POLYMER NANOCOMPOSITES AS ACTIVE FOOD PACKAGING MATERIALS TO IMPROVE THE SHELF LIFE OF FRUITS AND VEGETABLES

by

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ABSTRACT

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Keywords: Halloysite Nanotubes, Active Food Packaging, Waterborne Polyurethane Foam, Nanocomposites, Cinnamaldehyde, Ethylene production inhibition, Atmosphere Regulator, Moisture Absorption, Ethylene Absorption

In this thesis, important solutions to the concept of food safety and preservation of food quality, which has become increasingly important recently, has been offered with the development of multifunctional hybrid nanocomposite materials containing natural and environmentally-friendly components. Specifically, the studies have focused on the prevention of food spoilage and waste during post-harvest stages and two different hybrid nanocomposite materials that can protect and prolong the shelf-life of fresh produce during storage and transportation was designed. The first design included active food packaging films that can slowly release a natural active agent, which can slow down the ripening of fruits. Halloysite clay nanoparticles were impregnated with cinnamaldehyde essential oil and the obtained sustained release system was incorporated into polypropylene matrix, resulting in nanocomposite food packaging films that can release cinnamaldehyde to inhibit the production of fruit-ripening ethylene gas. The ripening of bananas packaged with these nanocomposite films was demonstrated to be delayed and bananas were shown to be stored fresh for a longer period of time than unpackaged bananas. In the second design, natural clay nanoparticles were integrated into foamed waterborne polyurethane matrix to produce novel, flexible, fresh-keeping and atmosphere regulating nanocomposite foams, which can be used as packaging inserts that can increase the shelf life of fruits. The nanocomposite foam was demonstrated to absorb both the fruit-ripening ethylene gas produced by the fruits and the excess moisture, thus delay the post-harvest ripening and spoilage in different fruits tested. The ethylene production inhibiting food packaging films and the ethylene and moisture absorbing foams presented in this thesis have a strong potential as food packaging materials that improve the shelf life of fresh produce and contribute to the prevention of food spoilage and waste.

ÖZET

MEYVE VE SEBZELERİN RAF ÖMRÜNÜ UZATMAK İÇİN AKTİF GIDA AMBALAJ MALZEMELERİ OLARAK POLİMER NANOKOMPOZİTLER

Sarp Kölgesiz

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Tez Danışmanı: Dr. Öğr. Üyesi Hayriye ÜNAL

Tez Eş Danışmanı: Dr. Öğr. Üyesi Serkan ÜNAL

Anahtar Kelimeler: Halloysit Nanotüpleri, Aktif Gıda Ambalajları, Su Bazlı Poliüretan Köpük, Nanokompozitler, Sinnamaldehit, Etilen Üretiminin Engellenmesi, Atmosfer Düzenleyici, Nem Absorpsiyonu, Etilen Absorpsiyonu, Gıda Raf Ömrü

Bu tezde, doğal ve çevre dostu bileşenler içeren, çok fonksiyonlu hibrit nanokompozit malzemelerin geliştirilmesiyle, son zamanlarda gittikçe önem arz etmeye başlayan gıda güvenliği ve gıda kalitesinin korunması kavramına yönelik çözümler sunulmuştur. Çalışmalar özellikle gıda tedarik zincirinin hasat sonrası aşamalarında gıdanın bozulmasını engellemeye odaklanılmış ve meyvelerin depolama ve taşıma aşamalarında raf ömrünü artırma özelliği gösteren iki farklı nanokompozit malzeme tasarlanmıştır.

Birinci tasarım, doğal bir malzemenin kontrollü salım sistemi ile gıdaların etilen gazı üretmesini yavaşlatabilmek için dizayn edilmiş aktif gıda ambalaj filmlerini içermektedir. Kontrollü salım sistemi, Sinamaldehit doğal yağı, Halloysit kil nanoparçacıkları içerisine emdirilmesiyle elde edildikten sonrasında, polipropilen matris içerisine entegre edilmiştir. Bu sayede elde edilen nanokompozite gıda ambalaj filmleri, sinamaldehitin ambalaj içerisine kontrollü salınmasıyla,

gıdaların etilen gazından kaynaklı olarak bozulmalarına engel olduğu gözlemlenmiştir. Üretilen nanokompozit filmlerle paketlenen muzlarda bozulmanın, bu ambalaj paketleriyle paketlenmeyenlere göre, yavaşlatıldığı ve bundan kaynaklı olarak gıdaların daha uzun süre bu ambalaj paketleri içerisinde taze ve sağlıklı kaldığı gösterilmiştir. İkinci tasarımda, gıdaların raf ömrünü ambalaj içerisinde bulunarak, yeni geliştirilen, esnek yapıda, gıdaların taze tutan ve ambalaj içerisindeki havayı düzenleyici özelliklere sahip nanokompozit köpük, doğal kil nanoparçacıklarının köpürtülmüş poliüretan matris içerisine entegre edilmesiyle üretilmiştir. Gıdaların olgunlaşmasını sağlayan etilen gazının ve ortamda fazladan bulunan nemi emme özelliği sayesinde, farklı gıdaların olgunlaşma ve bozulma durumları hasat sonrası süreçler için test edilmiştir. Gıdaların bozulma ve israf olmasını önleyici, aynı zamanda gıdaların raf ömrünü arttırmaya yönelik tasarlanmış, etilen gazı üretimini yavaşlatan ambalaj filmleri ve etilen ve nem absorp eden köpükler gıda ambalaj ürünleri arasında güçlü potansiyele sahip olan malzemelerdir.

“A matter can be the solution to any problem; we just don't know it so change your perspective.” (Mehmet Ali Gülgün)

To my family and my future self

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TABLE OF CONTENT

ABBREVIATIONS

AP : Active Food Packaging
EO : Essential Oil
CO_2 : Carbon dioxide
HNT : Halloysite Nanotubes
CA : Cinnamaldehyde
C_2H_4 : Ethylene
PP : Polypropylene
WPU : Waterborne Polyurethane
AS : Ammonium Stearate
$KMnO_4$: Potassium Permanganate
SEM : Scanning Electron Microscopy
TGA : Thermogravimetric Analysis
DSC : Differential Scanning Calorimetry

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CHAPTER 1. General Introduction

Food packaging materials are one of the important components of the food industry, as they not only provide protection of food from the external environment, but they also preserve the nutritional value of the food[1,2]. The main purpose of the design and production of food packaging materials is the protection of food from physical, chemical, and microbial damages[2]. The traditional approaches to the food packaging designs mostly do not satisfy public demands anymore, because they only fulfill the old-world requirements such as strength, and flexibility and acting as a passive physical barrier between the food and its environment. With the increase of the consciousness in terms of healthy and high-nutrition value food, the consumer demand has changed so that food packaging materials also provides preservation of the quality, safety, and freshness of the foods[3,4]. Food packaging technology has evolved by introducing new methods and innovations to be replace the traditional ones to meet these demands. One of the novel innovations in packaging technology is active food packaging (AP) which is designed to preserve and increase the quality, safety, and freshness of foods. This new technology can lead to increase in the shelf-life of the food by imparting new functionalities to the food packages[5].

