub>4</sub> (23 <sup>o</sup> C + H <sub>2</sub> O)	CL	0.5 ± 0.5 aA	0.5 ± 0.7 aA	0.5 ± 0.7 aA
	4A	5.8 ± 0.5 cA	5.8 ± 0.7 bcA	5.8 ± 0.7 cA
	СО	0.6 ± 0.1 aA	0.5 ± 0.1 aA	1.8 ± 1.7 aB
C <sub>2</sub> H <sub>4</sub> + CO <sub>2</sub> (7°C)	CL	1.8 ± 0.7 abA	1.2 ± 0.4 aA	2.3 ± 0.4 aA
	4A	3.2 ± 0.5 bA	4.5 ± 0.2 bB	6.6 ± 0.3 cC
	CO	0.2 ± 0.1 aA	0.1 ± 0.1 aA	1.1 ± 0.2 aA
C <sub>2</sub> H <sub>4</sub> (7 <sup>o</sup> C + H <sub>2</sub> O)	CL	0.4 ± 0.2 aA	0.5 ± 0.2 aA	3.6 ± 0.6 aA
	4A	2.9 ± 1.2 fA	4.1 ± 1.2 dB	6.6 ± 1.1 dB

Table A3.7. Summary of ethylene (nL) measurements taken for powder zeolites in chapter 3.

conditions	sample	normalized 5h $\Delta$ %	normalized total $\Delta$ %
	СО	0.6 ± 0.5 aA*	3.7 ± 0.5 aB
CO <sub>2</sub> (23°C)	CL	3.9 ± 0.4 abA	6.6 ± 0.6 aB
	4A	28.6 ± 2.4 efA	30.1 ± 1.9 dA
	CO	2.1 ± 0.5 abA	3.0 ± 1.1 aA
$CO_2 + C_2H_4$ (23°C)	CL	12.0 ± 0.9 cA	14.9 ± 0.9 bA
	4A	48.6± 3.0 hA	63.9 ± 5.5 eB
	CO	4.8 ± 1.4 abA	3.5 ± 0.1 aA
CO <sub>2</sub> + O <sub>2</sub> (23°C)	CL	21.1 ± 1.9 dA	21.3 ± 0.9 cA
	4A	59.3 ± 2.3 iA	73.0 ± 1.0 fB
	СО	1.0 ± 1.0 aA	1.3 ± 1.2 aA
CO <sub>2</sub> (23°C, H <sub>2</sub> O)	CL	4.2 ± 2.4 abA	4.3 ± 0.6 aA
	4A	31.5 ± 0.7 fA	30.3 ± 0.9 dA
	CO	1.7 ± 1.4 aA	2.2 ± 0.8 aA
$CO_2 + C_2H_4$ (7°C)	CL	14.1 ± 0.3 cA	18.6 ± 0.8 bcB
	4A	37.7 ± 2.4 gA	63.1 ± 2.4 eB
	CO	1.7 ± 0.7 aA	1.3 ± 0.6 aA
CO <sub>2</sub> (7°C, H <sub>2</sub> O)	CL	6.9 ± 1.3 bA	4.8 ± 0.8 aA
	4A	24.2 ± 1.1 deA	27.2 ± 2.4 dA

Table A3.8. Summary of carbon dioxide (%) measurements taken for powder zeolites in chapter 3.

time [h]	CO [ppm]	CL [ppm]	4A [ppm]
0	0	0	0
24	3.7 ± 2.5	172.2 ± 20.8	322.8 ± 48.7
48	5.1 ± 2.7	221.3 ± 21.0	342.7 ± 43.0
72	1.9 ± 1.3	249.4 ± 23.6	352.0 ± 37.7
96	5.9 ± 0.5	267.7 ± 24.9	357.8 ± 34.6

Table A3.1	LO. Amount	of ethylene	adsorption	(%) at room	temperature and 0% RH.

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
24	0.7 ± 0.5	32.7 ± 3.8	62.6 ± 9.6
48	$1.0 \pm 0.5$	42.1 ± 3.9	66.5 ± 8.5
72	$0.4 \pm 0.3$	47.4 ± 4.3	68.3 ± 7.5
96	$1.1 \pm 0.1$	50.9 ± 4.6	69.4 ± 6.9

time [h]	CO [ppm]	CL [ppm]	4A [ppm]
0	0	0	0
2.5	2.1 ± 0.8	3.6 ± 2.8	50.3 ± 3.7
5	$1.3 \pm 1.0$	5.1 ± 2.2	64.7 ± 5.0
7.5	$1.0 \pm 0.8$	6.6 ± 2.3	73.7 ± 5.5
24	2.2 ± 1.6	9.7 ± 2.5	99.7 ± 10.0
48	$1.5 \pm 0.6$	15.4 ± 5.2	113.3 ± 12.9
72	3.7 ± 2.4	17.9 ± 4.3	117.8 ± 13.1
96	3.6 ± 2.4	22.3 ± 7.8	122.9 ± 14.9
240	5.1 ± 5.9	29.7 ± 11.2	128.8 ± 15.4
264	3.3 ± 5.1	34.8 ± 9.6	129.8 ± 14.4
288	8.8 ± 7.8	37.0 ± 9.8	131.2 ± 15.6

Table A3.11. Amount of ethylene adsorption (ppm) at room temperature and 0% RH with carbon dioxide present.

Table A3.12. Amount of ethylene adsorption (%) at room temperature and 0% RH with carbon dioxide present.

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
2.5	0.9 ± 0.3	1.3 ± 0.9	$21.6 \pm 0.1$
5	$0.6 \pm 0.4$	2.0 ± 0.6	27.7 ± 0.2
7.5	0.4 ± 0.3	2.6 ± 0.5	31.6 ± 1.0
24	0.9 ± 0.7	3.8 ± 0.4	42.7 ± 1.4
48	0.6 ± 0.3	6.0 ± 1.2	48.5 ± 2.1
72	$1.6 \pm 1.0$	7.1 ± 0.7	50.4 ± 2.1
96	1.5 ± 1.0	8.7 ± 1.8	52.6 ± 2.6
240	2.1 ± 2.5	11.6 ± 2.8	55.1 ± 2.7
264	1.4 ± 2.2	13.7 ± 2.1	55.2 ± 2.4
288	3.7 ± 3.3	14.6 ± 2.0	55.6 ± 2.4

time [h]	CO [ppm]	CL [ppm]	4A [ppm]
0	0	0	0
2.5	11.6 ± 8.9	22.99 ± 8.4	27.0 ± 2.5
5	4.3 ± 3.0	23.24 ± 11.8	25.8 ± 8.1
7.5	30.7 ± 35.0	26.08 ± 20.3	65.6 ± 25.9
10	26.1 ± 17.4	9.67 ± 6.6	25.4 ± 10.0
24	22.4 ± 3.6	21.25 ± 8.2	67.2 ± 20.2
48	12.8 ± 2.6	33.74 ± 13.0	64.6 ± 9.5
72	8.5 ± 3.5	23.55 ± 9.5	78.8 ± 8.4
96	9.3 ± 2.5	24.2 ± 7.2	90.1 ± 4.9
120	0.0 ± 2.3	18.63 ± 4.8	89.6 ± 6.5
144	0.6 ± 2.4	21.31 ± 7.5	97.6 ± 9.3
168	4.7 ± 2.3	26.18 ± 5.4	102.3 ± 7.3
192	3.9 ± 4.1	23.69 ± 6.5	104.4 ± 5.9
216	8.5 ± 9.6	27.43 ± 4.7	108.8 ± 5.9
240	12.7 ± 9.1	35.76 ± 3.7	112.1 ± 6.3
264	11.3 ± 10.4	30.95 ± 2.5	113.0 ± 5.7
288	13.3 ± 12.0	34.55 ± 7.4	115.8 ± 4.3
312	19.1 ± 13.3	36.68 ± 2.1	117.1 ± 4.7
336	17.5 ± 21.5	37.31 ± 5.6	119.8 ± 6.2
360	24.2 ± 25.4	40.12 ± 6.3	121.5 ± 6.1
384	27.1 ± 31.2	44.20 ± 7.4	126.1 ± 7.6
408	29.5 ± 32.2	44.95 ± 7.3	126.6 ± 8.8
432	35.8 ± 33.5	46.55 ± 90.	131.0 ± 6.8

Table A3.13. Amount of ethylene adsorption (ppm) at 7°C and 0% RH with carbon dioxide present.

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
2.5	5.2 ± 3.8	9.3 ± 3.0	$12.0 \pm 0.8$
5	1.9 ± 1.3	9.3 ± 3.9	11.5 ± 3.3
7.5	13.3 ± 13.6	10.2 ± 7.2	29.1 ± 10.6
10	11.2 ± 7.2	4.0 ± 2.7	11.2 ± 4.1
24	9.8 ± 1.9	8.7 ± 3.3	29.9 ± 8.6
48	5.6 ± 1.4	13.6 ± 4.5	28.8 ± 3.6
72	3.7 ± 1.6	9.4 ± 3.1	35.1 ± 3.3
96	$4.0 \pm 1.0$	9.7 ± 2.4	40.2 ± 1.5
120	$0.0 \pm 1.0$	7.5 ± 1.3	40.0 ±2.0
144	0.3 ± 1.1	8.6 ± 2.8	43.5 ± 3.5
168	2.0 ± 1.0	10.6 ± 1.7	45.6 ± 2.4
192	1.7 ± 1.8	9.6 ± 2.3	46.5 ± 1.7
216	3.7 ± 4.1	11.1 ± 1.3	48.5 ± 1.8
240	5.5 ± 3.9	$14.6 \pm 1.4$	50.0 ± 1.5
264	4.9 ± 4.4	$12.6 \pm 0.9$	50.4 ± 1.5
288	5.8 ± 5.1	14.2 ± 3.4	51.7 ± 0.5
312	8.3 ± 5.6	15.0 ± 1.7	52.2 ± 0.6
336	7.6 ± 9.2	15.3 ± 3.0	53.5 ± 1.2
360	10.5 ± 10.8	16.6 ± 3.8	54.2 ± 1.2
384	11.7 ± 13.3	18.3 ± 4.5	56.3 ± 1.8
408	12.7 ± 13.7	18.6 ± 4.5	56.4 ± 2.4
432	15.4 ± 14.3	19.3 ± 5.4	58.4 ± 1.4

Table A3.14. Amount of ethylene adsorption (%) at 7°C and 0% RH with carbon dioxide present.

Table A3.15. Amount of ethylene adsorption (ppm) at room temperature and 100% RH.

time [h]	CO [ppm]	CL [ppm]	4A [ppm]
0	0	0	0
24	$1.5 \pm 0.6$	5.8 ± 8.4	165.4 ± 1.7
48	1.8 ± 2.6	9.8 ± 9.1	116.3 ± 10.4
72	2.3 ± 2.7	10.9 ± 8.8	113.1 ± 11.7
96	3.0 ± 2.9	9.4 ± 13.6	116.0 ± 13.2

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
24	$0.3 \pm 0.1$	1.3 ± 1.8	36.1 ± 0.6
48	$0.4 \pm 0.6$	2.1 ± 2.0	25.4 ± 2.4
72	0.5 ± 0.6	2.4 ± 1.9	24.7 ± 2.7
96	0.6 ± 0.6	2.0 ± 3.0	25.3 ± 3.0

Table A3.16. Amount of ethylene adsorption (%) at room temperature and 100% RH.

## Table A3.17. Amount of ethylene adsorption (ppm) at 7°C and 100% RH.

time [h]	CO [ppm]	CL [ppm]	4A [ppm]
0	0	0	0
24	5.3 ± 5.9	22.8 ± 5.3	324.5 ± 16.1
48	12.5 ± 9.7	$10.1 \pm 0.9$	293.6 ± 19.2
72	7.4 ± 4.9	5.8 ± 2.8	246.8 ± 16.3
96	8.3 ± 7.0	6.9 ± 1.7	220.2 ± 15.7

Table A3.18. Amount of ethylene adsorption (%) at 7°C and 100% RH.

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
24	$1.1 \pm 1.3$	4.9 ± 1.2	71.4 ± 4.2
48	2.7 ± 2.1	2.2 ± 0.2	64.6 ± 4.9
72	$1.6 \pm 1.0$	$1.3 \pm 0.6$	54.3 ± 4.1
96	1.8 ± 1.5	$1.5 \pm 0.4$	48.4 ± 3.8

Table A3.19. Amount of carbon dioxide adsorption (%) at room temperature and 0% RH.

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
2.5	0.8 ± 0.7	1.8 ± 1.9	19.9 ± 0.7
5	0.5 ± 0.5	1.6 ± 1.8	24.0 ± 2.1
7.5	$1.3 \pm 0.5$	2.6 ± 2.1	24.8 ± 2.1
10	3.2 ± 0.5	4.2 ± 1.6	25.2 ± 1.8

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
2.5	0.8 ± 0.5	$3.1 \pm 0.5$	$10.1 \pm 1.5$
5	$1.0 \pm 0.4$	3.2 ± 0.4	14.6 ± 1.3
7.5	0.6 ± 0.7	3.3 ± 0.7	16.6 ± 1.3
10	0.8 ± 0.2	3.3 ± 0.8	17.8 ± 1.2
12.5	0.7 ± 0.5	3.6 ± 0.8	18.7 ± 1.4
24	0.8 ± 0.4	3.9 ± 0.8	19.4 ± 0.9
48	0.9 ± 0.3	4.3 ± 0.3	20.2 ± 0.9

Table A3.20. Amount of carbon dioxide adsorption (%) at room temperature and 0% RH in presence of ethylene.

Table A3.21. Amount of carbon dioxide adsorption (%) at room temperature and 0% RH in presence of oxygen.

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
2.5	0.3 ± 0.3	$11.0 \pm 0.2$	7.7 ± 0.3
5	$0.5 \pm 0.1$	$11.0 \pm 0.7$	5.8 ± 0.3
7.5	0. ± 0.2	$11.0 \pm 0.3$	4.7 ± 0.2
10	$0.2 \pm 0.1$	$11.1 \pm 0.5$	4.2 ± 0.3
12.5	0.3 ± 0.2	$11.1 \pm 0.4$	3.8 ± 0.3
15	0.3 ± 0.2	$11.0 \pm 0.4$	3.8 ± 0.3

Table A3.22. Amount of carbon dioxide adsorption (%) at room temperature and 100% RH.

time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
2.5	3.0 ± 1.4	4.6 ± 3.1	28.8 ± 1.9
5	0.9 ± 1.0	4.1 ± 2.4	30.8 ± 0.6
7.5	1.3 ± 1.1	4.1 ± 0.3	29.7 ± 0.8

Table A3.23. Amount of carbon dioxide adso	ption (%) at 7°C and 0% RH in	presence of ethylene.
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time [h]	CO [%]	CL [%]	4A [%]
0	0	0	0
2.5	1.2 ± 0.8	8.0 ± 1.5	18.8 ± 1.2
5	1.1 ± 1.1	9.4 ± 1.1	27.6 ± 1.5
7.5	1.2 ± 0.6	10.3 ± 1.5	36.1 ± 2.3
10	1.1 ± 0.9	8.1 ± 2.3	36.7 ± 0.7
24	2.1 ± 1.0	10.6 ± 1.1	45.7 ± 2.3
48	$1.0 \pm 1.6$	12.4 ± 1.9	46.1 ± 1.0
time [h]	CO [%]	CL [%]	4A [%]
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0	0	0	0
2.5	0.8 ± 0.7	6.2 ± 1.3	15.1 ± 1.3
5	$1.4 \pm 0.6$	5.9 ± 1.1	20.8 ± 0.9
7.5	$1.1 \pm 1.1$	5.3 ± 0.7	22.6 ± 1.7
10	1.3 ± 0.8	5.0 ± 0.4	23.4 ± 1.5
12.5	$1.1 \pm 0.5$	4.2 ± 0.7	23.4 ± 2.0

Table A3.24. Amount of carbon dioxide adsorption (%) at 7°C and 100% RH.

REFERENCES

## REFERENCES

- 1. 2012 Production guide for Storage of Organic Fruits and Vegetables NYS IPM Publication no.10
- Coloma A., Rodriguez F.J., Bruna J.E., Guarda A., Galotto M.J. Development of an Active Film with Natural Zeolite as Ethylene Scavenger, Journal of the Chilean Chemical Society2014 (49) 2409-2414
- Patdhanagul N., Srithanratana T., Rangsriwatananon K., Hengrasmee S. Ethylene adsorption on cationic surfactant modified zeolite NaY, Microporous and Mesoporous Materials 2010 (131) 97-102
- 4. Erdogan B., Sakizci M., Yorukogullari E. Characterization and ethylene adsorption of natural and modified clinoptilolites, Applied Surface Science 2008 (254) 2450-2457
- Pham-Tuan H., Vercammen J., Devos C., Sandra P. Automated capillary gas chromatographic system to monitor ethylene emitted from biological materials, Journal of Chromatography A 2000 (868) 249-59
- 6. Cristescu S. M., Mandon J., Arslanov D., De Pessemier J., Hermans C., Harren F. J. Current methods for detecting ethylene in plants, Annals of Botany 2013 (111) 347-360
- 7. Suslow T. Performance of zeolite based products in ethylene removal, Perishables Handling Quarterly 1997 (92) 32-33
- 8. Meigh D. F. Use of gas chromatography in measuring the ethylene production of stored apples, Journal of the Science of Food and Agriculture 2006 (11) 381-385
- 9. Sklorz A., Miyashita N., Schäfer A., Lang W. Low Level Ethylene Detection Using Preconcentrator/Sensor Combinations IEEE SENSORS 2010 Conference 2494- 2499
- 10. De Greef J., De Proft M., De Winter F. Gas chromatographic determination of ethylene in large air volumes at fractional parts-per-billion level, Analytical Chemistry 1976 (48) 38–41
- 11. Sharma S., Sharma R. R., Pal R. K., Jhalegar M. J., Singh J., Srivastav M., Dhiman M. R. Ethylene absorbents influence fruit firmness and activity of enzymes involved in fruit softening of Japanese plum (Prunussalicina Lindell), Santa Rosa Fruits 2012 (67) 257–266
- 12. Peiser G., Suslow T. V. Factors Affecting Ethylene Adsorption by Zeolite: The Last Word (from us), Perishables Handling Quarterly 1998 (95) 17-19
- 13. Piergiovanni L., Scolaro M., Fava P. Measurement of ethylene permeability of plastic films, Packaging Technology and Science 1992 (5) 189-196
- 14. Potter, L., Campbell, A.J. and Cava, D. Active and Intelligent Packaging a Review. Review No. 62, Campden BRI 2008
- 15. Garrett E. H. Fresh-cut produce in Blakistone, B.A. (ed.) Principles and Application of Modified Atmosphere Packaging of Foods(125-134) Blackie Academic & Professional 1998

- van Dongen J. T., Gupta K. J., Ramirez-Aguilar S. J., Araujo W. L., Nunes-Nesi A., Fernie A. R. Regulation of respiration in plants: a role for alternative metabolic pathways, Journal of Plant Physiology 2011(12) 1434-1443
- 17. Kader A.A. Postharvest Biology and Technology: An Overview in Kader A.A. (ed.) Postharvest technology of horticultural crops (39-48) University of California Agriculture and Natural Resources Publication 3311 2002
- 18. Ozdemir M., Floros J. D. Active Food Packaging Technologies, Critical Reviews in Food Science and Nutrition, 2004 (44) 185-193
- 19. Yuzay I.E., Auras R., Selke S. Poly(lactic acid) and synthetic zeolite composites prepared by melt processing, Journal of Applied Polymer Science 2009 (115) 2262-2270
- 20. Elaiopoulos E. Operations involving organic gases and vapors in Inglezakis V. J., Zorpas A. A. (ed.) Handbook of Natural Zeolites (246-252) Bentham Science Publishers 2012
- Romero-Perez A., Aguilar-Armenta G. Adsorption kinetics and equilibria of carbon dioxide, ethylene and ethane on 4A(CECA) zeolite, Journal of Chemical and Engineering Data 2010 (55) 3625–3630
- 22. Rouquerol F., Rouquerol J., Sing K. Adsorption by Powders and Porous Solids. Principles, Methodology and Applications Academic Press 2014
- 23. Jinqu W., Yongchun Z. Adsorption equilibrium of ethylene-carbon dioxide mixture on zeolite ZSM5 and its correlation, Journal of Chemical Industry and Engineering (China) 1992 (7) 208-215
- 24. Sircar S., Myers A. L. Gas Separation by Zeolites in Auerbach S. M., Carrado K. A., Dutta P. K. (ed.) Handbook of Zeolite Science & Technology (1354-1406) Dekker2003
- Aguilar-Armenta G., Hernandez-Ramirez G., Flores-Loyola E., Ugarte-Castaneda A., Silva-Gonzalez R., Tabares-Munoz C., Jimenez-Lopez A., Rodriguez-Castellon E. Adsorption Kinetics of CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> in Cation-Exchanged Clinoptilolite, Journal of Physical Chemistry B 2001 (105) 1313-1319
- 26. http://helios.princeton.edu/zeomics/

#### CHAPTER 4

#### Effect of the processing method on the adsorbing gas capability of active films made of PLA/zeolite

### 4.1. Introduction

In chapter 3 sorption characteristics of two zeolites were investigated. Natural clinoptilolite (CL) and synthetic type 4A zeolites in the form of powder were proven to have simultaneous sorption capacities for ethylene and carbon dioxide. The next step was to incorporate them into plastic films so that they could be used as packaging materials for fresh produce. But first an appropriate method of production was needed. This method should not only result in a composite material made of PLA and zeolites but should not limit the sorption capacities of zeolites due to their incorporation into the polymer materials. PLA was chosen due to it being biobased and known to biodegrade reasonably quickly in commercial compost, and so it provides an alternative to commonly used petrochemical based polymers.

A commonly used technology for mixing polymers with additives is extrusion, preceded by production of a masterbatch [1]. Two zeolites, synthetic type 4A and natural chabazite, were used. First PLA and zeolites were placed in a micro extruder with co-rotating twin-screws; then the extrudate was transferred to a mini-injection molder and small discs were formed. To obtain thin films, the discs were compressed. No compatibilizer was needed [2-3].

Solvent coating is a known method of incorporating different materials on the surface of extruded films. Although it has not been commonly used for zeolites, it has been utilized in PLA production.

This chapter will show how different processing methods can produce films of varying sorption capacities for the two gases of interest. It will also show how small modifications within a given process can significantly change the sorption characteristics of a given film.

## 4.2. Experimental

## 4.2.1. Materials

## 4.2.1.1. Zeolites and Gases

Two zeolites were chosen, one synthetic - type 4A and one natural - clinoptilolite, and two adsorbents, ethylene and carbon dioxide, as described in chapter 3.

## 4.2.1.2. Poly(lactic acid)

PLA was used in two different forms - pellets and film. Pellets of PLA resin 4060 D were obtained from Nature Works LLC (Blair, NE, US). Film was purchased as a roll from Evlon (Wingham, Ontario, Canada) - F40EVHS, biaxially oriented with outside corona treatment to improve the surface adhesion of the coating.

Pellets were dried overnight in a vacuum oven at 60°C and stored in a desiccator. PLA film was coated with a zeolite/PLA coating solution on the outside.

## 4.2.2. Methods of thin film production

## 4.2.2.1. Extrusion, followed by injection molding and compression molding

PLA composites with 30 wt% of one of the zeolites, clinoptilolite or type 4A, were produced in the Composite Materials and Structures Center at Michigan State University. Both PLA and zeolites were dried in a vacuum oven before processing, as previously described, cooled and stored in a desiccator prior to use.

A DSM microextruder with co-rotating twin-screws (DSM Research, Netherlands) was used to mix PLA with the zeolites. Processing temperatures in the microextruder (top, middle, bottom) were all 190°C with melt temperature of 185°C. Screw speed was 100 rpm and retention time was 5 minutes. The resulting extrudate was collected from the die into a preheated transfer cylinder (195°C) and transferred into a mini injection molder (DSM Research, Netherlands). The applied injection pressure was 896 kPa with the mold kept at 30°C. Round micro discs were molded (figure 4.1). Dry ice was used to remove the discs from the mold.



Figure 4.1. Injection molded PLA, PLA/30% type 4A zeolite, PLA/30% clinoptilolite discs.

These discs were later dried overnight at 60°C in a vacuum oven and compression molded into thin films in a PHI Heated Press (model no. QL438-C, City of Industry, CA, US) (figure 4.2) at 320°F by applying a force of 25 tons for 5 minutes.



Figure 4.2. Heated press used to produce films from injection molded discs.

The resulting films had a thickness between 0.09 and 0.05 mm. In a similar manner PLA films with no additives were produced. Differences in thicknesses of resulting composite films might influence sorption measurements. Thicker films will have a larger barrier of PLA between the gases and the zeolites that might inhibit adsorption.

## 4.2.2.2. Bar coating

For bar coating, an instrument that allows accurate and reproducible prints was used (RK K303 Multicoater, United Kingdom) (figure 4.3). All coating solutions were prepared at room temperature and a mixing time of 45 minutes. The coating solution was 20 mL of acetone and various combinations of PLA and zeolites, as detailed in the results and discussion section. With this method, the thickness of the final film can be controlled by using different coating bars. The lower the number of the coating bar, the smaller is the thickness. Bars with numbers between 0 and 8 were used with speed set to 4 m/min. Coated films were dried in air and kept overnight in a desiccator before testing. Although PLA was coated with a solution containing both PLA and zeolites, the nomenclature has been shortened to PLA/zeolite coated film for simplicity.



Figure 4.3. Multicoater used to produce coated films.

# 4.2.2.3. Sample preparation

All films were cut into the same size samples (17.5 x 8 cm), stapled on the end to prevent rolling, and placed into 250 mL glass jars with metal closures. For filling and sampling purposes, holes were drilled in the lids and septa made of gray butyl rubber were inserted. The headspace was flushed with both gases ( $C_2H_4$  and  $CO_2$ ) and placed in a controlled temperature room (23°C).

# 4.2.3. Adsorption measurements

## 4.2.3.1. Gas Chromatography with Flame Ionization Detector (GC FID)

GC FID (Hewlett Packard GC 6890, Agilent Technologies, Santa Clara, CA, US) is used to detect  $C_2H_4$  concentration in the sampling systems (glass jars with aluminum closures and septa). The column used is Supelco Carboxen 1010 PLOT, L x I.D. 30m x 0.53 mm, packed with fused silica. The measuring method for  $C_2H_4$  was as follows: oven temperature of 150°C and a continuous run of 13 min, the retention time for a clear and symmetrical  $C_2H_4$  peak was 11 min. Both inlet and detector temperatures were 220°C.

#### 4.2.3.2. Gas Chromatography with Thermal Conductivity Detector (GC TCD)

GC TCD (ThermoScientific Trace GC Ultra GC with FID/TCD, Waltham, MA, US) was used to detect CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> concentrations in the sampling systems (same jars). The column used was as mentioned above. For detection of headspace gases (O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub>) the measuring method was as follows: temperature ramp from 45°C to 190°C and then to 230°C with a total run time of 9 min and retention times of 3.4 min for O<sub>2</sub>, 3.55 min for N<sub>2</sub> and 7.2 min for CO<sub>2</sub>. Inlet and detector temperatures were 200°C. For both measurements, 50 µL of sample was injected into the GC using a 100 µL gas tight syringe with needle valve (Supelco SGE, Australia).

Adsorption measurements were compared after 48 hours and after one week for all samples. Three replicates of each type of samples were tested. Results for  $C_2H_4$  are presented in % to show the proportion of the total headspace gas that was adsorbed and in nL to show the exact adsorbed volumes. For CO<sub>2</sub>, % and mL results are presented for the same reasons. Calibration curves can be found in appendix in chapter 3.

#### 4.2.4. Characterization of produced films

### 4.2.4.1. Thermogravimetric Analysis (TGA)

A TGA Q50 (TA Instruments, New Castle, DE, US) was used to determine the zeolite content in the PLA films. From five to ten g per sample was tested at a ramp of  $10^{\circ}$ C/min from  $23^{\circ}$ C to  $550^{\circ}$ C with constant N<sub>2</sub> flow of 70 mL/min. Zeolite content was measured for each sample.

## 4.2.4.2. Scanning Electron Microscopy (SEM)

SEM (Carl Zeiss Variable Pressure SEM EVO LS25, Germany) was used to determine how zeolites were distributed in/on the PLA surface. Images were acquired with an accelerating voltage of 20 kV and a working distance of 10 mm at 6 k and 11 k x magnification.

## 4.2.5. Statistical methods

Analysis of variance (ANOVA) was performed in the analytical software SPSS version 22 (SPSS Inc., Chicago, IL, US). Means were separated using the Tukey honestly significant difference (HSD) test (p < 0.05).

## 4.3. Results and discussion

## 4.3.1. Melt processing

Figures 4.4 and 4.5 show results for plain PLA and PLA/30 wt% zeolite composites with both zeolites. The first measurement was taken 48 hours after filling the jars with  $C_2H_4$  and  $CO_2$ , while the final measurement was taken after 6 weeks of storage. The adsorption percentage was calculated using equation 4.1.

 $\frac{\text{initial gas concentration-final gas concentration}}{\text{initial gas concentration}} \cdot \frac{1}{g \text{ zeolite in film}} \cdot 100\%$ (4.1)

While volume results (nL, mL) were normalized according to equation 4.2.

 $\frac{\text{initial volume of gas} - \text{final volume of gas}}{g \text{ zeolite in film}}$ (4.2)



Figure 4.4. Amount of ethylene (%) adsorbed by film samples at 2 different times.



Figure 4.5. Amount of ethylene (nL) adsorbed by film samples at 2 different times.



Figure 4.6. Amount of carbon dioxide (%) adsorbed by film samples at 2 different times.



Figure 4.7. Amount of carbon dioxide (mL) adsorbed by film samples at 2 different times.

Comparing all collected data (figures 4.4 - 4.7), it was shown that for both gases there was no significant amount adsorbed within the first two days (p < 0.05). C<sub>2</sub>H<sub>4</sub>adsorption of about 2% was observed for the composite materials and about 1% for plain PLA (figures 4.4 - 4.5). For CO<sub>2</sub> only 1% was sorbed by all the samples, with no significant difference whether samples contained zeolite or not (p >

0.05) (figures 4.6 - 4.7). Measurements carried out for multiple weeks showed almost no change in adsorption of  $C_2H_4$  for samples with zeolites incorporated into PLA. But the PLA itself seemed to sorb more than the investigated composites. For CO<sub>2</sub>, a similar situation was observed. PLA sorbed more than the zeolite composites. This time there was a significant difference between performance of the zeolites (p < 0.05); type 4A zeolite resulted in higher adsorption of CO<sub>2</sub> when compared to CL.

Supporting data for this chapter can be found in appendix below.

## 4.3.2. Surface characteristics

At that point it was suspected that zeolites that are incorporated too deeply into the polymer matrix have inhibited adsorption capacity for  $C_2H_4$ . To investigate, SEM images of both materials were taken (figure 4.8).



Figure 4.8. SEM images of PLA/30 wt% CL (on left) and PLA/30 wt% 4A (on right).

Figure 4.8 shows that in both cases zeolites are not on the surface of PLA but inside its matrix. Since PLA is a good barrier to  $C_2H_4$ , it blocks the adsorption capacities of both zeolites.