Active Food Packaging

The main purpose of using food packaging materials is to protect food throughout the food supply chain, which covers all stages from production to consumption. The features of traditional food packaging systems are no longer sufficient. However, active food packaging materials can be designed that can increase the shelf-life of food via incorporated active components. Active food packaging materials are designed by the integration of active components inside a polymeric matrix[6] resulting in materials that can absorb molecules that lead to spoilage of food or emit molecules that retard the spoilage, thus increase the shelf-life of food thanks to the active components[7]. By adding new features to the packaging and allowing it to interact with the food, the shelf life of the food is extended while enhancing its quality and freshness. The packaging is designed to protect the sensory properties of foods such as appearance, texture, and aroma, while at the same time increasing the shelf life by aiming to maintain the food quality and nutritional value[5].

There are many different studies related to active food packaging systems, that can be covered under three main groups which are active agent emitting systems, active agent absorbing systems, and systems that regulate the passage of gases. In active agent emitting systems, molecules, which are loaded, integrated, or naturally present inside the active agent such as antimicrobials, antioxidants, or carbon dioxide, directly interact with the food while being releasing onto the surface of the food or released slowly to the headspace of the package. In active agent absorbing systems, active agents scavenge the undesired molecules that are produced by food during the storage periods such as ethylene, oxygen, odor, and carbon dioxide. In gas regulating systems, the packaging is designed so that it acts as a barrier against gases.

In the food packaging industry, there are several different packaging types that have been designed and used according to the requirements of the food. Active food packaging materials are mostly produced by the incorporation of active agent to these package types by using different methods and processes. Incorporation of active agents into any polymeric matrix by using melt process methods, coating of package surfaces with active agents, or supercritical carbon dioxide methods are some of the examples of methods that are used to develop active food packaging materials.

Because of the increasing demand for high-quality, and healthy food, new types of active food packaging systems have been developed in more recent times. In the literature, several active food packaging systems are investigated. Here, they will be categorized according to their functions, such as being antioxidant, antimicrobial, ethylene absorbing, oxygen absorbing, carbon dioxide absorbing, odor absorbing, and presenting barrier properties.

1.1.2 Antioxidant Food Packaging Materials

Food spoilage can be observed in any stage of the food supply chain and the phenomenon directly has an impact on the quality and safety of food. There are many reasons for the decrease in shelf-life of foods and one of the main reasons for spoilage is oxidation[8]. The impact of oxidation on the food is that the important nutritional values, which are essential fatty acids, proteins, and lipids, are destroyed or damaged in the presence of the reactive oxygen compounds[9]. Oxidation not only causes degradation of the nutritional value, but also leads to a decrease in the energy content, formation of odors, and change in color sensory properties [10,11]. These facts are one of the key parameters in the decision steps of purchasing any food by the consumer[11] , thus there has also been an economic impact. Oxidation of essential fatty acids, proteins, and lipids, which are important nutritional values, can be prevented with direct application of antioxidant agents to food. However, the direct interaction of the synthetic antioxidant can cause potential risks to human health with the toxicity problem because of the migration of the additives into the food. Polyphenol, organophosphate, and thioester compounds are some examples of traditional antioxidant agents[11]. However, strict legal controls are a necessary request in the case of the use of synthetic antioxidants in food applications to prevent undesired consequences because of potential toxicity problems[11]. An alternative approach to this problem is the use of natural antioxidants, especially tocopherol, plant extracts, and essential oils from herbs and spices[12–17]. In addition, some of the antioxidant agents have been produced by utilizing industrial food wastes[18–20].

Another approach for using antioxidant material in food applications is active food packaging. Basically, antioxidant food packaging materials can be categorized into two groups in terms of their designs. In one of the designs, antioxidants are released from the food packaging and react with oxygen or reactive oxygen species in the headspace or directly in the food[21–24]. One of the main advantages of active food packaging with an antioxidant-controlled release system is that antioxidant agents are released from the system through food, gradually. This control over the release mechanism is to provide the presence of the active agents during all storage and transformation time which means that the protection functions would be present in the packaging material for a longer time when comparing the direct application of antioxidants. In the other design approach, oxygen-related substances are scavenged by the antioxidant scavengers, which have been incorporated into the food packaging[21–28]. In addition to these studies, many different methods and techniques are being tested to reduce the effects of oxidation reactions on food products and improve the stability of these new alternative packaging technologies for improving the quality and safety of oxidation-sensitive food products, e.g., modified atmosphere packaging for optimizing oxygen and related substance level[29], and encapsulation of the active agent in order to control the release rate for the increasing the presence of the active agent during the packaging[30].

In the literature, there are many different studies related to the application of different types of antioxidants with different applications. For example, the suitable antioxidants for food such as butylated hydroxytoluene (BHT) or butylated hydroxyanisole (BHA), have been addressed while reducing the risk of undesired consequences of the toxicity problem of synthetic compounds[8,31].

Another example is that a-tocopherol-loaded poly(lactic)acid microparticles containing 40 wt% of the natural antioxidant agent are produced for the biodegradable an oxygen scavenger system[32], the blend coextruded film (low-density polyethylene and polyamide6/66) is produced with the 0,8 and 14 mg/g butylated hydroxytoluene (BHT) for active food packacing[33], three different antioxidants, which are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tertiary butylated hydroquinone (TBHQ), are incorporated inside the polypropylene active packaging via extrusion molding process[34]. For this perspective, there are many different studies that are submitted to the literature with different methods[35–39] and alternatively, bio-based antioxidants and essential oils are good candidates to substitute synthetic antioxidant compounds[40,41]. In addition to these studies, antioxidant agents can be extracted from agricultural and industrial waste[42]. The motivation/aim of all these studies that knowledge about the positive antioxidant activities on the quality of food products while the interaction of agents with the reactive oxygen compounds that the reduction in the rate of the lipid oxidation of the food can be observed and the shelf-life of the food can be increased thanks to the presence of the antioxidation agents without any risk for the human health[11].

It is important to make this statement as well that there are some limitations due to the material or working principle of the systems. The preservation and stabilization of the food quality is provided by the presence of the active agent in the package and its activation. In case of depletion or absence of the active agent, nutrient degradation is observed because the functions gained in the presence of the agent will not work. The other limitation is that the material used cannot homogeneously interact with the entire food surface. Therefore, deterioration will occur in areas where the active agent is not present, which will negatively affect the quality of the food and thereby human health[43]. In addition, the direct use of some of the antioxidant agents on the food or food surface has been restricted because of toxicity problems and while optimizing the oxygen content in the package has an effect on the control of oxidation reactions, for the same cases, this cannot entirely be sufficient because oxygen dissolved in the food is very difficult to detect or completely remove during packaging[11,43,44]. Due to these limitations, studies should be conducted on these systems and new systems should be developed that are more innovative, economical, and aimed at protecting human health.