## 4.3.3. Solution coating

There was a need for a new method that would allow zeolites to be deposited as much on the surface of the PLA as possible. Methods considered included bar coating, spin coating, knife coating, plasma application, cast extrusion, blown film and extrusion of a bilayer. It was decided to start with bar coating as a widely used method that could be evaluated relatively quickly.

When comparing all samples, extruded and coated, after 2 days increased adsorption in the coated films compared to the extruded films was observed (figures 4.9 and 4.12). It should be also noted that although both zeolites were coated similarly on the PLA surface they displayed different adsorption behavior. Natural clinoptilolite was more active with  $CO_2$ , while synthetic 4A was more active for  $C_2H_4$ .



Figure 4.9. Amount of ethylene (%) adsorbed by extruded (ext) and coated (coat)film samples.



Figure 4.10. Amount of ethylene (nL) adsorbed by extruded and coated film samples.



Figure 4.11. Amount of carbon dioxide (%) adsorbed by extruded and coated film samples.



Figure 4.12. Amount of carbon dioxide (mL) adsorbed by extruded and coated film samples.

As those initial measurements showed promise that coating was a more appropriate method of production for PLA/zeolite composites than extrusion, it was further investigated.

The next step was to try different coating solutions, to determine if an increase in wt% of zeolite would increase adsorption. Solutions of 30, 60 and 90 wt% of both zeolites were prepared and tested. Coating solutions were modified only by adding more zeolites, 20 mL of acetone, 1 g of PLA and 0.3, 0.6 or 0.9 g of zeolite, respectively. Also different coating bars were used, to see how the thickness of the resulting film influenced wt% and adsorption capacity, all with the goal of increasing the exposure of zeolites on the surface of the PLA film. Tested combinations of coating solutions and bars used for coating are listed in table 4.1.

sample	bar	% zeolite
PLA+30%CL	0	0.98
PLA+30%CL	7	2.69
PLA+30%CL	8	3.14
PLA+60%CL	7	5.07
PLA+60%CL	8	5.93
PLA+90%CL	8	7.02
PLA+30%4A	7	3.34
PLA+60%4A	7	4.33
PLA+60%4A	8	2.37
PLA+90%4A	8	7.48

Table 4.1. List of combination of wt% of zeolite in coating solution and bar used for coating and % of zeolite in obtained film.

Mixing different coating solutions and using different bars for coating did not give conclusive results, as shown in figures 4.13 and 4.16. There was too much variation in preparation of film samples. Since two variables were changed at the same time, the coating solution together with the bar, it was not easy to see which of these had the actual effect on adsorption capacity of the investigated samples. Nevertheless, for most samples it was observed that after a week their adsorption capacity was significantly increased when compared to data collected after 48 hours (p < 0.05). What was interesting is that natural zeolite (CL), which when investigated as powder always displayed worse adsorption capacity than synthetic one (4A), this time, when incorporated into film, CL could compete with 4A and in few cases be a more active compound. This was noted for both  $C_2H_4$  and  $CO_2$ . The main difference between CL and 4A is that natural zeolite is hydrophilic and the synthetic one is hydrophobic. Due to having PLA on the surface, covering the zeolites, any  $H_2O$  molecules have to get through the PLA first before getting into the zeolites and this way, sorption sites in CL are not blocked by moisture.



Figure 4.13. Amount of ethylene (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars.



Figure 4.14. Amount of ethylene (nL) adsorbed by coated film samples prepared using different coating solutions and different coating bars.



Figure 4.15. Amount of carbon dioxide (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars.



Figure 4.16. Amount of carbon dioxide (mL) adsorbed by coated film samples prepared using different coating solutions and different coating bars.

Due to the inconclusiveness of the data shown in figures 4.13 - 4.16, it was decided to try to use as little PLA and as much zeolite in the coating solution as possible, so that the PLA would not block the zeolites but still enough PLA so that a uniform coating was obtained. Different combinations of PLA and zeolite weights that were tested in coating solutions are listed in table 4.2. TGA was used to determine the zeolite % in each film. Using a bar with a smaller number resulted in a thinner layer of PLA on top of the zeolites, allowing for less coverage of the particles with PLA. Adsorption measurements were carried out for a maximum of three weeks so that adsorption characteristics of all materials could be fully discovered. Results are shown in figures 4.17 - 4.20.

Table 4.2. List of combination of PLA and zeolite weights in coating solution along with bar used for coating and % of zeolite in obtained film.

sample	bar	% zeolite
PLA+ CL (1g + 0.3g)	8	3.67
PLA + CL (0.2g + 1g)	2	2.55
PLA + CL (0.2g + 1g)	3	3.56
PLA+ 4A (1g + 0.3g)	8	3.79
PLA + 4A (0.2g + 1g)	2	2.05
PLA + 4A (0.2g + 1g)	3	3.49
PLA + 4A (0.8g + 1g)	3	4.26

Analyzing samples with CL, it can be seen that although initially (after 2 days) there was no significant difference between the four samples (p < 0.05), after one week one of the combinations (PLA + CL (0.2 g + 1 g) and B3) started to show superior behavior due to the higher amount of CL and lower amount of PLA, which continued in the next two weeks. This happened for both gases, which also proves that adsorption was not selective to only one gas at a time but happened simultaneously for C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub>. Results for 4A composites seemed similar to what was observed for CL. For the 2-day measurement, there was no significant difference between the samples for both gases (p > 0.05). But it gets more interesting when comparing data after one, two and three weeks. One sample (PLA+ 4A (1 g + 0.3 g) and B8) seemed more prone to adsorb C<sub>2</sub>H<sub>4</sub> and a little bit less CO<sub>2</sub> while another (PLA + 4A (0.2 g + 1 g) and B2) was exactly the opposite. All of this happened because of the processing differences. Bar 8 resulted in a higher thickness of the final material than bar 2, so larger CO<sub>2</sub> molecules will have more

issues in getting to the zeolites. The same goes for having 5 times higher content of PLA in the coating solution. Remembering that PLA is a good barrier to  $C_2H_4$  and  $CO_2$  is also important [4-5]. A higher content of zeolite means more available adsorption sites. Since in active packaging of fresh produce,  $C_2H_4$  has more negative effects than  $CO_2$  does, the better option here is the first sample.



Figure 4.17. Amount of ethylene (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars at four sampling times.



Figure 4.18. Amount of ethylene (nL) adsorbed by coated film samples prepared using different coating solutions and different coating bars at four sampling times.



Figure 4.19. Amount of carbon dioxide (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars at four sampling times.



Figure 4.20. Amount of carbon dioxide (mL) adsorbed by coated film samples prepared using different coating solutions and different coating bars at four sampling times.

Based on the results shown in figures 4.17 to 4.20 and visual evaluation of the homogeneity of the coating, it was concluded that for each zeolite different combinations of coating solution and bar were optimal. For CL the best results were obtained with 0.2 g of PLA and 1 g of zeolite and bar no. 3, while for type 4A more PLA was required in solution, 1g of PLA mixed with 0.3 g of zeolite and coated with bar no. 8. Measured using TGA, both options resulted in a similar wt% of zeolite, 3.56% of CL and 3.79% of 4A. Both values are smaller than the wt% for commercially available film that was tested in the same manner, LDPE with 5 wt% of zeolite as determined by TGA. For this film, the producer does not provide information about what zeolite is used or by what process the film is produced.

## 4.4. Conclusions

Bar coating is a superior method for preparing PLA/zeolite composite materials for adsorption of  $C_2H_4$  and  $CO_2$  compared to extrusion followed by injection molding and compression. Films obtained by the first method allow zeolites to be more on the surface of the films rather than being too deeply incorporated into the polymer matrix, which eventually blocks their adsorption capacity due to PLA being a good barrier to  $C_2H_4$ .

Varying the composition of coating solution (amounts of PLA and zeolites) but also changing the thickness of the coating by using different bars strongly influenced the adsorption capacities of the resulting films. Natural clinoptilolite needs much less PLA and a thinner coating layer than does synthetic 4A, which suggests that CL blends better with PLA.

Further studies should be done to evaluate the adsorption capacities of the investigated films in real life situations relevant to packing fresh produce (low temperature and high relative humidity).

APPENDIX

% eth	2 days	6weeks		
PLA	0.9 ± 0.3 a1*	5.1 ± 2.2 a2		
PLA+30%CL	2.1 ± 0.6 a1	2.7 ± 1.2 a1		
PLA+30%4A	2.4 ± 1.2 a1	2.7 ± 1.9 a1		

Table A4.1. Amount of ethylene (%) adsorbed by film samples at two different times.

Table A4.2. Amount of et	nylene (nl	) adsorbed by	y film sam	ples at two different times.
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% eth	2 days	6 weeks
PLA	0.2 ± 0.1 a1*	0.5 ± 0.3 a2
PLA+30%CL	0.4 ± 0.2 a1	$0.4 \pm 0.2 a1$
PLA+30%4A	0.4 ± 0.2 a1	0.5 ± 0.3 a1

\* means followed by the same lower case letter in column, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A4.3. Amount of carbon dioxide (70) ausorbed by mini samples at two different times	Table A4.3. Amount of carbon dioxide	(%)	adsorbed by	y film sam	ples at two	different times.
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% CO <sub>2</sub>	2 days	6 weeks
PLA	1.1 ± 0.4 a1*	5.7 ± 2.6 ab2
PLA+30%CL	1.3 ± 0.7 a1	2.2 ± 1.6 b1
PLA+30%4A	1.5 ± 1.8 a1	3.8 ± 0.2 a2

\* means followed by the same lower case letter in column, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A4.4. Amount of carbon dioxide (%) adsorbed by film sa	mples at two different times.
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% CO <sub>2</sub>	2 days	6 weeks
PLA	2.7 ± 0.9 a1*	14.3 ± 6.6 ab2
PLA+30%CL	3.2 ± 1.7 a1	5.6 ± 3.9 b1
PLA+30%4A	3.6 ± 4.5 a1	3.4 ± 0.4 a2

% eth	2 days
PLA (ext)	0.9 ± 0.3 a*
PLA+30%CL (ext)	2.1 ± 0.6 a
PLA+30%4A (ext)	2.4 ± 1.2 a
PLA+30%CL (coat)	2.0 ± 0.6 a
PLA+30%4A (coat)	3.0 ± 1.0 a

Table A4.5. Amount of ethylene (%) adsorbed by extruded and coated film samples.

Table A4.6. Amount of ethylene (nL) adsorbed by extruded and coated film samples.

nL eth	2 days
PLA (ext)	0.2 ± 0.1 a*
PLA+30%CL (ext)	0.4 ± 0.2 a
PLA+30%4A (ext)	0.4 ± 0.2 a
PLA+30%CL (coat)	0.3 ± 0.1 a
PLA+30%4A (coat)	0.5 ± 0.2 a

\* means followed by the same lower case letter in column are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A4.7. Amount of Carbon dioxide (%) adsorbed by extruded and coaled him samples	Table A4.7. Amount of carbon	dioxide (%) adsorbed b	y extruded and coated film samples.
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% CO <sub>2</sub>	2 days
PLA (ext)	1.1 ± 0.4 a*
PLA+30%CL (ext)	1.3 ± 0.7 a
PLA+30%4A (ext)	1.5 ± 1.8 a
PLA+30%CL (coat)	3.2 ± 1.3 a
PLA+30%4A (coat)	1.7 ± 0.2 a

\* means followed by the same lower case letter in column are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

|--|

mL CO <sub>2</sub>	2 days
PLA (ext)	2.7 ± 0.9 a*
PLA+30%CL (ext)	3.2 ± 1.7 a
PLA+30%4A (ext)	3.6 ± 4.5 a
PLA+30%CL (coat)	8.0 ± 3.3 a
PLA+30%4A (coat)	4.3 ± 0.5 a

% eth	2 days	week
PLA+PLA B3	0.6 ± 0.1 a1*	2.0 ± 1.5 a2
PLA+30%CL B0	0.8 ± 0.5 a1	4.5 ± 1.0 a2
PLA+30%CL B7	1.8 ± 0.9 a1	4.1 ± 0.4 a2
PLA+30%CL B8	2.0 ± 0.6 a1	7.4 ± 1.2 a2
PLA+60%CL B7	1.4 ± 0.3 a1	3.8 ± 1.3 a2
PLA+60%CL B8	2.6±0.7 ab1	2.6 ± 0.7 a1
PLA+90%CL B8	4.0 ± 1.1 b1	4.9 ± 1.3 a1
PLA+30%4A B7	3.0 ± 1.0 ab1	5.1 ± 2.3 a1
PLA+60%4A B7	1.4 ± 0.5 a1	5.7 ± 3.2 a2
PLA+60%4A B8	1.7 ± 0.6 a1	4.2 ± 1.1 a2
PLA+90%4A B8	2.8 ± 1.0 ab1	5.5 ± 1.0 a2

Table A4.9. Amount of ethylene (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars.

Table A	<b>\4.10</b> . <i>I</i>	Amount	of ethylene	(nL)	adsorbed	by	coated	film	samples	prepared	using	different
coating	solutio	ons and d	ifferent coat	ing b	ars.							

nL eth	2 days	week
PLA+PLA B3	$0.1 \pm 0.0 a1^*$	0.2 ± 0.2 a2
PLA+30%CL B0	0.1 ± 0.1 a1	0.5 ± 0.1 a2
PLA+30%CL B7	0.2 ± 0.1 a1	0.5 ± 0.0 a2
PLA+30%CL B8	0.2 ± 0.1 a1	0.8 ± 0.1 a2
PLA+60%CL B7	0.2 ± 0.0 a1	0.4 ± 0.1 a2
PLA+60%CL B8	0.3 ± 0.1 ab1	0.3 ± 0.1 a1
PLA+90%CL B8	0.4 ± 0.1 b1	0.5 ± 0.1 a1
PLA+30%4A B7	0.3 ± 0.1 ab1	0.6 ± 0.3 a1
PLA+60%4A B7	0.2 ± 0.1 a1	0.6 ± 0.4 a2
PLA+60%4A B8	0.2 ± 0.1 a1	0.5 ± 0.1 a2
PLA+90%4A B8	0.3±0.1 ab1	0.6 ± 0.1 a2

% CO <sub>2</sub>	2 days	week
PLA+PLA B3	1.6 ± 0.5 a1*	3.0 ± 0.1 a2
PLA+30%CL B0	0.8 ± 0.5 a1	4.0 ± 0.7 a2
PLA+30%CL B7	3.2 ± 1.3 b1	5.3 ± 1.4 a1
PLA+30%CL B8	2.1 ± 0.7 ab1	6.1 ± 1.0 a2
PLA+60%CL B7	2.6 ± 0.4 ab1	3.6 ± 0.7 a1
PLA+60%CL B8	3.5 ± 0.2 b1	3.9 ± 1.5 a1
PLA+90%CL B8	2.1 ± 0.7 ab1	4.2 ± 1.5 a1
PLA+30%4A B7	1.7 ± 0.2 ab1	3.8 ± 1.3 a1
PLA+60%4A B7	2.4 ± 1.5 ab1	5.3 ± 1.8 a1
PLA+60%4A B8	2.7 ± 1.3 ab1	3.7 ± 1.0 a1
PLA+90%4A B8	1.6 ± 1.0 ab1	4.4 ± 1.8 a1

Table A4.11. Amount of carbon dioxide (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars.

unierent coating solut	merent coating solutions and unrerent coating bars.							
mL CO <sub>2</sub>	2 days	week						
PLA+PLA B3	4.0 ± 1.2 a1*	7.4 ± 0.3 a2						
PLA+30%CL B0	2.0 ± 1.2 a1	9.9 ± 1.6 a2						
PLA+30%CL B7	8.0 ± 3.3 b1	13.3 ± 3.6 a1						
PLA+30%CL B8	5.3 ± 1.7 ab1	15.2 ± 2.4 a2						
PLA+60%CL B7	6.5 ± 1.0 ab1	8.9 ± 1.8 a1						
PLA+60%CL B8	8.8 ± 0.6 b1	9.7 ± 3.7 a1						
PLA+90%CL B8	5.2 ± 1.7 ab1	10.5 ± 3.6 a1						
PLA+30%4A B7	4.3 ± 0.5 ab1	9.4 ± 3.2 a1						
PLA+60%4A B7	5.9 ± 3.8 ab1	13.1 ± 4.5 a1						
PLA+60%4A B8	6.6 ± 3.3 ab1	9.2 ± 2.4 a1						
PLA+90%4A B8	4.0 ± 2.5 ab1	10.9 ± 4.4 a1						

Table A4.12. Amount of carbon dioxide (mL) adsorbed by coated film samples prepared using different coating solutions and different coating bars.

0	0			
% eth	2 days	week	2 weeks	3 weeks
PLA + PLA (1g) B3	0.5 ± 0.3 a1*	1.0 ± 0.7 a1	2.3 ± 1.1 a2	3.5 ± 1.4 a2
PLA+ CL (1g + 0.3g) B8	2.4 ± 0.3 a1	2.3 ± 0.7 a1	2.7 ± 0.5 a1	6.1 ± 0.3 a2
PLA + CL (0.2g+1g) B2	1.8 ± 0.8 a1	2.5 ± 0.3 a1	4.7 ± 0.7 b2	7.8 ± 1.0 a3
PLA + CL (0.2g+1g) B3	3.1 ± 1.3 a1	5.1 ± 0.6 b1	8.6 ± 0.8 c2	10.4 ± 1.6 b2
PLA+ 4A (1g + 0.3g) B8	2.5 ± 1.2 a1	4.5 ± 0.6 b12	6.1 ± 0.6 d23	7.3 ± 0.6 a3
PLA + 4A (0.2g+1g) B2	1.2 ± 0.2 a1	2.2 ± 0.2 a1	4.2 ± 0.3 b2	6.9 ± 1.0 a3
PLA + 4A (0.2g+1g) B3	1.8 ± 0.7 a1	2.2 ± 0.4 a1	4.5 ± 0.4 b2	6.5 ± 0.5 a3
PLA + 4A (0.8g+1g) B3	1.8 ± 0.3 a1	3.3 ± 0.1 a2	3.4 ± 0.3 ab2	3.6 ± 0.1 c2

Table A4.13. Amount of ethylene (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars at four different times.

Table A4.14.	Amount of	ethylene	(nL)	adsorbed	by	coated	film	samples	prepared	using	different
coating solut	ions and diff	erent coati	ing b	ars at four	diff	ferent ti	mes.				

nL eth	2 days	week	2 weeks	3 weeks
PLA + PLA (1g) B3	0.1 ± 0.0 a1*	0.1 ± 0.1 a1	0.3 ± 0.1 a2	0.4 ± 0.2 a2
PLA+ CL (1g + 0.3g) B8	0.3 ± 0.0 a1	0.3 ± 0.1 a1	0.3 ± 0.1 a1	0.7 ± 0.0 a2
PLA + CL (0.2g+1g) B2	0.2 ± 0.1 a1	0.3 ± 0.0 a1	0.5 ± 0.1 b2	0.9 ± 0.1 a3
PLA + CL (0.2g+1g) B3	0.3 ± 0.1 a1	0.6 ± 0.1 b1	1.0 ± 0.1 c2	1.1 ± 0.2 b2
PLA+ 4A (1g + 0.3g) B8	0.3 ± 0.1 a1	0.5 ± 0.1 b12	0.7 ± 0.1 d23	0.8 ± 0.1 a3
PLA + 4A (0.2g+1g) B2	0.1 ± 0.0 a1	0.2 ± 0.0 a1	0.5 ± 0.0 b2	0.8 ± 0.1 a3
PLA + 4A (0.2g+1g) B3	0.2 ± 0.1 a1	0.3 ± 0.0 a1	0.5 ± 0.0 b2	0.7 ± 0.1 a3
PLA + 4A (0.8g+1g) B3	0.2 ± 0.0 a1	0.4 ± 0.0 a2	0.4 ± 0.0 ab2	0.4 ± 0.0 c2

\* means followed by the same lower case letter in column, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

% CO <sub>2</sub>	2 days	week	2 weeks	3 weeks
PLA + PLA (1g) B3	0.7 ± 0.6 a1*	1.8 ± 0.2 a2	1.2 ± 1.1 a12	1.8 ± 1.0 a1
PLA+ CL (1g + 0.3g) B8	2.2 ± 0.6 a1	2.8 ± 0.4 a1	5.3 ± 0.0 ab2	9.4 ± 0.7 ab3
PLA + CL (0.2g+1g) B2	2.7 ± 0.5 ab1	3.7 ± 0.4 ab1	7.0 ± 0.8 ac2	11.3 ± 0.6 a3
PLA + CL (0.2g+1g) B3	4.2 ± 0.5 b1	8.9 ± 0.8 c2	12.4 ± 0.9 d3	16.5 ± 0.7 c4
PLA+ 4A (1g + 0.3g) B8	2.6 ± 0.8 ab1	4.5 ± 0.2 bd2	7.9 ± 0.8 ce3	11.6 ± 0.8 a4
PLA + 4A (0.2g+1g) B2	2.8 ± 0.7 ab1	2.9 ± 0.7 a1	6.4 ± 0.3 abc2	8.7 ± 0.9 b3
PLA + 4A (0.2g+1g) B3	4.2 ± 1.1 b1	5.5 ± 0.6 d1	9.7 ± 0.9 e2	11.7 ± 0.6 a2
PLA + 4A (0.8g+1g) B3	2.8 ± 0.3 ab1	3.3 ± 0.2 ab12	4.7 ± 1.0 b2	5.0 ± 0.5 d2

Table A4.15. Amount of carbon dioxide (%) adsorbed by coated film samples prepared using different coating solutions and different coating bars at four different times.

· · · · · · · · · · · · · · · · · · ·						
mL CO <sub>2</sub>	2 days	week	2 weeks	3 weeks		
PLA + PLA (1g) B3	1.7 ± 1.4 a1*	4.5 ± 0.5 a2	3.0 ± 2.6 a12	4.6 ± 2.5 a1		
PLA+ CL (1g + 0.3g) B8	5.5 ± 1.5 a1	7.0 ± 0.9 a1	13.1 ± 0.0 ab2	23.6 ± 1.8 ab3		
PLA + CL (0.2g+1g) B2	6.7 ± 1.3 ab1	9.2 ± 1.0 ab1	17.5 ± 2.0 ac2	28.1 ± 1.6 a3		
PLA + CL (0.2g+1g) B3	10.6 ± 1.3 b1	22.2 ± 2.1 c2	31.0 ± 2.3 d3	41.2 ± 1.7 c4		
PLA+ 4A (1g + 0.3g) B8	6.5 ± 2.0 ab1	11.2 ± 0.5 bd2	19.7 ± 2.0 ce3	28.9 ± 2.1 a4		
PLA + 4A (0.2g+1g) B2	7.1 ± 1.8 ab1	7.3 ± 1.7 a1	16.0 ± 0.6 abc2	21.8 ± 2.3 b3		
PLA + 4A (0.2g+1g) B3	10.4 ± 2.6 b1	13.6 ± 1.6 d1	24.2 ± 2.1 e2	29.3 ± 1.6 a2		
PLA + 4A (0.8g+1g) B3	7.0 ± 0.8 ab1	8.2 ± 0.4 ab12	11.7 ± 2.4 b2	12.5 ± 1.2 d2		

Table A4.16. Amount of carbon dioxide (mL) adsorbed by coated film samples prepared using different coating solutions and different coating bars at four different times.

REFERENCES

## REFERENCES

- Coloma A., Rodriguez F.J., Bruna J.E., Guarda A., Galotto M.J. Development of an Active Film with Natural Zeolite as Ethylene Scavenger, Journal of the Chilean Chemical Society 2014 (49) 2409-2414
- Yuzay I. E., Auras R., Selke S. Poly(lactic acid) and Zeolite Composites Prepared by Melt Processing: Morphological and Physical–Mechanical Properties, Journal of Applied Polymer Science 2009 (115) 2262–2270
- Yuzay, I. E., Auras R., Soto-Valdez H., Selke S. Effects of synthetic and natural zeolites on morphology and thermal degradation of poly(lactic acid) composites, Polymer Degradation and Stability 2010 (95) 1769–1777
- Domenek S., Courgneau C., Ducruet V. Characteristics and Applications of PLA in Kalia S., Averous L. (ed.) Biopolymers: Biomedical and Environmental Applications (183-223) Wiley-Scrivener 2011
- Almenar E., Auras R. Permeation, sorption, and diffusion in poly(lactic acid) in Auras R., Lim L.-T., Selke S., Tsuji H. (ed.) Poly(lactic acid) Synthesis, Structures, Properties, Processing and Applications (155-179) John Willey and Sons 2010

#### CHAPTER 5

# New active packaging materials made of PLA films coated with solutions of PLA and natural or synthetic zeolites characterized as ethylene and carbon dioxide scavengers

#### 5.1. Introduction

One type of active packaging (AP) involves additives incorporated as a part of the packaging material or placed inside of a container to modify or to interact with the headspace and extend product shelf life. It is very important in fresh produce packaging. The main purpose of many AP systems is to extend the shelf life of fresh produce while preventing loss of nutritional quality and freshness, and at the same time inhibit the growth of pathogens. The market for active packages has been growing in the last several decades [1-3].

Until now, the most popular way of creating an active packaging system was to place additives in the form of a sachet inside of a package. Sachets may not be the safest due to the danger of being eaten or ruptured and allowing active components to contact the food. The newer option is to incorporate active elements directly into the material or on the surface of it [1-3].

Ethylene is a plant hormone that accelerates ripening and senescence of climacteric fruits and vegetables by increasing their respiration rate. It is a colorless gas which is produced by plants as they ripen. Too high levels of ethylene during storage can shorten shelf life and also produce physiological defects of the harvest. Even a very low concentration of ethylene, at the level of parts per billion (ppb) and parts per million (ppm), can be critical [4-7].

Although high levels of CO<sub>2</sub> in the headspace might be beneficial in many cases (slow down respiration and lipid oxidation, reduce color change, inhibit growth of molds, yeasts and bacteria),

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excessive concentrations of  $CO_2$  inside the package might reduce the pH of the product, which will result in development of an acid taste or cause flavor tainting and drip loss. Also if the wrong packaging material is used, especially with high respiration classes of perishables, there is a danger of blowing up the package by excessive package expansion [4].

Zeolites are crystalline aluminosilicates of alkali and alkaline earth elements. They are characterized by unique three-dimensional framework structures composed of SiO<sub>4</sub> and AlO<sub>4</sub>. Within zeolites, we can differentiate types based on the framework structure. Many zeolites are also modified by exchanging cations, in order to increase their specific activity. Zeolites have been commonly used for a variety of purposes, including gas separation, gas adsorption, antimicrobials, removal of odors, etc. [6-7]. Zeolites have been successfully used as C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> scavengers. They have also been used to produce polymer/zeolite films and their adsorption capacities have been investigated. Polymers commonly mixed with zeolites include LDPE, HDPE, PP, PC, and PS [1,5,11].

Poly(lactic acid) is a biobased polymer, which can be obtained from renewable resources like corn, potato or sugar beets. Its high cost of production used to limit its application as a packaging material in general. But as the cost has been continuing to decrease, PLA is more and more used. Nowadays it is commercially used as a retail package in the form of clamshell containers, thermoformed foam trays or pouches made of film. With growing public concern about eliminating petrochemical based polymers from the food industry, PLA has become a material of interest [8-9]. PLA is a good barrier to CO<sub>2</sub>, O<sub>2</sub>, and ethanol but a poor barrier to H<sub>2</sub>O [9]. This is why if PLA is to be used as an active packaging material, it has to be modified. It has been proved that PLA/zeolite composite materials can be produced by melt processing without compatibilizers [10].

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The objective of this study was to determine how well newly developed PLA films coated with PLA/zeolite solutions can be used as ethylene and carbon dioxide scavengers in conditions relevant to fresh produce.

### 5.2. Experimental

## 5.2.1. Materials

### 5.2.1.1. Zeolites and gases

Synthetic type 4A and natural clinoptilolite, and ethylene and carbon dioxide, as described in chapter 3.

## 5.2.1.2. Poly(lactic acid)

PLA was used in two different forms - pellets and film, as described in chapter 4.

## 5.2.1.3. Commercial bags

Two commercial materials were chosen for comparison, PeakFresh (PeakFresh Produce Bags, Australia) and Green bags (Evert-Fresh Corporation, Katy, TX, US).

### 5.2.2. Bar coating

A multicoater (RK K303, United Kingdom) was used as described in chapter 4. For CL the coating solution contained 0.2 g of PLA, 1 g of zeolite and bar no. 3 was used for distributing it on the polymer surface, while for type 4A the coating solution was composed of 1 g of PLA mixed with 0.3 g of zeolite and coated with bar no. 8.

Coated films were dried in air and kept overnight in a desiccator before testing.

#### 5.2.3. Adsorption measurements

Gas Chromatography with Flame Ionization Detector (GC FID) and Gas Chromatography with Thermal Conductivity Detector (GC TCD) were used to quantify  $C_2H_4$  and  $CO_2$ , as described in chapters 3 and 4.

To validate if acetone was still present in the PLA films coated with PLA/zeolite solutions (PLA/zeolite coated films in short) the headspace of PLA/coated film was injected into GC FID equipped with an HP-5 column at 40°C with inlet temperature of 250°C and detector temperature of 280°C. The same was done with headspace coming from a bottle of acetone. Retention time for acetone was 2.1 min. Three replicates of each sample type were measured. Calibration curves for  $C_2H_4$ ,  $CO_2$ ,  $O_2$  and  $N_2$  are in appendix in chapter 3.

#### 5.2.4. Desorption measurements

For the purpose of reusing samples, desorption studies were carried out. After adsorption studies were completed, film samples were placed into new jars with no headspace gases present ( $C_2H_4$  or  $CO_2$ ), closed and left for a week at 23°C. A second set of desorption jars involved the same handling of the already used samples, but at the end they were placed in a chamber at 37.8°C.

### 5.2.5. Sample preparation

Some standard samples were chosen to compare performance of investigated PLA films coated with the two types of zeolites. An empty jar flushed with the same gases as all the other samples was used as a control. The designation PLA indicates a piece of film cut from the same roll as the coated films. 2PLA denotes film prepared by coating PLA with a coating solution that contained PLA but no zeolite. PLA+CL and PLA+4A denote films coated with natural and synthetic zeolites, respectively. Commercial films chosen for evaluation were Green Bags and Peakfresh bags, both made of LDPE and zeolites. Standard neat LDPE film was evaluated for comparison.

For the adsorption/desorption experiments, films were cut into the same size samples (17.5 x 8 cm), stapled on end to prevent rolling, and placed into 250 mL glass jars with metal closures. For filling and sampling purposes, holes were drilled in the lids and septa made of gray butyl rubber were inserted. The headspace was flushed with both gases ( $C_2H_4$  and  $CO_2$ ).