1.1.3 Antimicrobial Food Packaging Materials

Foods are perishable products that can be spoiled or deteriorated by any environmental effect during the food supply chain[45]. One of the main reasons for food spoilage is foodborne pathogenic microorganisms. Campylobacter and Salmonella species, *Yersinia enterocolitica*, *Escherichia coli*, and *Listeria monocytogenes*, are some examples of spoilage microorganisms that affect the food quality[45]. Traditional methods, such as freezing, and drying[45], used for food preservation and preservation are needed to improve sufficient protection under the motivation of prolonging the shelf-life of foods. However, active food packaging can provide various functions such as scavenging oxygen, moisture, or ethylene, as well as being designed to demonstrate antimicrobial activity. In addition to that, active food packaging can be utilized with different material forms such as films, and sachets.

Antimicrobial food packaging materials which mostly utilized in the form of film that can be produced by incorporating natural or synthetic antimicrobial agents to prevent food against microbial activities[45].Natural antimicrobial agents obtained from natural sources by different methods are relatively safer for the food packaging application in the case of toxicity problems[46]. In addition, the extraction of natural antimicrobial agents from nature may require complicated extraction procedures. The fact that the natural source may be rare and valuable at the point of production of natural antimicrobial agents may cause problems in the production and use of these agents at some points[45]. However, with the increasing interest in food production and packaging demand, natural antimicrobial materials are insufficient to provide the demand. Therefore, the development of organic or inorganic synthetic antimicrobial agents and the development of usable systems are also important. Ethylene diamine tetraacetic acid (EDTA), fungicides, parabens, and other chemicals are examples of the main antibacterial agents for food packaging applications. Organic acids have been used to prolong the shelf life of foods by preventing the growth of fungi and bacteria that cause spoilage. Sorbic acid also is utilized as an inhibition agent for the germination of bacterial spores. The inhibitory effect of organic acids is associated with the passage of its protonated form to the plasma membrane. Because of the high pH in the cell, the acid decomposes. Protons and anions are released due to the high pH of the environment. As a result, metabolic growth is inhibited[47–51]. In addition, bacteriocins, which have hydrophobic and positively charged compounds, interact with the negatively charged sides of the cell membranes and bind to the membrane. By penetrating the membrane of hydrophobic components in bacteriocins, pores can be formed in the membrane[52,53].

There are many different methods to improve and design effective antimicrobial packaging systems. Volatile antimicrobial or nonvolatile compounds included sachets/pads, polymeric materials which are incorporated with volatile and nonvolatile antimicrobial ingredients, using coating or adsorbing methods to apply the agent to the surfaces of the polymers, immobilization of antimicrobial substances in polymers with the presence of ion or covalent bonds, the use of natural antimicrobial materials in the polymer structure, such as chitosan[54].

Another antimicrobial compound, which is essential natural oils, which have an inherent ability to inhibit microbial growth, are used as antimicrobial agents in active food packaging. In general, active components such as aldehydes, phenols, and oxygenated terpenoids found in EOs are the basis of their antimicrobial properties. In addition, due to their hydrophobic components, EOs prevent microbial growth by interacting with the cell membrane and mitochondrial lipids of microbial cells, increasing the permeability of the cell membrane, and causing ion losses, which are important for the life of cells[55]. Thanks to the presence of hydrocarbon monoterpenes inside the EOs, microorganism cells can be stimulated to passage other antimicrobial agents that are used in the application to increase the impact of the antimicrobial agent on the microorganisms[56,57]. For example, known components of carvacrol and thymol, which are found in the structure of EOs, may facilitate the entry of components such as eugenol into *E.coli*, leading to the breakdown of the cell membrane[58].

Another potential antimicrobial agent, which is based on biodegradable polysaccharides, is chitosan and its derivatives that are to have inhibited activity to gram-positive and negative bacteria, fungi, and also viruses[54,59]. For example, the compounds of chitosan such as glucosamine monomer that can react with the cell membrane because of the presence of positive and negative charges on the mentioned two that can induce killing bacteria and such by outflowing vital compounds from the cell[54,60]. In addition, the chitosan concentration that is used in the antimicrobial application directly affects the activity[54,61]. Chitosan has been known as an antioxidant, anti-tumor, antifungal, antibacterial, anti-inflammatory, anti-thrombogenic, immunoadjuvant, and anti-cholesteric agent, and has also many green attributes such as nontoxicity, biocompatibility, non-allergenicity, and biodegradability. Therefore, it is widely used in medicine, agriculture, paper, textile, etc. It is also used in different fields such as the pharmaceutical and food industries[62]. Chitin, which is a significant natural polymer that has been known, is used to produce chitosan by deacetylation. Chitin is a naturally available component that can produce from the presence of numerous living organisms or waste seafood industry [63,64]. Consequently, chitosan is an affordable and easily accessible polysaccharide. Chitosan is a semi-crystalline material in the solid phase that is typically soluble in diluted organic acids such as acetic, citric, formic, lactic, malic, or tartaric acid, among others. [63,65] The use of chitosan as a material for food packaging films or coatings is becoming more popular as a result of the aforementioned chitosan qualities [59]. In the literature, antioxidant and/or antimicrobial films are the most common active films created utilization of chitosan as the polymeric matrix. The main reason for that there has been a lot of interest in recent years regarding the use of active agents which are derived from natural sources, such as essential oils and phenolic compounds found in large quantities in a variety of fruits, vegetables, legumes, and seeds, among other things [59]. These active ingredients, when combined with biodegradable polymeric matrices, have potential antibacterial and/or antioxidant characteristics and are suggested as a promising technique for creating food coatings or films. These active ingredients, which are used directly in food, increase its shelf life while ensuring its quality and safety. There are many examples of chitosan films, which are incorporated with tree tea, bergamot, clove bud, cinnamon, or Eucalyptus globulus among other essential oils, to perform as antimicrobial and antioxidant activity on the food[59,66–70]. As microorganisms gain new resistance to agents with antimicrobial properties, it is necessary to produce effective AP materials with new antimicrobial agents with new methods in the food packaging industry. In this context, the use of substances with potential antimicrobial effects against a wide variety of microorganisms in food packaging has become one of the important techniques used to prevent food spoilage.

1.1.4. Carbon dioxide Emitting/Absorbing Food Packaging Materials

Carbon dioxide is an important ingredient for food such as fish, meat, bakery, and dairy products and their preservation against microbial activity can be provided with desired carbon dioxide concentration. Thus, carbon dioxide can perform an antimicrobial activity to prolong the shelf-life of foods[71], and also the carbon dioxide, which is produced by the packaged foods during storage, helps to suppress physiologically reactive deterioration[71]. It is clear that carbon dioxide has a positive impact on food.