For the adsorption/permeation experiments, samples were cut into circles of 10 cm diameter and placed into the middle of 150 mL permeation cells. The permeation cells were divided into two separate compartments by placing the film in between. The bottom of the cells was flushed with C<sub>2</sub>H<sub>4</sub> (500 ppm in N<sub>2</sub>) for 30 seconds, while the top was left containing room air. The coated side of the film was exposed to the flushed side of the cell. Septa placed on the sides of the cells were used for sampling purposes. In an attempt to obtain permeability data, gas concentrations in two of the four available cells were measured at selected times (K1 and K4), the same as with the jars (2, 7, 14 and 21 days). Two cells were measured only during the first and last week (K2 and K3) to avoid any leakage that might be associated with repeated measurements. PLA coated films were prepared according to the same method as before. Two cells contained CL coated films (K3 and K4), and the remaining two contained 4A coated films (K1 and K2).

All samples, jars and permeation cells were placed in controlled temperature rooms (23°C or 7°C). All jars kept at low temperature had small vials filled with 3mL of deionized water placed inside to assure 100% relative humidity. Adsorption measurements were carried out at set intervals: after 48 hours, one, two and three weeks for all samples.

Adsorption measurements carried out in jars had three replicates of each sample type, while measurements done in permeation cells were performed in single cells. Results for  $C_2H_4$  are presented as %, ppm and nL; those for  $CO_2$  are given in % and mL.

Calibration curves can be found in appendix in chapter 3

## 5.2.6. Characterization of produced films

### 5.2.6.1. Thermogravimetric Analysis (TGA)

A TGA Q50 (TA Instruments, New Castle DE, US) was used to determine the % content of zeolite in coated PLA films, as described in chapter 4.

## 5.2.6.2. Differential Scanning Calorimetry (DSC)

A DSC Q100 (TA Instruments, New Castle DE, US) was used to determine the glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ) and melting enthalpy ( $\Delta H_m$ ). Between 5and10g of sample were heated from 23°C to 190°C at rate of 10°C/min under a constant N<sub>2</sub> flow of 70mL/min. The degree of crystallinity ( $X_c$ ) of all samples was calculated using equation 5.1.

$$\% X_C = \left(\frac{\Delta H_m - \Delta H_C}{93.1 \cdot X_{PLA}}\right) \cdot 100\%$$
(5.1)

where  $\Delta H_m$ ,  $\Delta H_c$  and  $X_{PLA}$  are melting enthalpy, crystallization enthalpy and PLA content, respectively. 93.1 J/g is the literature value for the melting enthalpy for 100% crystalline PLA [12].

### 5.2.6.3. Scanning Electron Microscopy (SEM)

A scanning electron microscope (Carl Zeiss Variable Pressure SEM EVO LS2, Germany) was used to determine the particle size of the zeolites and their size and distribution on the PLA surface. To prevent PLA melting under the electron beam, the sample holder was cooled down to -16°C before the measurements. Images were acquired with an accelerating voltage of 20 kV and a working distance of 10 mm at 6 k and 11 k x magnification.

#### 5.2.6.4. Tensile Testing

An Instron Universal Testing Machine (Model 5567, Instron, Norwood, MA, US) was used to test the tensile properties of the PLA/zeolite films. ASTM D 882 (2002) was followed as a standard test method for determination of tensile properties of plastics in the form of thin sheeting.

### 5.2.6.5. Fourier Transform Infrared Spectroscopy (FTIR)

A Shimadzu IRPrestige-21 spectrometer (Shimadzu, Japan) was used in the attenuated total reflection mode to examine the surface structure of PLA films coated with clinoptilolite and type 4A zeolite. Spectra were collected at a 4cm<sup>-1</sup> resolution, a scan rate of 40 and wavenumber 400-4000 cm<sup>-1</sup>. Exactly the same samples were used for measurements after adsorption tests were completed and they were remeasured after overnight degassing in vacuum oven at room temperature.

#### 5.2.7. Statistical methods

Analysis of variance (ANOVA) was performed in the analytical software SPSS version 22 (SPSS Inc., Chicago, IL, US). Means were separated using the Tukey honestly significant difference (HSD) test (p < 0.05).

### 5.3. Results and discussion

### 5.3.1. Adsorption measurements

All % results were normalized to mass as in the equation 5.2 below:

$$\frac{\text{initial gas concentration}-\text{final gas concentration}}{\text{initial gas concentration}} \cdot \frac{1}{g \text{ zeolite}} \cdot 100\%$$
(5.2)

For ppm results, they were normalized as in equation 5.3:

$$\frac{(initial gas concentration-final gas concentration)}{g zeolite}$$
(5.3)

(5.4)

While volume results (nL, mL) were normalized according to equation 5.4.

initial volume of gas – final volume of gas g zeolite

Figures 5.1 - 5.3 compare  $C_2H_4$  adsorption of all tested materials in % of total concentration of  $C_2H_4$  in the jar and specific ppm and nL corresponding to those concentrations. It is apparent that there was no significant difference between the control, PLA, 2PLA, LDPE and Peakfresh samples for any of the times investigated (p > 0.05). Only the Green bags have adsorption comparable to the PLA/zeolite materials. There is no significant difference between any of three materials; CL and 4A coatings on PLA gave similar results of  $C_2H_4$  adsorption to commercial Green bags (p > 0.05).

Supporting data for this chapter can be found in appendix below.



Figure 5.1. Amount of ethylene (%) adsorbed by commercial and coated films and values for control at four sampling times at 23°C and 0% RH.



Figure 5.2. Amount of ethylene (ppm) absorbed by commercial and coated films and values for control at four sampling times at 23°C and 0% RH.



Figure 5.3. Amount of ethylene (nL) absorbed by commercial and coated films and values for control at four sampling times at 23°C and 0% RH.

Looking at a similar set of data (figures 5.4 - 5.5), this time measuring CO<sub>2</sub> adsorption, superior performance of the new-coated films can be observed. Starting with the initial measurement after 48 hours of flushing the jars with both gases, both zeolites significantly increased the adsorption capacities of the PLA (p < 0.05). Again most control samples showed no significant adsorption (p > 0.05), except for the Green bags (p < 0.05). There was also a noticeable increase in adsorption in the 4A coated material after 2 weeks (p < 0.05), showing that the PLA coating may be causing a delay in reaching the total adsorption capacity of the synthetic zeolites. The higher PLA content in the coating solution for the 4A material and the higher thickness of the final film (2 mils compared to 1.7 mils for CL coated and 1.6 mils for neat PLA film), may explain that result, especially since PLA is known for its good barrier properties towards C<sub>2</sub>H<sub>4</sub> (6.8·10<sup>-18</sup> m<sup>3</sup> m/m<sup>2</sup> s Pa) [13].



Figure 5.4. Amount of carbon dioxide (%) adsorbed by commercial and coated films and values for control at four sampling times at 23°C and 0% RH.



Figure 5.5. Amount of carbon dioxide (mL) adsorbed by commercial and coated films and values for control at four sampling times at 23°C and 0% RH.

A similar set of materials was used for testing in more realistic fresh produce conditions, 7°C and 100% RH (figures 5.6 - 5.8). The presence of water could be responsible for the higher adsorption capacities measured for both gases for all investigated cases. It is suspected that  $C_2H_4$  and  $CO_2$  were soluble in the deionized water used to fill the small vials in the jars, evidenced by the apparent adsorption in the control jars. Only three materials had noticeably higher  $C_2H_4$  adsorption (p < 0.05). These are again PLA films coated with synthetic and natural zeolites and Green bags. Although there were no significant differences between the samples for the first two time periods, 2 and 7 days (p > 0.05), there was a significant difference for the last two samplings at 2 and 3 weeks (p < 0.05). In chapter 3 it was shown that presence of  $H_2O$  molecules inhibited adsorption of  $C_2H_4$  in CL and caused desorption of initially adsorbed  $C_2H_4$  in 4A. In the coated films the situation was the opposite—in the presence of  $H_2O$  there was no desorption of adsorbed gases, moreover adsorption continued until the experiment was stopped. All of this was likely due to presence of the polymer in the samples. Adsorption of  $C_2H_4$  in both powder zeolites decreased when the temperature was decreased, while in coated films it actually increased, although in general increase in temperature increases permeability of polymers.



Figure 5.6. Amount of ethylene (%) adsorbed by commercial and coated films and values for control at four sampling times at 7°C and 100% RH.



Figure 5.7. Amount of ethylene (ppm) adsorbed by commercial and coated films and values for control at four sampling times at 7°C and 100% RH.



Figure 5.8. Amount of ethylene (nL) adsorbed by commercial and coated films and values for control at four sampling times at 7°C and 100% RH.

A little different situation can be noticed for the  $CO_2$ adsorption data (figures 5.9 - 5.10). Already within the first week, the experimental PLA films coated with zeolites and the Green bags had superior performance compared to any other samples (p < 0.05). As expected from previous experiments carried out with only zeolites present in the jars, the initial high adsorption became steady over time, indicating that low temperature and high relative humidity limit the CO<sub>2</sub> adsorption capacities of the zeolites in any material in which they are incorporated.



Figure 5.9. Amount of carbon dioxide (%) adsorbed by commercial and coated films and values for control at four sampling times at 7°C and 100% RH.



Figure 5.10. Amount of carbon dioxide (mL) adsorbed by commercial and coated films and values for control at four sampling times at 7°C and 100% RH.

The producers of the commercially available films advertised them as reusable packaging materials. Following the same thinking, two of the previously tested films, each with different zeolites, along with one of the commercial films that showed similar adsorption capacities, were reused. Prior to the adsorption determination, the films were dried overnight in a vacuum oven at 60°C, cooled down and kept in a desiccator prior to testing. And finally, the same testing conditions were applied as when they were tested the first time(the same jars, same gases and environmental conditions).  $C_2H_4$  and  $CO_2$  were added to the jar headspace and they were kept at 23°C and 0% RH.

The results presented in figures 5.11 - 5.13 show that for most investigated samples, the adsorption capacity did not change. Also, the rate of adsorption was similar since the % changes at equal times were very similar. Natural zeolite (CL) had no significant differences within the first three measurements. Only the last measurement, after three weeks, showed a significant increase for the used material. It is suspected that degassing in the vacuum oven removes more of the H<sub>2</sub>O than keeping

the material in the desiccator right after production. Moisture might be getting into the zeolites during the coating process and cannot be removed without degassing in vacuum oven.

There is no doubt these PLA/zeolite films can be reused. Very similar situations can be observed for the synthetic zeolite (4A) and the commercial films. There were no significant differences for the 2, 7 and 14 day measurements (p < 0.05) with a significant increase in adsorption at 3 weeks (p > 0.05). The explanation seems to be the same as in the case of clinoptilolite.



Figure 5.11. Amount of ethylene (%) adsorbed by the same commercial and coated films and values for control, used first time after coating and second time after drying, at four sampling times at 23°C and 0% RH.



Figure 5.12. Amount of ethylene (ppm) adsorbed by the same commercial and coated films and values for control, used first time after coating and second time after drying, at four sampling times at 23°C and 0% RH.



Figure 5.13. Amount of ethylene (ppm) adsorbed by the same commercial and coated films and values for control, used first time after coating and second time after drying, at four sampling times at 23°C and 0% RH.

As for  $CO_2$ , different observations can be drawn from figures 5.14 and 5.15. The natural zeolite and the commercial film had similar adsorption capacities for both uses. There was no significant difference between the first and second use at any time point (p < 0.05), while the synthetic zeolite (4A) seemed to be losing its adsorption capacity when reused (p > 0.05). This could be due to stronger interactions between the type 4A zeolite and CO<sub>2</sub> than was observed for the natural zeolite and commercial film. Probably degassing in vacuum oven did not remove all the previously adsorbed CO<sub>2</sub> and H<sub>2</sub>O, which limited the adsorption capacity when reusing the film.



Figure 5.14. Amount of carbon dioxide (%) adsorbed by the same commercial and coated films and values for control, used first time after coating and second time after drying, at four sampling times at 23°C and 0% RH.



Figure 5.15. Amount of carbon dioxide (mL) adsorbed by the same commercial and coated films and values for control, used first time after coating and second time after drying, at four sampling times at 23°C and 0% RH.

Figures 5.1 - 5.18 present data collected at room temperature, while figures 5.19 - 5.21 present

data collected at 7°C. In both cases there was no water present in the cells, so 0% RH was assumed.

C<sub>2</sub>H<sub>4</sub> adsorption taking place at room temperature showed a steady increase in adsorption for

both zeolites during the first two weeks of the experiment. A higher increase was noted for the synthetic

zeolite at 3 weeks. This could be explained again by more PLA covering and blocking the type 4A zeolite

from reaching its maximum adsorption capacity.



Figure 5.16. Amount of ethylene (%) adsorbed by coated films in permeation cells at four sampling times at 23°C and 0% RH.



Figure 5.17. Amount of ethylene (ppm) absorbed by coated films in permeation cells at four sampling times at 23°C and 0% RH.



Figure 5.18. Amount of ethylene (nL) absorbed by coated films in permeation cells at four sampling times at 23°C and 0% RH.

What is interesting when looking at a similar experiment carried out at low temperature (figures 5.12 - 5.13), is that  $C_2H_4$  adsorption was higher but also grew more steadily with time than at room temperature. Again, two types of cells, those measured periodically and just at the beginning and end, showed very similar results for both zeolites, which means the conditions were repeatable. Also, comparing this behavior to what occurred in the jars at 7°C but in the presence of water indicates that even a small amount of water can have a large impact on the adsorption capacities of both zeolites. Water seems to work as a competitive molecule to  $C_2H_4$  and  $CO_2$  (figures 5.6 - 5.9). There is no similar set of conditions in the experiments reported in chapter 3 to compare to these data, so it cannot be stated how lowering temperature influence adsorption in zeolites when used as fine powders versus when they were incorporated onto the PLA film.



Figure 5.19. Amount of ethylene (%) adsorbed by coated films in permeation cells at four sampling times at  $7^{\circ}C$  and 0% RH.



Figure 5.20. Amount of ethylene (ppm) adsorbed by coated films in permeation cells at four sampling times at 7°C and 0% RH.



Figure 5.21. Amount of ethylene (nL) adsorbed by coated films in permeation cells at four sampling times at 7°C and 0% RH.

As found in the literature, the adsorption isotherms for  $C_2H_4$  and  $CO_2$ in clinoptilolite have a classic isotherm form (type II) as is characteristic for adsorbents with a wide range of pore sizes, such as natural zeolites. These isotherms are observed when adsorbate molecules are small enough to enter the zeolite micropore systems. Literature kinetic diameters of  $CO_2$  (3.3 Å) and  $C_2H_4$  (3.9 Å) are both smaller than the average pore radius measured in clinoptilolite (5.5 ± 0.8 Å), which was actually larger than literature reports (3.5 Å) [22-23]. This allows both gases to get inside the cages and cavities in the zeolite framework. Physisorption taking place inside zeolites resulted in higher adsorption energy and lower adsorption isotherm for  $CO_2$  also has the characteristic type II shape while the one for  $C_2H_4$  has the type I shape and follows Henry's law. Again comparing pore openings in 4A measured by Quantachrome and listed in chapter 3 (2.3 ± 0.7 Å) to those found in literature (4 Å) shows that the actual pore radius was much smaller, probably due to different cations occupying the corner sites in cavities and cages resulting in channel size reduction. This could result in all physisorption happening on the external surface of the zeolite and be characterized by low adsorption energy and high adsorption rate [19-20]. All of the above

supports the experimental results. Water having the smallest kinetic diameter of all investigated gases (2.65 Å) makes it even easier for  $H_2O$  to enter the pores in clinoptilolite and block adsorption sites for  $C_2H_4$  and  $CO_2$ , while it is often too large for 4A zeolite pores and this is why the effect of water is not as critical to adsorption as in the case of the natural zeolite. Decreased adsorption of  $C_2H_4$  when compared to  $CO_2$  could be due to lower polarizability associated with smaller ionic radius [21, 23].