Chemically, carbon dioxide is known as nonpolar gas and is heavier when compared with oxygen and nitrogen. Because of the higher molecular weight of the carbon dioxide (44 g/mol), the diffusion of carbon dioxide will be slower in the air[72]. However, the reason that it shows effective antimicrobial activity against gram-negative bacteria and molds is the unique high solubility property of carbon dioxide in watery and fatty foods. According to the literature, there is a reverse relationship between the temperature and solubility of carbon dioxide, the solubility of the carbon dioxide is increased when the temperature decreases. Also, the inhibition property and antimicrobial property against the microbial is higher at reduced temperature. The high solubility property of CO_2 can be important for some food such as roasted coffee. In some cases, due to high solubility, CO_2 concentration in the package may decrease, in these cases a CO_2 emitter placed in the package helps to release CO_2, slowing down physiological reactions such as respiration and/or ethylene production that cause food spoilage. However, the high CO_2 level inside the headspace of the package has also drawbacks on food such as browning and off-odor development when the CO_2 concentration exceed the 20% of the tolerance limit. As mentioned above, carbon dioxide is an important factor in food spoilage. However, since it must be at a certain concentration, carbon dioxide emitters and absorbers as active agents can be utilized to design active food packaging systems in order to increase the quality and shelf life of foods.

CO_2 absorbers have been mainly utilized to prevent volume expansion because of the production of carbon dioxide, to control the concentration of CO_2 inside the headspace, and to preserve the iron-based oxygen scavenger against CO_2[72]. The required application in terms of quality preservation or package integrity, CO_2 absorbers can be employed in food packaging systems as sachets, pouches, and/or labels to absorb CO_2 physically or chemically. The gas adsorbents such as metal oxides and metal hydroxides can be included in sachets or active food films to absorb physically the CO_2. In addition, the natural material chitin has a component named D-glucosamine that is utilized to scavenge the released CO_2 by roasted coffee beans [73].

In order to absorb the CO_2 chemically, most of the CO_2 absorbers, which are performed in active food packaging, have specifically reacted with CO_2. CO_2 inherently is an acidic gas so there are many alkaline earth solutions and salts that give a reaction with CO_2 in the case of an acid-base neutralization reaction. There are many different compounds that are used to absorb CO_2 chemically. Calcium hydroxide is one of them that is used frequently in the application. The reaction between them leads to the formation of calcium carbonate and water which means, it is safe to apply food packaging applications[71]. The commonly used other compound is calcium oxide during food transportation[71]. Sodium carbonate, a type of widely used food additive, is another promising CO_2 absorber that may react with CO_2 when supplied with moisture [74]. In addition to these compounds, because of the safety and the capability of the absorption of the CO_2, that sodium glycinate can be utilized in the food packaging application in the form of sachets, pouches, or film [75].

Activated carbon and zeolite are typical examples of physical gas adsorbents[71], and physical gas-absorbing materials in the porous structure are also performed for CO_2 absorption. The main difference between the chemical CO_2 absorbers and physicals, there is an adsorption equilibrium for the CO_2 absorption. The level of CO_2 absorption and the partial pressure of CO_2 have a relationship in that the CO_2 absorption has been increased when the partial pressure of CO_2 increases. For the explanation of the relationship between the CO_2 and absorbers, Henry's law, Langmuir isotherm, and other adsorption equations can be utilized to analyze the CO_2 adsorption capabilities of the materials. In addition, there are other parameters that have affected the relationship such as microporous structure, temperature, and humidity. The physical absorption of CO_2 phenomena can be called an intrinsically reversible process that is the increase in the adsorption of CO_2 with increases in partial pressure of CO_2, and the reduction of partial pressure of the CO_2 in the environment may cause the reduction in the absorbed amount.

1.1.5. Ethylene Scavenging Food Packaging Systems

Ethylene (C2H4), which is known as pure unsaturated hydrocarbons and as a plant hormone, is present in nature. It is a volatile substance that is extremely important for the plants[76]. This hormone, produced by plants, regulates the cycle of plants from their development to their aging, and ethylene also controls physiological mechanisms[77,78]. Ethylene induces physiological responses in plants such as geotropism, maturation, senescence, dormancy, and flowering[79–81]. In some cases, low concentration of ethylene gas is known to be used to activate the physiological activities of nutrients after harvest[82,83]. However, the food loss and contamination of food by microorganisms are observed because of the exposure to a high level of ethylene with increasing the ripening of food during the post-harvest stage[84]. Active food packaging is one of the important solutions for the contamination or deterioration of food by ethylene gas. The ethylene scavenger is required for prolonging the quality and safety of the food[76,85,86] while absorbing the exceeded ethylene level produced by food[87,88]. The ethylene scavenger materials commonly used in the type of sachets, films, or boxes that are utilized to control the ethylene concentration in packaging headspace to prevent food spoilage[89].

As mentioned for the CO_2 active food packaging system, ethylene scavengers also reacted with the ethylene gas to the absorption in two specific ways such as physical or chemical. The basic approach for the ethylene-removing system is that the different gases are applied to the headspace to regulate the exceeded amount of ethylene inside the headspace, then the perforation process is applied on the packaging material for the passage of the gases and lastly, ethylene scavenger is utilized for the removing of the ethylene gases from the system[76].

Some of the supermarket chains such as Tesco and M&S are utilized ethylene scavengers and absorbers for fresh fruit and vegetable to control their spoilage and even prolong their shelf-life [90–92]. The ethylene scavengers are effective agents that are used to eliminate the exceeded ethylene concentration level in the headspace of packages[93]. Because of the presence of the double bound in the chemical structure of the ethylene gases, degradation or change can occur in the structure while the reaction between the reactive compounds[94]. Thanks to the chemical structure of ethylene, many different methods can be performed for the disposal of ethylene. Chemical and physical methods are utilized during the food application to scavenge ethylene[95]. The ethylene scavenging system can be designed as an incorporation of suitable agents inside the small sachets or into packaging material. The high permeability property of the sachet can allow the passage of ethylene gas toward sachets for scavenging[95,96].

Potassium permanganate ($KMnO_4$)-based systems, a dependable agent that chemically scavenges C_2H_4 via oxidation process, have been the most well-known, affordable, and commonly utilized ethylene cleaning systems for last years[93,97]. The improvement of the gas absorption efficiency of some of the materials such as silica gel or alumina, which are functionalized with $KMnO_4$ for increasing the surface area, are utilized as ethylene scavengers via oxidization phenomena.

According to the literature[98], $KMnO_4$ incorporation on the silica and alumina ethylene scavenging system is developed for ethylene scavenging.