Injection of samples of the headspace into the GC FID in order to determine if there was any acetone content left after coated samples were dried in air showed small amounts of acetone was present after the film samples were stored for about two months inside the jar. One way to remove acetone would be to heat the sample, which in case of PLA would not be recommended. PLA is not very heat resistant; its melting temperatures are between 150-160°C [8]. Although the amount was not quantified, even trace amounts of acetone are not tolerated in food packaging, which means that a different solvent should be investigated if the coating approach is used.

### 5.3.2. Desorption studies

For coated samples after adsorption studies were done, no desorption was noticed, since no significant amounts of  $C_2H_4$  or  $CO_2$  were present in the headspace when samples were kept at 23°C or at 37.8°C. This was the reason for degassing the samples in a vacuum oven before reusing.

#### 5.3.3. Thermal analysis

TGA analysis was performed to determine the percent of zeolites in both the newly developed films and the commercially available ones. For all samples it was observed that coating or impregnation did not result in very uniform distribution of the zeolites. However, a more uniform distribution was achieved in the experimental samples than in the commercial ones. The data are listed in table 5.1 and show that the % zeolites in all samples were similar.

sample	% zeolite
PLA + CL	$3.40 \pm 0.40$
PLA + 4A	4.45 ± 1.44
Peakfresh	3.30 ± 2.16
Green bags	4.55 ± 2.95

Table 5.1. Percent of zeolite content in investigated films measured by TGA.

Sample thermograms for zeolite coated films and commercial bags are shown in figure 5.22. Since coated films are PLA and commercial ones are LDPE there are obvious differences in the thermograms between these two polymers. Both commercial films display similar thermograms, with both having onset temperatures higher than those for coated films for PLA, meaning LDPE is a more thermally stable polymer than PLA. Comparing the effect of the coating on PLA shows that the onset temperature of degradation of PLA in the 4A sample was 50°C, while for the CL sample it was 100°C. Degradation of PLA ended at 360°C for 4A coating and at 380°C for CL coating. This means that PLA coated with 4A had lower thermal stability than PLA coated with CL.



Figure 5.22. TGA thermograms of two zeolite coated films and two commercial films.

To further investigate the influence of zeolite coatings on PLA, DSC analysis was done. The resulting thermograms are shown in figure 5.23, and thermal properties are listed in table 5.2. The most obvious difference in the DSC thermograms is that all the samples except the PLA pellets had two glass transition temperatures and both were higher than the T<sub>g</sub> of the pellets. On the website for Evlon [14], producer of our PLA film, it can be found that the one side heat sealable polylactide film is composed of three parts: the PLA treated surface, the PLA sealant layer and the PLA core. All coatings were applied to the treated surface and their interaction with PLA might have caused some changes in the first T<sub>g</sub> and the presence of an apparent second T<sub>g</sub>. For three of the investigated samples, PLA film, PLA film coated with PLA and PLA film coated with CL, there was no difference between T<sub>g</sub> values (p < 0.05). In the case of PLA coated with 4A, the T<sub>g</sub> value was very close to the PLA pellet T<sub>g</sub>, and both were significantly different than those for the other films (p < 0.05). There was no significant difference between the

melting temperatures ( $T_m$ ) for any of the samples tested (p > 0.05). But the % crystallinity of the films coated with 4A zeolite was significantly different than that of all other samples (p < 0.05), having the lowest crystallinity, except for the pellets having no crystallinity. Changes in  $T_g$  values can be related to permeabilities of gases. Increase of  $T_g$  means chain separation and mobility in the polymer chain is decreased which can make it more challenging for  $C_2H_4$  and  $CO_2$  molecules to pass through PLA and get close to the zeolites. Within all film samples, PLA coated with 4A had the lowest  $T_g$ , and this is in accord with those materials being often the most effective scavengers of  $C_2H_4$  and  $CO_2$ .



Figure 5.23. DSC thermograms (1st cycle) of standard samples and PLA films coated with zeolites.

sample	T <sub>g1</sub> [°C]	T <sub>g2</sub> [°C]	T <sub>m</sub> [°C]	∆H <sub>m</sub> [J/g]	%X <sub>c</sub>
PLA pellet	59.1 ± 0.0 a*	-	-	-	0
PLA film	65.1 ± 0.1 b	71.2 ± 0.2 a	165.8 ± 0.2 a	35.7 ± 0.8 ab	38.3 ± 0.9 a
2PLA	65.1 ± 0.1 b	71.3 ± 0.2 a	166.3 ± 0.1 a	36.1 ± 0.4 a	39.6 ± 0.5 a
PLA + CL	65.0 ± 0.0 b	71.3 ± 0.1 a	165.8 ± 0.2 a	35.1 ± 0.3 b	38.3 ± 0.3 a
PLA + 4A	60.4 ± 1.0 c	70.1 ± 0.7 b	165.9 ±0.2 a	32.2 ± 0.2 c	35.0 ± 0.2 a

Table 5.2. Thermal properties of investigated PLA films coated with zeolites along with standard samples.

\* means followed by the same lower case letter in column are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

### 5.3.4. FTIR analysis

FTIR spectra were recorded to determine whether or not  $C_2H_4$  was absorbed on the zeolite coated films. The FTIR spectra of the same films exposed to  $C_2H_4$  and after degassing after adsorption were compared. Different peaks observed for the differing zeolites suggest that adsorption happened differently depending on the zeolite involved. Recorded spectra were compared to literature spectra for  $C_2H_4$  [15-16]. Figures 5.24a and b shows the effects in CL coated films. The intensive absorption band at 1000 cm<sup>-1</sup> is even more intense when  $C_2H_4$  is present (figure 5.24b), which could suggest that it is resulting from the CH<sub>2</sub> twist in the  $C_2H_4$  molecules. This suggests that  $C_2H_4$  molecules are free to twist which can be possible more on the external surface of the zeolite than inside pores and cavities.



Figure 5.24. FTIR spectra of PLA film coated with clinoptilolite, after adsorption of ethylene and after degassing.

Figure 5.25 (a-d) shows what happened in the type 4A coated PLA films. Here the opposite situation was observed; the absorption band right after 1000 cm<sup>-1</sup>decreased in the presence of  $C_2H_4$  (figure 5.25d), meaning that  $C_2H_4$  limited the stretching of the Si-O and Al-O bonds belonging to the SiO<sub>4</sub> and AlO<sub>4</sub>tetrahedra, which are associated with those bands [17]. Also, new absorption peaks at 1200 cm<sup>-1</sup> and 1300 cm<sup>-1</sup>appeared in the spectra of the exposed sample (figure 5.25c), which could be attributed to CH<sub>2</sub> rock and CH<sub>2</sub> scissor vibrations in the C<sub>2</sub>H<sub>4</sub> molecules, respectively. The increased intensity of the 1700 cm<sup>-1</sup> peak could be explained by the C-C stretch in the C<sub>2</sub>H<sub>4</sub> molecules (figure 5.25b). Relatively high intensity changes in some peaks in the case of both zeolite coated films might suggest that C<sub>2</sub>H<sub>4</sub> molecules are adsorbed rather than absorbed, due to their possible movements and limiting movements of zeolites, since the pore openings in the zeolites are very close to the size of the C<sub>2</sub>H<sub>4</sub> molecules.



Figure 5.25. FTIR spectra of PLA film coated with type 4A zeolite, after adsorption of ethylene and after degassing.

# 5.3.5. Mechanical characterization

Results for the mechanical properties of the uncoated and coated samples are provided in table

5.3. Data were recorded for the samples in the machine direction (MD) and cross machine direction

(CD). In general, most mechanical properties of the PLA film changed with coating, having different changes associated with different coating solution compositions. Tensile strength in all cases but one (PLA coated with PLA in CD) decreased, with the lowest values for the 4A coatings, and the highest for the PLA coating. A decrease in the modulus of elasticity, break strength, and tensile stress at yield was observed for all samples. The maximum load was the only property that was not changed with coating (p > 0.05), while elongation at break was the only one that increased with coating, being highest for 4A and lowest for PLA coating. These changes could be due to the different characteristics of the materials involved. PLA is hydrophobic and the zeolites are hydrophilic. The coating made PLA films less breakable (due to lower values of energy to break) and more flexible.

sample	tensile strength [MPa]	elongation at break [%]	modulus of elasticity [GPa]	maximum load [N]	break strength [MPa]	energy to break [in-lbf/in <sup>3</sup> ]	extension at yield (zero slope) [mm]	tensile stress at yield (zero slope) [MPa]
MD								
PLA	143.3 ± 5.2 a*	55.5 ± 2.5 a	5.0 ± 0.1 a	93.7 ± 1.0 a	90.1 ± 33.3 ab	577.7 ± 273.8 a	3.9 ± 0.1 a	134.4 ± 24.7 a
2PLA	100.6 ± 24.7 bc	124.4 ± 1.4 de	3.2 ± 0.6 a	87.1 ± 3.3 a	81.9 ± 19.6 a	1362.9 ± 260.9 de	7.0 ± 0.3 b	92.5 ± 23.4 b
PLA + CL	84.7 ± 2.2 bd	103.5 ± 25.9 cd	3.1 ± 0.1 a	92.9 ± 2.4 a	65.1 ± 4.1 a	807.6 ± 260.4 ab	4.1 ± 0.27 a	84.7 ± 2.2 b
PLA + 4A	71.2 ± 1.9 cd	141.6 ± 5.3 e	2.6 ± 0.1 a	91.9 ± 2.5 a	67.3 ± 6.4 a	1010.0 ± 42.2 bcd	4.5 ± 0.1 a	70.7 ± 1.5 b
CD								
PLA	180.2 ± 10.5 e	75.8 ± 4.2 ab	6.8 ± 0.3 b	116.3 ± 6.8 a	175.1 ± 20.0 c	1300.6 ± 100.1 cde	3.0 ± 0.1 a	155.4 ± 1.4 a
2PLA	188.2 ± 7.5 e	96.4 ± 12.1 bc	6.6 ± 0.5 b	121.4 ± 4.8 ab	184.6 ± 10.7 c	1648.7 ± 198.8 e	3.1 ± 0.2 a	150.2 ± 2.8 a
PLA + CL	116.4 ± 4.2 c	88.0 ± 4.5 bc	4.1 ± 0.2 a	127.7 ± 4.6 b	116.9 ± 4.0 b	959.0 ± 36.7 bc	2.9 ± 0.1 a	91.8 ± 2.0 b
PLA + 4A	96.6 ± 3.7 bc	95.4 ± 8.4 bc	3.3 ± 0.2 a	124.7 ± 4.7 ab	94.2 ± 3.9 ab	827.1 ± 59.4 ab	3.9 ± 0.2 a	76.3 ± 1.4 b

Table 5.3. Tensile properties of standard samples and PLA films coated with zeolites.

\* means followed by the same lower case letter in column are not statistically different from each other (Tukey,

α= 0.05)

### 5.3.6. Surface characteristics

SEM images of the zeolite-coated films were taken to help understand if there might be any surface reasons for affecting adsorption in these films. Figures 5.26 and 5.27 show how differently the coated surfaces appeared, depending on the type of zeolite. Clinoptilolite blended very well with PLA and formed a uniform layer on the surface of the PLA film with almost no uncovered spaces, while type 4A zeolites formed clusters of particles. The images show how uniformly the zeolites were dispersed throughout the surface and also how much the zeolite molecules were covered by the PLA. Those images are in concordance with the previously discussed adsorption capacities and behavior of the investigated films. CL was more exposed to the headspace gases and so the adsorption was not as much influenced by PLA as in the case of 4A. Cubic 4A molecules were not only blocked by the PLA but also by other 4A molecules, so adsorption of  $C_2H_4$  and  $CO_2$  did not occur as fast as in CL.



Figure 5.26. SEM images of PLA films coated with clinoptilolite.



Figure 5.27. SEM images of PLA films coated with type 4A zeolite.

### 5.4. Conclusions

Zeolite coatings allowed PLA films to be successful  $C_2H_4$  and  $CO_2$  scavengers in two sets of conditions for packing of fresh produce (23°C, 0% RH and 7°C, 100% RH). The latter is the more relevant to commodities and it was showed that lowering temperature actually increased adsorption of both gases, by a factor of 2 for  $C_2H_4$  and by a few percent for  $CO_2$ . One of the commercial films did not appear to work, while the other one was comparable to the coated films in sorption capacities and %wt zeolite content. There is a possibility of reusing two zeolite coated films in the same manner and efficiency as the commercial Green bags. Solution coating was more repeatable than commercial impregnation with zeolites, as the standard deviations of the %wt of zeolites were smaller. SEM images showed that there is a better distribution of CL coating than 4A which, as shown in the adsorption measurements, greatly improved the sorption capacities of the resulting films. Thermal and tensile properties were not greatly affected by the zeolite coatings.

While the mechanism of action of the zeolites as gas scavengers is still not fully known, PLA films coated with zeolites show promise in providing a new biobased and biodegradable alternative to commercially available bags and should be further investigated.

APPENDIX

% CO <sub>2</sub>	2 days	7 days	14 days	21 days	
Control	0.7 ± 0.5 aA*	0.8 ± 0.5 aA	1.8 ± 0.6 aA	1.2 ± 0.1 aA	
PLA	0.6 ± 0.9 aA	1.1 ± 0.7 aA	1.5 ± 0.5 aA	2.4 ± 1.1 abA	
2PLA	0.7 ± 0.6 aA	1.8 ± 0.2 aA	1.2 ± 1.1 aA	1.8 ± 1.0 abA	
CL	1.9 ± 0.7 aA	3.5 ± 0.3 bB	5.2 ± 0.6 bC	5.1 ± 0.4 bC	
4A	3.1 ± 0.8 bA	4.3 ± 0.8 bA	8.9 ± 0.5 cB	9.9 ± 1.3 cB	
LDPE	1.2 ± 0.8 aA	1.6 ± 0.5 aA	1.7 ± 0.9 aA	2.2 ± 1.5 abA	
Green bags	0.4 ± 0.3 aA	1.7 ± 0.1 aA	2.2 ± 1.5 aA	3.9 ± 2.2 abA	
Peakfresh	1.4 ± 0.6 aA	1.7 ± 0.4 aA	1.9 ± 0.5 aA	2.5 ± 1.5 abA	

Table A5.1. Amount of carbon dioxide (%) adsorbed by commercial and coated films and values for control at four different times at 23°C and 0% RH.

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.2. Amount of carbon dioxide (mL) adsorbed by commercial and coated films and values f	or
control at four different times at 23°C and 0% RH.	

mL CO <sub>2</sub>	2 days	7 days	14 days	21 days
Control	1.6 ± 1.2 aA*	2.0 ± 1.3 aA	4.4 ± 1.6 aA	3.0 ± 0.3 aA
PLA	1.5 ± 2.3 aA	2.7 ± 1.7 aA	3.9 ± 1.2 aA	5.9 ± 2.9 abA
2PLA	1.7 ± 1.4 aA	4.5 ± 0.5 aA	3.0 ± 2.6 aA	4.6 ± 2.5 abA
CL	4.7 ± 1.7 aA	8.8 ± 0.7 bB	13.1 ± 1.6 bC	12.8 ± 1.1 bC
4A	7.7 ± 2.1 bA	10.6 ± 2.1 bA	22.2 ± 1.3 cB	24.6 ± 3.2 cB
LDPE	3.1 ± 2.0 aA	3.9 ± 1.2 aA	4.3 ± 2.3 aA	5.6 ± 3.6 abA
Green bags	1.1 ± 0.7 aA	4.1 ± 3.1 aA	5.5 ± 3.8 aA	9.8 ± 5.4 abA
Peakfresh	3.6 ± 1.4 aA	4.3 ± 1.0 aA	4.7 ± 2.2 aA	6.3 ± 3.7 abA

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)
ppm eth	2 days	7 days	14 days	21 days
Control	3.2± 2.3 aA*	2.5 ± 0.8 aA	3.1 ± 1.6 aA	4.9 ± 1.1 aA
PLA	3.3 ± 0.8 aA	1.0 ± 1.3 aA	3.1 ± 1.5 aA	4.8 ± 4.2 aA
2PLA	1.3 ± 0.8 aA	2.2 ± 1.5 aA	5.4 ± 2.4 aAB	8.2 ± 2.6 aB
CL	5.3 ± 1.5 aA	8.6 ± 1.6 bA	13.2 ± 0.8 bB	22.8 ± 0.5 bC
4A	4.2 ± 1.1 aA	10.7 ± 1.1 bB	13.6 ± 2.7 bB	26.9 ± 6.8 bC
LDPE	4.9 ± 1.8 aA	5.6 ± 1.8 aA	6.2 ± 1.6 aA	8.3 ± 0.8 aA
Green bags	3.3 ± 0.8 aA	3.0 ± 0.5 aA	11.8 ± 3.6 bB	23.8 ± 8.7 bC
Peakfresh	3.0 ± 2.1 aA	0.5 ± 0.5 aA	2.6 ± 0.2 bA	4.1 ± 5.8 aA

Table A5.3. Amount of ethylene (ppm) adsorbed by commercial and coated films and values for control at four different times at 23°C and 0% RH.