In literature, there are several clay-based materials, which are consisted of aluminosilicates tetrahedral and octahedral layers, that are known for their ability to absorb the ethylene gas[99]. Si^{4+} is included in the tetrahedral layers with the presence of Al^{3+} commonly and Mg^{2+} and Al^{3+} ions can also be found in the octahedral layers although the other ions Fe^{2+}, Ni^{2+}, Li^{+}, Fe^{3+}, Cr^{3+} can be observed in this layer[100]. Activated carbon, zeolites, and other types of clay-based material adsorbents are utilized to remove physically the ethylene from the system by the presence of the active surfaces that can be performed in the sachets or incorporated into the polymeric films by applying polymer melt process[99,101]. Zeolite has been utilized as an ethylene absorber because of the interior hollow structure that naturally existed on the material. This unique property of the zeolite, the hollow and the porous structure, that the zeolite is applied in food packaging applications[97]. Zeolite is not only a clay-based material having such unique properties. Halloysite nanotubes and montmorillonite are examples of natural clay-based materials that are commonly used in active food packaging applications[99,102,103].

Halloysite nanotubes (HNTs) are natural clay-based materials that can be extracted from nature. Because of its unique properties such as its high aspect ratio and the tubular structure, HNTs are utilized in a wide range of applications[99,104–107]. Specifically, HNTs are used as nanocarriers[104,105,108–111] because of their tubular structure and high loading capacity, and because of their high aspect ratio, they are utilized as reinforcing agents in composite materials[112–115]. According to the literature, there is no evidence that HNT is toxic or dangerous for human health because of that reason, HNT is widely used in food packaging applications as a reinforcer and ethylene absorber. For example, different amounts of HNTs are incorporated into the low-density polyethylene film, via melt extrusion process, to increase the shelf life of food by the ethylene absorbing property of HNTs[77] and the alkali-treatment of HNTs has been demonstrated to increase the ethylene absorption capacity to increase the shelf-life of food [101].

Another ethylene scavenger material is a new palladium-promoted material, that is to have remarkable ethylene scavenging capabilities at even room temperature[76]the palladium-based ethylene scavenger, which is applied on climacteric fruit, is enhanced to scavenge the produced ethylene by fruits and as a result, the ripening of the fruits is delayed with the presence of the ethylene scavenger[116]. In another study, a palladium-promoted ethylene scavenger is developed in the form of powder with high ethylene adsorption efficiency (4162 μL g^{-1}) when compared with $KMnO_4$ ethylene scavenger at 20 °C[117]. The palladium is also incorporated with other materials such as activated carbon to analyze the synergic effect of the ethylene scavenging capacity. According to the studies, the synergic effect is occurred with the combination of palladium and activated carbon with different concentrations that have a positive effect on the quality of foods over time[118–120].

Basically, the existence of ethylene inside the headspace of the food package can be scavenged with the ethylene scavenger or absorber to prolong the safety, quality, and shelf life of the fresh food. There are some parameters that are directly effective on the scavenging efficiency of the compounds that are used in the food packaging application such as concentration or the amount of the scavenger or absorber, the efficiency of the material, which is able to work at high relative humidity, and lastly the temperature that is applied during the storage process of the food[82,96].

The designed system, which has the ethylene scavenging ability to prolong the shelf-life of food, should be carefully designed. Specific parameters such as intended fruit/vegetable application and expected shelf life of food determine the design of an ethylene scavenging system and the ethylene absorption capacity of an ethylene scavenger, which is utilized in the system, is considerable for the application. For these purposes, the material that is performed in this application is in the form of sachets and plastic films[76].

Sachet forms of ethylene scavengers are mainly utilized in food packaging applications in order to remove ethylene from the headspace or minimize the ethylene activity while decreasing the ethylene level inside the headspace[97]. Porous structure-based sachets are utilized to ensure the passage of the ethylene gas and the materials, which are used as ethylene scavengers, can be applied in different forms such as powder, granules, and beads[76]. Additionally, there are new attempts to use ethylene scavenging sachets for cold stores and shipping containers in the form of porous slabs and blankets[76]. There are many examples of commercial ethylene scavengers. Sachets and SendoMate, Evert-Fresh, Biofresh are examples of those products. However, there is a need for some consideration about the use of the sachets because of some of the parameters that are directly related to the performance of the sachet such as high relative humidity, dimensions, the type of fruits and vegetables, exposure time to the ethylene, and many other parameters[76].

Polymer films are very common materials that can be observed at almost any stage of the food supply chain to increase the shelf-life of food or protect the quality/freshness of the food. Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) are examples of polymer that can be utilized during the film production process for packaging. The thickness of the films can be found in the range of 10–60 μm with a high-water vapor transmission rate (WVTR)[76]. Thanks to technology improvements, several clays-based and other types of ethylene scavengers such as zeolite[121], HNT[99], and $KMnO_4$[122] can be embedded inside the polymeric film via different methods. Although, the main criteria of the applied methods are related to the incorporation of the ethylene scavenger agents inside the polymeric matrix whereas the coating method can be utilized for the preparation of the active food packaging[76]. The solvent casting method is utilized for the production of the chitosan-titanium dioxide nanocomposite film[123], and melt and blowing extrusion methods are performed for the fabrication of polyethylene-halloysite nanotubes nanocomposite film[99]. The drawback of such kind of application is the limitation of the incorporation amount of the ethylene scavenger inside the film because exceeding the limitation of the additive concentration that can negatively affect the polymeric material such as barrier, and mechanical properties[99,124]. In addition to that agglomeration problems directly have an impact on the barrier properties of the polymeric films while causing damage to the polymer matrix[76].

1.1.6. Flavor and Odor Scavenging Food Packaging Systems

Flavor and odor absorbers are one of the popular materials that are utilized to absorb undesired gases in the package. Volatile package ingredients, gases with chemical and microbial activity, respiration products, or off-flavors in raw foods are examples of such gases [125]. There are some compounds that induce some chemical reactions occurring in food. For example, after the protein decomposition, sulfurous and amine gases are released into the environment and the oxidation of lipids can lead to emitting aldehydes and ketones compounds[126].

The main mechanism to explain the formation of the flavors and the reduction in the food quality in the food packaging is the mass transfer phenomena in the packaged food while interaction between the food and package materials[126]. Migration, flavor scalping, selective permeability, and transferring the contents that are present in the heterogeneous region of food is the familiar phenomenon that are occurring in food packaging systems. Because of the direct interaction of the food and food packaging materials, the migration of the compounds that are present in the packaging toward food is a very commonly observed phenomenon. For this reason, it should be considered that the phenomena can be a risk to human health, in the case of the presence of the food packaging compounds after migration inside the edible food[126]. Monomers, dimers, oligomers, solvent residues, and other additives such as scavengers are examples of the migrants that can be migrated after the interaction. In addition, the migration phenomenon of chemicals can be considered in specific ways such as the total migration and specific migration of the chemicals[126].