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.4. Amount of ethylene (%) adsorbed by commercial and coated films and values for control
at four different times at 23°C and 0% RH.

% eth	2 days	7 days	14 days	21 days
control	1.3 ± 0.8 aA*	1.1 ± 0.4 aA	1.3 ± 0.7 aA	2.1 ± 0.5 aA
PLA	1.4 ± 0.1 aA	0.4 ± 0.5 aA	1.3 ± 0.7 aA	2.1 ± 1.9 aA
2PLA	0.5 ± 0.3 aA	1.0 ± 0.7 aA	2.3 ± 1.1 aAB	3.5 ± 1.4 aB
CL	2.2 ± 0.5 aA	3.6 ± 0.8 bB	5.5 ± 0.4 bC	9.6 ± 0.4 bD
4A	1.8 ± 0.4 aA	4.5 ± 0.5 bB	5.8 ± 1.4 bB	11.5 ± 3.4 bC
LDPE	2.0 ± 0.8 aA	2.3 ± 0.8 aA	2.5 ± 0.7 aAB	3.3 ± 0.5 aB
Green bags	1.4 ± 0.1 aA	1.2 ± 0.9 aB	5.1 ± 0.9 bC	10.1 ± 2.2 bD
Peakfresh	1.2 ± 0.8 aA	1.2 ± 1.6 aA	3.2 ± 3.6 aA	1.7 ± 2.4 aA

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

nL eth	2 days	7 days	14 days	21 days
control	0.2 ± 0.1 aA*	0.1 ± 0.0 aA	0.2 ± 0.1 aA	0.2 ± 0.1 aA
PLA	0.2 ± 0.1 aA	0.0 ± 0.1 aA	0.2 ± 0.1 aA	0.2 ± 0.2 aA
2PLA	0.1 ± 0.0 aA	0.1 ± 0.1 aA	0.3 ± 0.1 aAB	0.4 ± 0.1 aB
CL	0.3 ± 0.1 aA	0.4 ± 0.1 bB	0.7 ± 0.0 bC	$1.1 \pm 0.0 \text{ bD}$
4A	0.2 ± 0.1 aA	0.5 ± 0.1 bB	0.7 ± 0.1 bB	1.3 ± 0.3 bC
LDPE	0.2 ± 0.1 aA	0.1 ± 0.1 aA	0.2 ± 0.2 aAB	0.3 ± 0.2 aB
Green bags	0.2 ± 0.0 aA	0.1 ± 0.1 aB	0.6 ± 0.2 bC	1.2 ± 0.4 bD
Peakfresh	0.1 ± 0.0 aA	0.1 ± 0.1 aA	0.2 ± 0.2 aA	0.1 ± 0.1 aA

Table A5.5. Amount of ethylene (nL) adsorbed by commercial and coated films and values for control at four different times at 23°C and 0% RH.

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

% CO₂	2 days	7 days	14 days	21 days
control	3.9± 0.4 aA*	4.2 ± 0.9 aA	5.5 <b>±</b> 1.3 aA	5.5 ± 1.8 aA
PLA	2.2 ± 0.6 aA	4.5 ± 0.3 aB	6.0 ± 0.7 aC	5.4 ± 2.9 aC
2PLA	4.2 ± 0.9 aA	4.0 ± 1.0 aA	6.0 ± 1.2 aBC	7.5 ± 1.5 aC
CL	9.9 ± 0.5 bA	13.1 ± 1.4 bB	13.3 ± 1.7 bB	14.7 ± 1.4 bB
4A	8.4 ± 0.8 bA	12.1 ± 1.1 bB	13.3 ±1.4 bB	14.3 ± 1.1 bB
LDPE	2.4 ± 0.6 aA	4.8 ± 1.6 aB	6.0 ± 2.2 aB	6.2 ± 2.4 aB
Green bags	11.4 ± 0.2 bA	9.5 ± 2.1 bA	12.0 ± 1.6 bA	14.4 ± 3.8 bA
Peakfresh	3.1 ± 2.0 aA	6.2 ± 2.3 a	5.4 ± 2.7 a	5.8 ± 1.0 aA

Table A5.6. Amount of carbon dioxide (%) adsorbed by commercial and coated films and values for control at four different times at 7°C and 100% RH.

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.7. Amount of carbon dioxide (mL) adsorbed by	y commercial and coated films and values for
control at four different times at 7°C and 100% RH.	

mL CO <sub>2</sub>	2 days	7 days	14 days	21 days
control	9.7 ± 1.0 aA*	10.4 ± 2.2 aA	13.8 ± 3.2 aA	13.9 ± 4.6 aA
PLA	5.5 ± 1.6 aA	11.2 ± 0.8 aB	15.1 ± 1.6 aC	13.5 ± 7.2 aC
2PLA	10.5 ± 2.3 aA	9.9 ± 2.5 aA	15.1 ± 2.9 aBC	18.8 ± 3.8 aC
CL	24.7 ± 1.3 bA	32.6 ± 3.5 bB	33.2 ± 4.1 bB	36.7 ± 3.6 bB
4A	21.1 ± 2.1 bA	30.3 ± 2.8 bB	33.3 ± 3.4 bB	35.8 ± 2.9 bB
LDPE	6.0 ± 1.4 aA	11.9 ± 4.1 aB	14.9 ± 5.4 aB	15.6 ± 6.1 aB
Green bags	28.5 ± 0.5 bA	23.7 ± 5.2 bA	30.0 ± 4.0 bA	36.0 ± 9.4 bA
Peakfresh	7.8 ± 4.9 aA	15.6 ± 5.7 a	13.6 ± 6.8 a	14.4 ± 2.4 aA

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.8. Amount of ethylene (ppm) adsorbed by commercial and coated films and values for control at four different times at 7°C and 100% RH.

ppm eth	2 days	7 days	14 days	21 days
control	11.9 ± 2.1aA*	15.7 ± 1.9 aA	11.1 ± 3.0 aA	13.5 ± 4.1 aA
PLA	12.7 ± 4.2 aA	14.8 ± 1.8 aA	18.5 ± 1.9 aB	22.6 ± 3.8 aB
2PLA	14.0 ± 5.4 aA	17.5 ± 3.8 aA	20.2 ± 5.5 aA	18.4 ± 6.0 aA
CL	17.2 ± 3.7 aA	23.9 ± 3.2 bA	47.9 ± 3.1 bB	50.7 ± 2.6 bB
4A	16.1 ± 4.4 aA	26.5 ± 8.4 bA	51.2 ± 11.4 bB	55.2 ± 16.6 bB
LDPE	12.8 ± 1.3 aA	14.5 ± 0.3 aA	14.9 ± 6.3 aA	17.4 ± 5.3 aA
Green bags	11.3 ± 0.6 aA	15.5 ± 1.9 aA	34.7 ± 2.3 bB	40.2 ± 2.1 bB
Peakfresh	13.0 ± 2.8 aA	15.1 ± 0.7 aA	19.0 ± 6.3 aA	19.9 ± 8.0 aA

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

% eth	2 days	7 days	14 days	21 days
control	5.4 ± 1.1 aA*	7.1 ± 1.1 aA	5.0 ± 1.4 aA	6.1 ± 2.0 aA
PLA	5.7 ± 1.8 aA	6.7 ± 0.6 aA	8.4 ± 0.6 aB	10.2 ± 1.4 aB
2PLA	6.3 ± 2.2 aA	8.0 ± 1.4 aA	9.2 ± 2.1 aA	8.3 ± 2.4 aA
CL	7.6 ± 1.3 aA	10.5± 0.9 bB	21.2 ± 0.8 bC	22.4 ± 0.9 bC
4A	6.7 ± 1.3aA	11.0 ± 2.8 bB	21.3 ± 3.0 bC	22.9 ± 5.1 bC
LDPE	5.8 ± 0.8 aA	6.6 ± 0.1 aA	6.7 ± 2.6 aA	7.9 ± 2.3 aA
Green bags	5.6 ± 0.5 aA	7.8 ± 1.8 aA	17.2 ± 1.2 bB	20.0 ± 3.1 bB
Peakfresh	5.6 ± 1.0 aA	6.4 ± 0.3 aA	8.0 ± 2.3 aA	8.4 ± 3.0 aA

Table A5.9. Amount of ethylene (%) adsorbed by commercial and coated films and values for control at four different times at 7°C and 100% RH.

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table	A5.10.	Amount	of	ethylene	(nL)	adsorbed	by	commercial	and	coated	films	and	values	for
contro	l at four	different	tin	nes at 7°C	and	100% RH.								

nL eth	2 days	7 days	14 days	21 days
control	0.6 ± 0.1 aA*	0.8 ± 0.1 aA	0.6 ± 0.2 aA	0.7 ± 0.2 aA
PLA	0.6 ± 0.2 aA	0.7 ± 0.1 aA	0.9 ± 0.1 aB	1.1 ± 0.2 aB
2PLA	0.7 ± 0.3 aA	0.9 ± 0.2 aA	1.0 ± 0.3 aA	0.9 ± 0.3 aA
CL	0.9 ± 0.2 aA	1.2 ± 0.2 bB	2.4 ± 0.2 bC	2.5 ± 0.1 bC
4A	0.8 ± 0.2 aA	1.3 ± 0.4 bB	2.6 ± 0.6 bC	2.8 ± 0.8 bC
LDPE	0.6 ± 0.1 aA	0.7 ± 0.0 aA	0.7 ± 0.3 aA	0.9 ± 0.3 aA
Green bags	0.6 ± 0.0 aA	0.8 ± 0.1 aA	1.7 ± 0.1 bB	2.0 ± 0.1 bB
Peakfresh	0.7 ± 0.1 aA	0.8 ± 0.0 aA	1.0 ± 0.3 aA	1.0 ± 0.4 aA

\* means followed by the same lower case letter in column, upper case in rows are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.11. Amount of carbon dioxide (%) adsorbed by the same commercial and coated films and values for control, used first time after
coating and second time after degassing, at four different times at 23°C and 0% RH.

% CO2	2 days		week		2 weeks		3 weeks	
	1st time	2nd time	1st time	2nd time	1st time	2nd time	1st time	2nd time
СО	0.7 ± 0.5aA1*	0.5 ± 0.2aA1	0.8 ± 0.5aA1	1.3 ± 0.7aA1	1.8 ± 0.6aA1	1.4 ± 0.7aA1	1.2 ± 0.1aA1	1.6 ± 1.1aA1
CL	1.9 ± 0.7aA1	3.9 ± 0.9bA2	3.5 ± 0.3bB1	4.1 ± 0.7bA1	5.2 ± 0.6bC1	5.2 ± 1.0bA1	5.1 ± 0.4bC1	6.2 ± 2.2bA1
4A	3.1± 0.8bA1	2.2 ± 1.2bA1	4.3 ± 0.8bA1	3.8 ± 1.9bcAB1	8.9 ± 0.5cB1	5.0 ± 1.3bB2	9.9 ± 1.3cB1	5.8 ± 1.7bB2
Green								
bags	0.4 ± 0.3aA1	0.9 ± 0.5aA1	1.7 ± 1.2aA1	1.9 ± 0.8acA1	2.2 ± 1.5aA1	2.2 ± 1.4aA1	3.9 ± 2.2abA1	6.3 ± 2.2bB2

\* means followed by the same lower case letter in column, upper case in rows, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.12. Amount of carbon dioxide (mL) adsorbed by the same commercial and coated films and values for control, used first time after
coating and second time after degassing, at four different times at 23°C and 0% RH.

mL								
CO <sub>2</sub>	2 days		week		2 weeks		3 weeks	
	1st time	2nd time	1st time	2nd time	1st time	2nd time	1st time	2nd time
СО	1.6 ± 1.2 aA1*	1.3 ± 0.5 aA1	2.0 ± 1.3 aA1	3.3 ± 1.7 aA1	4.4 ± 1.6 aA1	3.6 ± 1.7 aA1	3.0 ± 0.3 aA1	4.1 ± 2.7 aA1
CL	4.7 ± 1.7 aA1	9.6 ± 2.2 bA2	8.8 ± 0.7 bB1	10.2 ± 1.8 bA1	13.1 ± 1.6 bC1	13.1 ± 2.4 bA1	12.8 ± 1.1 bC1	15.5 ± 5.4 bA1
4A	7.7 ± 2.1 bA1	5.5 ± 3.1 bA1	10.6 ± 2.1 bA1	9.4 ± 4.8 bcAB1	22.2 ± 1.3 cB1	12.5 ± 3.3 bB2	24.6 ± 3.1 cB1	14.5 ± 4.2 bB2
Green								
bags	1.1 ± 0.7 aA1	2.3 ± 1.3 aA1	4.1 ± 3.1 aA1	4.8 ± 1.9 acA1	5.5 ± 3.8 aA1	5.4 ± 3.5 aA1	9.8 ± 5.4 abA1	15.8 ± 5.5 bB2

\* means followed by the same lower case letter in column, upper case in rows, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.13. Amount of ethylene (ppm) adsorbed by the same commercial and coated films and values for control, used first time after coating and second time after degassing, at four different times at 23°C and 0% RH.

ppm eth	2 davs		week		2 weeks		3 weeks	
	1st time	2nd time	1st time	2nd time	1st time	2nd time	1st time	2nd time
СО	3.2 ± 2.3 aA1*	3.1 ± 1.3 aA1	2.5 ± 0.8 aA1	2.8 ± 1.6 aA1	3.1 ± 1.6 aA1	3.1 ± 4.2 aA1	4.9 ± 1.1 aA1	5.5 ± 3.2 aA1
CL	5.3 ± 1.5 aA1	7.7 ± 0.4 bA2	8.6 ± 1.6 bA1	8.8 ± 0.9 bA1	13.2 ± 0.8 bB1	12.5 ± 1.0 bB1	22.8 ± 0.5 bC1	33.5 ± 0.7 bC2
4A	4.2 ± 1.1 aA1	7.1 ± 0.3 bA2	10.7 ± 1.1 bB1	11.4 ± 2.1 bB1	13.6 ± 2.7 bB1	14.2 ± 2.2 bB1	26.9 ± 6.8 bC1	33.0 ± 2.4 bC1
Green								
bags	3.3 ± 0.8 aA1	4.6 ± 0.6 aA1	3.0 ± 0.5 aA1	3.5 ± 2.0 aA1	11.8 ± 3.6 bB1	12.4 ± 0.7 bB1	23.8 ± 8.7 bC1	31.2 ± 2.8 bC1

\* means followed by the same lower case letter in column, upper case in rows, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.14. Amount of ethylene (%) adsorbed by the same commercial and coated films and values for control, used first time after coatin
and second time after degassing, at four different times at 23°C and 0% RH.