Various parameters including the interaction area of food with the food package, interaction time, food ingredients, concentration or amount of chemicals (migrants), temperature, morphology, and polarity of the package[127,128] have an impact on the level of migration of compounds. Flavor scalping is one of the undesired phenomena that some of the desirable volatile food flavors, such as flavors of orange juice[126,129], can be absorbed by food packaging materials. Polyethylene (PE) is one of the most popular package materials for the food packaging industry whereas PE is known as scalper in the literature in the case of flavor scalping[129]. The specific knowledge about PE as a flavor scalping comes from its inherent polyolefinic nature because of that property, the nonpolar compounds as the aroma and volatile flavors can be retained, and consequently, food quality reduction can be observed. In order to solve such kind of problems, increasing the barrier properties of the packaging material can be a useful solution for the prevention of absorption of desired volatile compounds.

Flavor and odor absorbers which are encountered in the form of sachets, tapes, trays, and films, have also been utilized with the same mechanism to prolong the shelf life of food while removing undesired flavors or odors. The general usage type of the absorber that can be found in the application is the presence of the absorber inside the food package or porous materials. The absorption ability of porous-type materials, such as zeolite and HNT, arises from specific high surface areas. Films are also utilized with the incorporation of the absorbers and the absorbing efficiency can be examined with the arranging of the thickness of films because the higher thickness is to give the film a chance to absorb a high degree of flavors whereas the rate of adsorption and the diffusion of the flavors are not correlated with the thickness of the film in the case of high absorption efficiency. The degree of the absorption rate such as the adsorption rate of the surface and the diffusion property is related to flavors molecules' size, the chemical composition, the type of packaging materials, and physical properties of the packaging such as morphology, porosity, and crystallinity[126]. High barrier properties or polar-type packaging material can be performed to restrain the absorption of non-polar flavor. On the other hand, non-porous plastic materials can also absorb flavor molecules and no chemical reaction is observed during the absorption event. When absorption occurs, an increase in adsorption kinetics and diffusion kinetics begins to occur, which gradually leads to an increase in the absorption rate. When a chemical reaction between the packaging material and the flavor exists, it directly has an impact on the kinetics of the phenomena. The acidic agents can be utilized to absorb or neutralize some alkali chemicals such as ammonia and amines in the presence of the packaging material[126,130]. There are also many different commercial products that are used for the absorption of odor and flavor such as ABSCENTS, Aroma-Can®, ATCO® oxygen scavengers, CompelAroma®, ODORLESS D, and Sincera®[131]. One of the ethylene absorbers known as Retarder® can be utilized to remove the off odor. A combination of the clays and activated carbon or silicate with different concentrations can be performed as a flavor and odor absorber. Another commercial material Natrasorb with moisture, odor, and oxygen absorber can be utilized inside package[131]. There are also flavors and odors emitters for increasing the attention of the consumer to the food while increasing the aroma or flavor of food as in some packaging the encapsulated flavors or odors active agents can be found[131].

1.1.7. Barrier Packaging Materials

There is a certain difference between the polymeric and the metal or glass food packaging materials which is the permeability property of the polymeric food packaging materials. Polymeric packaging films are mostly permeable to small molecules such as gases, water, and organic vapor, flavor/odor, and other food additives to different degrees. Thanks to the barrier properties of the packaging material, the passage of the molecules can be transferred from high to low[132]. The regulation of such kinds of gas molecules inside the package is an important phenomenon because the excess levels of these can induce food spoilage and decrease the shelf life of the food. For these reasons, behaviors of gas molecules such as solution, diffusion, or permeation under different conditions are one of the main research areas for the food packaging industry. The barrier property of the films can be affected by the polymer processing conditions and also the polymer properties such as crystallinity ratio, the distribution of the crystalline and amorphous regions, inherent structure, chemical groups, polarity, crosslinking degree, and glass transition temperature[133,134]. Moreover, the sorption properties of the polymeric packaging materials can be directly affected by the nature of the food such as pH, fat content, and aroma compound and the gas barrier properties of the packaging material can be also affected by environmental circumstances such as fluctuations on temperature and relative humidity[133].

Film structure, thickness, surface areas, temperature, and pressure are directly related to the diffusion of any permeates through the film. The film permeability is basically the permeation of any gases, across the material[135,136]. The passage of any gas molecules across a film that has any deformation on the matrix is known as activated discussion which means that the permeate can be dissolved inside the polymeric matrix from the high to low concentration region then evaporate the other surface. The solubility differences between the gases are another specification for the diffusion-ability of the gases from the one side the other side[135]. The next phenomenon is permeability, which is the diffusion of the gases, that is directly related to the size, shape, and polarity of the permeant molecules and the matrix properties such as crystallinity and crosslinking degrees. The permeation of the gas molecules is inhibited in the crystalline region of the polymeric matrix because of the solubility problem of the gases in that region[137]. The amorphous regions in the semicrystalline polymers are utilized for the permeation of the gases. The decrease in the permeability is related to the reduction of the suitable volume inside the polymer (increasing the crystallinity of the matrix) and the large tortuous path between the crystallites. In other words, the permeability of the polymer matrix decreases when the crystalline phases in the matrix are increased. The permeation rates of the gas molecules across the polymer films are dependent on film area and thickness and can be explained by Henry and Fick's laws [138]. Further calculations and the explanation of diffusion are explained in the article by Siracusa[132].

However, reducing the gas permeability properties of packages is one of the important research topics for prolonging the shelf life of food. In the food packaging industry, because of the protection functions of the packaging material against the mechanical, chemical, and microbial damages which can be occurred by external forces, synthetic-based polymeric materials are commonly utilized[139]. In the industry, several kinds of polymeric materials almost more than 40%, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET), have been utilized in different types of package forms such as films, sheets, bottles[140–143]. As mentioned before that the permeability of small molecules such as gases and vapors that are to consist of oxygen, carbon dioxide, flavor, and organic vapors by food package materials that one of the drawbacks of the usage of polymer materials for the food packaging industry[141].

Different industrial areas such as construction, water, gas transportation, electronics, and aerospace, have tried to deal with the permeability performance problem of materials. In addition, the issue of the permeability in the food packaging materials, pharmaceuticals, and electronic devices[141,144,145] is an urgent problem that can be solved for the stable protection functions of the materials. In order to solve this problem, diffusion of the small molecules can be inhibited by using polymer nanocomposite films or multilayer films which are produced with different methods such as coating or blends with high barrier properties[141]. The drawbacks of using blended polymer and multilayer composited films compared with the nanocomposite polymeric material that is the higher cost, additives, and other additional polymers, and because of such additives the recycling problems[146]. Nanocomposite polymer films and materials are also preferred when comparing the cost and recycling problems, whereas there is a need the improvements for properties of these materials such as barrier properties that can be improved by using new methods and new strategies[139,146–154].

Designing the nanocomposite material with the incorporation of the additives such as montmorillonite, which is a lamellar additive and has a high aspect ratio, can increase the pathway of the small molecules [155]. The barrier properties of the polymeric material can be increased with the presence of additives which are utilized to decrease the permeability of the film. There are important considerations for the nanocomposite material that the dispersion and exfoliation behavior of nanoparticles inside the polymer matrix. The additives are not only for improving the barrier properties of the materials while increasing the diffusion pathway of the gas molecules, even if the nanoparticle, which is to have a high aspect ratio, well aligned inside the matrix during the manufacturing process, has a positive impact on the mechanical properties of the materials[99,156].

Additives such as nanoparticles can give a threshold for the gas molecules for their diffusion mechanism while increasing the tortuosity of the diffusion pathway. Consequently, the presence of the nanoparticle inside the polymer nanocomposite material tends to increase the gas barrier properties of the materials because of the expansion and tortuous diffusion pathway[154]. In addition, the presence of the nanoparticle (in the form of a sheet/plate inside) of the polymer matrix can form an interaction between the particles and matrix; therefore, the motion of the polymer chains is affected by this interaction. Because of the presence of nanoparticles and also the interaction, the available volume for the diffusion of small molecules and their solubility will be altered[157]. According to the studies, high aspect ratio nanoparticles are required to improve the gas barrier properties and their alignments on the matrix would be perpendicular to the pathway of the diffusion of the gas molecules. The interfacial interaction between the nanoparticle and the polymer matrix is another important key factor for the increase in the gas barrier properties of the polymer nanocomposite materials[152,158–162]. The clay-based material such as mica, talc, and montmorillonite are also utilized as reinforcement agents to produce better-performance nanocomposites[163,164]. For example, to the statement, different halloysite nanocomposite content is incorporated into the LDPE matrix to increase the mechanical, thermal, and barrier properties of the nanocomposite films[99]. High mechanical, gas barrier, and thermal properties of the nanocomposite can be obtained by the incorporation of the clay nanoparticle inside the polymer matrix[165]. In other studies, the exhibition of the high strength, stiffness, and high aspect ratio Na^+-montmorillonite (Na^+-MMT) clay with its unique lamellar structure is performed as an additive to increase the performance of the polymer nanocomposite[166].

1.2. Dissertation Overview:

In the thesis, development of food packaging materials, which are suitable for delaying food spoilage and waste, are the main objective of the studies. The two essential factors in the deterioration of fruits and vegetables are fruit-ripening ethylene gas and excess level of humidity. Here, two different types of hybrid nanocomposite materials were designed for preventing factors' negative effect on food, while integrating active agents that have an impact on the shelf life of fruits into a polymer matrix.

The first nanohybrid nanocomposite material was designed to include a sustained release system prepared by the impregnation of cinnamaldehyde essential oil into halloysite nanotubes, that was integrated into polypropylene matrix. The resulting flexible food packaging films slowly released cinnamaldehyde, which was shown to inhibit ethylene release from fruits, thus delay the ripening and increase the shelf-life of bananas while inhibition of the ethylene production by bananas. The second hybrid nanocomposite material was a novel, flexible, waterborne polyurethane nanocomposite foam incorporated with halloysite nanotubes that can keep fruits fresh via regulation of the package atmosphere by absorbing ethylene gas and excess humidity. Two different solutions to the problem of post-harvest food spoilage and food waste during storage and transportation have been provided by the design of hybrid nanocomposite materials.

CHAPTER 2. Extending the Shelf Life of Bananas with Cinnamaldehyde Essential Oil Impregnated Halloysite Nanotubes/Polypropylene Nanocomposite Films

2.1 Introduction

Food waste due to premature spoilage often arises from improper handling of food until it reaches the consumer and constitutes a major economic problem. According to research, approximately one-third of the food produced is wasted before consumption every year[167] . In different food categories such as eggs and egg products, dairy products, and fruits & vegetables, the food loss ratio is recorded at about 40 %[168–170]. Particularly, fruits and vegetables are among the main sources of nutrients for human life in terms of their high nutritional value[171], and their proper preservation from spoilage and waste reduction is important both to prevent economic problems and foodborne diseases[172–174]. Many different research studies have been carried out to prevent food loss due to spoilage. One of the innovative approaches developed by material scientists is active food packaging technology for safer, fresher, and higher-quality foods. The purpose of active food packaging (AP) is to solve the problem of food loss by incorporating additives, such as antimicrobial compounds, preservatives, oxygen absorbers, water vapor absorbers, and ethylene scavengers into the packaging materials to extend the shelf life of food. AP not only extends the shelf life of foods but also prevents foodborne diseases and preserves the nutritional quality of foods[2,175,176].

Fruits and vegetables are naturally perishable foods, whose spoilage is induced by different parameters related to inappropriate growth environment, pre-, and post-harvest conditions, storage conditions, packaging process/conditions, package atmosphere and supply chains[177]. Ethylene gas released from fruits and vegetables is another major factor causing their deterioration [178,179]. Ethylene is actually a natural plant hormone produced for growing and ripening during the pre- and post-harvest stages by climacteric foods. However, excessive exposure to ethylene gas within the packaging headspace causes overripening, which results in faster deterioration, thus decreasing the shelf life. In the literature, many different studies have been reported that aim for the inhibition of the ethylene production, its oxidation or its scavenging [180–183]. Incorporation of ethylene absorbers such as zeolite and halloysite nanotubes (HNT) or oxidizing agents such as potassium permanganate and titanium dioxide, into food packaging materials constitutes one of the most efficient methods to keep ethylene-sensitive fruits and vegetables fresh for longer [99,184–187]. Furthermore, treating ethylene-sensitive food products with mimics of ethylene gas such as 1-methyl-cyclopropene and Aloe vera gel has been demonstrated to inhibit the ethylene action by binding to the ethylene receptors and prevent ripening [180,188,189]. The effect of some ethylene production inhibition agents on the ripening of fruits and vegetables has also been studied. For example, the physio-biochemical response of mango fruit to 6-Benzylaminopurine is investigated during storage conditions [181]. There have also been studies on the inhibition effect of essential oils on the ethylene production of fruits and vegetables. While essential oils, non-toxic, eco-friendly natural plant extracts have been widely utilized in different food applications mainly as antimicrobial and antioxidant agents for maintaining food quality [190–194], there have also been studies on the inhibition effect of essential oils on the ethylene production of fruits and vegetables [194–199]. However, the demonstration of the incorporation of essential oils into food packaging materials as ethylene release inhibiting agents has been limited[198,200,201], mainly because the direct incorporation of volatile essential oils into packaging materials is not possible due to the high-temperature polymer processing conditions. Incorporation of an ethylene-release inhibiting agent into food packaging films via a sustained release system that allows its long-term, slow release from the packaging film can allow the release of the ethylene-release inhibiting agent into packaging headspace and delay the ripening of the packaged food product.

In this study, cinnamaldehyde (CA), the active component of the cinnamon essential oil, was investigated in terms of its ethylene production inhibition properties and encapsulated in natural halloysite nanotubes (HNT) to obtain a sustained CA release system. Resulting HNT-CA nanohybrids were embedded into polypropylene (PP) matrix and polymeric nanocomposite films that can slowly release an ethylene production inhibition agent were obtained. The effectiveness of the PP/HNT-CA nanocomposite films on the shelf life of banana, an ethylene-sensitive fruit, was investigated.