% eth	2 days		week		2 weeks		3 weeks	
	1st time	2nd time	1st time	2nd time	1st time	2nd time	1st time	2nd time
СО	1.3 ± 0.8 aA1*	1.4 ± 0.5 aA1	1.1 ± 0.4 aA1	1.2 ± 0.7 aA1	1.3 ± 0.7 aA1	1.4± 1.8 aA1	2.1 ± 0.5 aA1	2.5 ± 1.4 aA1
CL	2.2 ± 0.5 aA1	3.5 ± 0.3 bA2	3.6 ± 0.8 bB1	4.3 ± 0.6 bA1	5.5 ± 0.4 bC1	4.6 ± 0.9 bA1	9.6 ± 0.4 bD1	15.1 ± 0.4 bB2
4A	1.8 ± 0.4 aA1	3.2 ± 0.1 bA2	4.5 ± 0.5 bB1	4.2 ± 1.0 bA1	5.8 ± 1.4 bB1	5.5 ± 3.0 bA1	11.5 ± 3.4 bC1	14.9 ± 1.2 bB1
Green								
bags	1.4 ± 0.1 aA1	2.1 ± 0.2 aA2	1.2 ± 0.9 aB1	1.6 ± 1.0 aA1	5.1 ± 0.9 bC1	5.3 ± 0.7 b1	10.1 ± 2.2 bD1	14.1 ± 1.2 bC2

\* means followed by the same lower case letter in column, upper case in rows, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

Table A5.15. Amount of ethylene (nL) adsorbed by the same commercial and coated films and values for control, used first time after coating and second time after degassing, at four different times at 23°C and 0% RH.

nL eth	2 days		week		2 weeks		3 weeks	
	1st time	2nd time	1st time	2nd time	1st time	2nd time	1st time	2nd time
СО	0.2 ± 0.1 aA1*	0.2 ± 0.1 aA1	0.2 ± 0.1 aA1	0.2 ± 0.2 aA1	0.2 ± 0.1 aA1	0.2 ± 0.2 aA1	0.2 ± 0.1 aA1	0.3 ± 0.2 aA1
CL	0.3 ± 0.1 aA1	0.4 ± 0.0 bA2	0.7 ± 0.0 bB1	0.6 ± 0.1 bA1	0.7 ± 0.0 bC1	0.6 ± 0.1 bA1	$1.1 \pm 0.0 \text{ bD1}$	1.7 ± 0.0 bB2
4A	0.2 ± 0.1 aA1	0.4 ± 0.0 bA2	0.7 ± 0.1 bB1	0.7 ± 0.3 bA1	0.7 ± 0.1 bB1	0.7 ± 0.3 bA1	1.3 ± 0.3 bC1	1.6 ± 0.1 bB1
Green								
bags	0.2 ± 0.0 aA1	0.2 ± 0.0 aA2	0.6 ± 0.2 aB1	0.6 ± 0.1 aA1	0.6 ± 0.2 bC1	0.6 ± 0.1 b1	1.2 ± 0.4 bD1	1.6 ± 0.1 bC2

\* means followed by the same lower case letter in column, upper case in rows, numbers between times, are not statistically different from each other (Tukey,  $\alpha$ = 0.05)

sampling times at 25°C and 0% Kin.								
2 days	% eth	ppm eth	nL eth					
4A (K1)	0.4	1.7	0.1					
CL (K4)	0.2	4.0	0.0					
7 days	% eth	ppm eth	nL eth					
4A (K1)	2.7	12.4	0.6					
CL (K4)	2.5	15.7	0.6					
14 days	% eth	ppm eth	nL eth					
4A (K1)	3.5	15.9	0.8					
CL (K4)	4.6	21.0	1.0					
21 days	% eth	ppm eth	nL eth					
4A (K1)	12.1	55.4	2.7					
4A (K2)	12.1	52.7	2.7					
CL (K3)	10.3	35.8	2.3					
CL (K4)	9.2	31.6	2.1					

Table A5.16. Amount of ethylene (%, ppm, nL) adsorbed by coated films in permeation cells at four sampling times at 23°C and 0% RH.

Table A5.17. Amount of ethylene (%, ppm, nL) adsorbed by coated films in permeation cells at four sampling times at  $7^{\circ}$ C and 0% RH.

2 days	% eth	ppm eth	nL eth
4A (K1)	9.9	44.3	2.2
CL (K4)	10.5	47.2	2.4
7 days	% eth	ppm eth	nL eth
4A (K1)	19.5	86.8	4.3
CL (K4)	16.4	73.4	3.7
14 days	% eth	ppm eth	nL eth
4A (K1)	29.3	143.2	7.1
CL (K4)	24.9	124.2	6.2
21 days	% eth	ppm eth	nL eth
4A (K1)	33.4	161.6	8.0
4A (K2)	32.1	154.2	7.7
CL (K3)	28.4	137.1	6.9
CL (K4)	26	129.4	6.5

REFERENCES

## REFERENCES

- 1. Ozdemir M., Floros J. D. Active Food Packaging Technologies Critical Reviews in Food Science and Nutrition, 2004 (44) 185-193
- Wilson C. L. (ed.) Intelligent and Active Packaging for Fruits and Vegetables CRC Press 2007 (57-71)
- 3. Zagory D. Ethylene-removing packaging in Rooney M.L. (ed.) Active Food Packaging (38-54)
- 4. Chapman& Hall 19952012 Production guide for Storage of Organic Fruits and Vegetables NYS IPM Publication no.10
- Coloma A., Rodriguez F.J., Bruna J.E., Guarda A., Galotto M.J. Development of an Active Film with Natural Zeolite as Ethylene Scavenger, Journal of Chilean Chemical Society2014 (49) 2409-2414
- Patdhanagul N., Srithanratana T., Rangsriwatananon K., Hengrasmee S. Ethylene adsorption on cationic surfactant modified zeolite NaY, Microporous and Mesoporous Materials 2010 (131) 97-102
- 7. Erdogan B., Sakizci M., Yorukogullari E. Characterization and ethylene adsorption of natural and modified clinoptilolites, Applied Surface Science 2008 (254) 2450-2457
- Sodergard A., Stolt M. Industrial production of high molecular weight poly(lactic acid) in Auras R., Lim L.-T., Selke S., Tsuji H. (ed.) Poly(lactic acid) Synthesis, Structures, Properties, Processing and Applications (27-41) John Willey and Sons 2010
- Gonzales-Buesa J., Page N., Kaminski C., Ryser E.T., Beaudry R., Almenar E. Effect of nonconventional atmospheres and bio-based packaging on the quality and safety of *Listeria monocytogenes*-inoculated fresh-cut celery (*Apiumgraveolens L*.)during storage Postharvest Biology and Technology 2014 (93) 29-37
- 10. Yuzay I.E., Auras R., Selke S. Poly(lactic acid) and synthetic zeolite composites prepared by melt processing, Journal of Applied Polymer Science 2009 (115) 2262-2270
- 11. Esturk O., Ayhan Z., Gokkurt T. Production and Application of Active Packaging Film with Ethylene Adsorber to Increase the Shelf Life of Broccoli (*Brassica oleracea* L. var. Italica), Packaging Technology and Science 2013 (27) 179-191
- 12. Mohanty A., Misra M., Drzal L. (ed.) Natural Fibers, Biopolymers, and Biocomposites CRC Press 2005
- 13. Domenek S., Courgneau C., Ducruet V. Characteristics and Applications of PLA inKalia S., Averous L. (ed.) Biopolymers: Biomedical and Environmental Applications (183-223) Wiley-Scrivener 2011
- 14. http://evlon.ca/specifications.php

- 15. http://vpl.astro.washington.edu/spectra/c2h4.htm
- 16. http://webbook.nist.gov/cgi/cbook.cgi?ID=C74851&Units=SI&Type=IR-SPEC&Index=O#IR-SPEC
- Aronne A., Esposito S., Ferone C., Pansini M., Pernice P. FTIR study of the thermal transformation of barium-exchanged zeolite A to celsian, Journal of Materials Chemistry 2002 (12) 3039-3045
- 18. Elaiopoulos E. Operations involving organic gases and vapors in Inglezakis V. J., Zorpas A. A. (ed.) Handbook of Natural Zeolites (246-252) Bentham Science Publishers 2012
- Romero-Perez A., Aguilar-Armenta G. Adsorption kinetics and equilibria of carbon dioxide, ethylene and ethane on 4A (CECA) zeolite, Journal of Chemical and Engineering Data 2010 (55) 3625–3630
- Adsorption by Clays, Pillared Clays, Zeolites and Aluminophosphates in Rouquerol F., Rouquerol J., Sing K. Adsorption by Powders and Porous Solids. Principles, Methodology and Applications (490-519) Elsevier 1999
- 21. Jinqu W., Yongchun Z. Adsorption equilibrium of ethylene-carbon dioxide mixture on zeolite ZSM5 and its correlation, Journal of Chemical Industry and Engineering (China) 1992 (7) 208-215
- 22. Sircar S., Myers A. L. Gas Separation by Zeolites in Auerbach S. M., Carrado K. A., Dutta P. K. (ed.) Handbook of Zeolite Science & Technology(1354-1406) Dekker 2003
- Aguilar-Armenta G., Hernandez-Ramirez G., Flores-Loyola E., Ugarte-Castaneda A., Silva-Gonzalez R., Tabares-Munoz C., Jimenez-Lopez A., Rodriguez-Castellon E. Adsorption Kinetics of CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> in Cation-Exchanged Clinoptilolite, Journal of Physical Chemistry B 2001 (105) 1313-1319

## CHAPTER 6

## Summary, general conclusions and recommendations for future work

In food packaging, the composition and relative concentrations of headspace gases play an important role in extending the shelf life of perishables. Some gases, like oxygen, nitrogen or carbon dioxide, will be placed in the packages during the packaging process; others (especially ethylene but also carbon dioxide) will be produced by the fresh produce itself. Presence of specific gases or too high concentrations of already present gases will play a critical role in keeping fruits and vegetables both fresh and safe.

Active packaging systems are efficiently used in food packaging. Due to growing interest in using PLA as a replacement packaging material for petrochemical based polymers, there is also a question if PLA can be used as a part of active packaging systems. Zeolites, having many different structures and frameworks, make themselves ideal sorbents for many volatiles. They have been proven to act as ethylene and CO<sub>2</sub> scavengers. Studies show that PLA and zeolites can be combined into one material by extrusion. Now the question is if they can act as an efficient active packaging system.

In chapter 3, two zeolites were chosen for investigation, due to their popularity and common utilization in many fields. These were natural clinoptilolite (CL) and synthetic type 4A zeolite. Experiments were focused on determination of their adsorption capacities for ethylene ( $C_2H_4$ ) and carbon dioxide ( $CO_2$ ) at different conditions (temperature, humidity, composition of headspace gases). It was proven that both zeolites can be successfully used as ethylene and carbon dioxide scavengers and are promising alternatives to currently used materials. The largest adsorption capacities were recorded for room temperature and 0% relative humidity and the smallest for the conditions most relevant to fresh produce (7°C and 100% RH). But all investigated cases showed that the amounts adsorbed are in a range that corresponds to concentrations produced and are above amounts tolerated by fresh produce. Zeolites were active for different times, between 2 days for carbon dioxide and up to three weeks for ethylene. Commodities are not usually stored this long. All of those results proved that zeolites could be used for the purpose needed in this research.

Chapter 4 describes two ways of incorporating zeolites into/onto poly(lactic acid). The first processing method was based on research done before at the School of Packaging and involved extrusion, injection molding and compression. Ethylene and carbon dioxide adsorption of the produced films were investigated and no significant adsorption was observed. This was due to the zeolites being too deeply incorporated into the PLA matrix. Since PLA is a good barrier to ethylene, it was blocking the zeolites. The second method tried was solution coating. This method proved to be successful in incorporating zeolites on the surface of the PLA film and also not blocking their activity as a gas scavenger. Different combinations of zeolite and polymer contents were investigated in the adsorption studies. At the end, two coating solutions and conditions were developed for each zeolite and were proven to be most effective for further studies.

In chapter 5 details about adsorption characteristics, thermal and tensile properties of the newly developed zeolite coated PLA films are provided. For the adsorption studies, also two commercially available bags, PeakFresh and Green bags, which are claimed to be ethylene scavengers that extend fresh produce shelf life, were evaluated. There were also several control samples: PLA film without coating, PLA film coated with the same coating solution just not containing zeolites, and LDPE film as a control for the commercial films, since they are LDPE with impregnated zeolites. Adsorption studies were run in two conditions, 23°C and 0% RH, and 7°C and 100% RH. Most control samples did not show significant adsorption of the two investigated gases, while coated films and Green bags did. In both

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testing conditions our films were comparable to each other and one of commercial bags in adsorption of ethylene and carbon dioxide. Since producers of commercial films advertise them as reusable bags, an experiment was performed to compare the reusability of coated films and one of the commercial bags that was comparable in adsorption capacity to our samples. It was proven that at room temperature all samples could be successfully reused after proper desorption in vacuum oven. Experiments involving permeation cells also proved that zeolite coated PLA films can be successful in scavenging C<sub>2</sub>H<sub>4</sub> at 23°C and 7°C with no water present. Thermal properties were minimally changed when compared to PLA films that were uncoated or coated without zeolite. Tensile properties were more significantly affected by the presence of zeolites. Tensile strength and modulus of elasticity were decreased while elongation at break was increased, meaning our films were less breakable and more flexible.

In conclusion, this research has shown that zeolites in the form of powder are powerful ethylene and carbon dioxide scavengers in different conditions of temperature, relative humidity and headspace gases. Decreasing the temperature from 23°C to 7°C decreased sorption of ethylene for both zeolites, and decreased sorption of carbon dioxide in 4A, while increasing sorption of carbon dioxide in CL. The presence of water inhibited adsorption of ethylene in CL, decreased adsorption of carbon dioxide in CL, and reversed ethylene adsorption in 4A but did not affect adsorption of carbon dioxide in 4A. The presence of additional headspace gases in most cases increased sorption of larger molecules and extended adsorption times for smaller molecules. Since fresh produce is usually kept at low temperatures and with high humidities inside packages with few gases present inside the headspace, all those changes are relevant. Decreased temperature will have a positive effect while increased RH and more headspace gases might have detrimental effects.

Further, solution coating is a method of choice to incorporate zeolites on the surface of PLA films without blocking their adsorption capacities by incorporating them too deeply into the polymer

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matrix. Zeolite coated PLA films demonstrated lower adsorption capacities than zeolites by themselves but were still relevant for the concentrations produced and are above amounts tolerated by fresh produce, with the length of action longer than would be typical in applications. While the mechanism of action of zeolites as gas scavengers is still not fully known, PLA films coated with zeolites should be further investigated as a new biobased and biodegradable alternative to commercially available LDPE bags.

Many questions have been answered by this research, but there are still more questions to be asked. It would be definitely beneficial to investigate more different zeolites. There are over 150 synthetic and 40 natural zeolites and we have tested only two of them. Depending on the type of framework, zeolites can have different pore openings; modified zeolites can also have variable ions. All of these will definitely change their adsorption capacities. As for the production method, only extrusion with injection molding followed by compression and solution coating have been tried. There are also other methods available like spin coating, knife coating, bilayer cast film extrusion on PLA film, etc. To improve the homogeneity of coating solutions, sonication could be utilized. No matter the method, the adsorption mechanism should be further investigated. Experiments involving kinetics characterization as well as building sorption isotherms for the new films should be carried out. As much as adsorption is very important in extending the shelf life of fresh produce, desorption measurements could help in developing films that could be utilized as reusable packages, which would help in being a competitive alternative to commercially available systems.