2.2 Experimental

2.2.1. Chemicals

Halloysite nanotubes mined from Balıkesir, Turkey were supplied by ESAN Eczacıbaşı. PP pellets (521 P (MFR = 3 g/10 min; density= 905 kg/m^3), particularly designed for biaxially oriented PP film extrusion with a very specific molecular structure providing the ultimate properties required for the stretching process, were obtained from Sabic Polyolefins, Germany. CA was purchased from Tokyo Chemical Industry Co., LTD. Extra pure methanol (99.8%) was purchased from Tekkim Ltd. (Bursa/Turkey). All chemicals were used without any further purification.

2.2.2. Preparation and Characterization of HNT-CA nanohybrids

Prior to the impregnation, HNTs were dried in a vacuum oven at 100 °C for 24 h. HNTs were impregnated with CA via solvent-assisted impregnation methodology [202]. 0.3 g of CA dissolved in 10 ml of methanol was mixed with 0.7 g of HNTs. The HNT-CA mixture was sonicated in a bath sonicator for 20 min, placed in a water bath at 70 °C, and vacuum was applied to the mixture to remove the methanol by decreasing the pressure to 0.3 kPa. The resulting HNT-CA powder was dried overnight at room temperature and stored in a sealed container at 4 °C.

The Shimadzu Corp. DTG-60H (TGA-DTA) was used to determine the amount of CA impregnated in HNTs. The sample was heated to 1000 °C at 10 °C/min under nitrogen flow. The impregnation percentage was calculated by the difference of the total weight loss of raw HNTs and HNT-CA nanohybrids in the range of 25 to 1000 °C [203].

Differential Scanning Calorimetry (DSC) (Thermal Analysis MDSC TAQ2000) was performed to evaluate the CA content of HNT-CA nanohybrids via calculation of evaporation enthalpy of CA. The temperature was set up between 50 and 320 °C at a rate of 10 °C/min under an inert atmosphere. The CA evaporation enthalpy was calculated through the tangent method [204]. Eq. 1 was used to determine the CA amount in the nanohybrids.

$$X_{\mathrm{CA}}: (\mathit{\Delta}\mathrm{H}_{\mathrm{HNT\text{-}CA}} / \mathit{\Delta}\mathrm{H}_{\mathrm{pure\ CA}}) \times 100 \qquad \text{Eq.1}$$

where the X_{CA} denotes the percentage of CA, $\mathit{\Delta}\mathrm{H}_{\mathrm{HNT\text{-}CA}}$ denotes the evaporation enthalpy of the HNT-CA nanohybrid, and $\mathit{\Delta}\mathrm{H}_{\mathrm{CA}}$ denotes the enthalpy of evaporation pure CA. The calculations were completed using TA Universal Analysis software.

2.2.3. Release of CA from HNT-CA nanohybrids

DSC analysis, which was used to detect the evaporation enthalpy of CA, was applied to investigate the sustained release of CA from the HNT-CA nanohybrids. HNT-CA nanohybrids were placed in an unsealed dish and kept at room temperature and 53 % humidity. At each time point, three samples were taken from the different parts of the dish before the analysis and DSC was performed. The results were constructed using the average of three measurements. The release profile of CA from the HNTs was determined by using Eq. 2.

$$\%R_{CA} = 100 - (\mathit{\Delta}\mathrm{H}_t / \mathit{\Delta}\mathrm{H}_0) \times 100 \qquad \text{Eq. 2}$$

where $\%R_{CA}$ denotes percentage of released CA, ΔH_0 denotes the initial evaporation enthalpy of CA and ΔH_t denotes the evaporation enthalpy of CA at the time point [115].

2.2.4. Ethylene production inhibition properties of HNT-CA nanohybrids

The ethylene inhibition property of HNT-CA nanohybrids was investigated using F-950 Three Gas Analyzer (Felix Instruments) on continuous sampling mode. The analyzer was connected to an airtight chamber into which two apples were placed and the increase in the ethylene concentration in the chamber was monitored for 24 h. Then, the same process was repeated with 0.5 g neat HNT powder and 0.5 g HNT-CA nanohybrids in the sealed chamber, respectively, using the same apples. Changes in ethylene concentrations (%) were calculated relative to the ethylene concentrations in the chamber containing apples only. For all experiments, with and without the HNT-CA or HNTs, the process was repeated three times, and averages of three ethylene release profiles were reported for each set.

The ethylene production inhibition properties were further characterized by monitoring the ripening process of ethylene-treated bananas in the presence and absence of the HNT-CA nanohybrids. *Grand Naine* bananas were harvested from the greenhouses in Antalya, Turkey and transferred to the laboratory within 24 h. Bananas were exposed to 100 ppm ethylene gas in an airtight container for 24 h to mimic the commercial ethylene treatment applied to bananas in ripening rooms. Five bananas of the same size, weight, and color were placed in a sealed PP box (15 × 20 cm). Two sets of banana-containing boxes were prepared where 0.5 g HNT-CA nanohybrid was placed into one of the boxes, and the other box did not contain HNT-CA nanohybrids. The quality of the bananas was investigated for 7 d.

2.2.5. Preparation and characterization of PP/ HNT-CA nanocomposite films

PP/HNT-CA masterbatch was prepared using a twin-screw extruder with a 12 mm screw diameter and L/D ratio of 40 (Zamac, Mercator). The mixture of HNT-CA nanohybrids and PP granules containing 15 wt. % HNT-CA was poured inside the extruder through the feeding zone. The temperature and rpm of the screw were set between 190-240 °C and 650 rpm, respectively. A water bath was used to cool the produced nanocomposite and a cutter was used to pelletize.

The blends of PP/HNT-CA masterbatch and PP pellets were extruded using a 110kg/h capacity corotating-screw extruder with 40 mm screw diameter and L/D ratio of 32/1 at 250 ºC and 75 rpm screw speed into cast films of 1 mm thickness and 200 mm width. Nanocomposite bioriented PP/HNT-CA films were manufactured on a pilot bioriented PP manufacturing line on which the cast films are stretched in both machine direction (MD) and transverse direction (TD). The stretching ratio in MD and TD were set to 4:1 and 10:1, respectively. The processing

temperatures of MD and TD stretching are presented in Table 1. Nanocomposite bioriented films with 20 ± 0.6 µm thickness and 1200 mm width were obtained.

Table 1. Processing conditions of the bioriented PP/HNT-CA films.

MD	**Roll 2**	**Roll 3**	**Roll 4**	**Roll 5**	**Roll 6**	**Roll 7**	**Roll 9**	**Roll 10**	**Annealing**
	104 °C	104 °C	105 °C	103 °C	103 °C	85 °C	100 °C	100 °C	90 °C
TD	**Zone 1**	**Zone 2**	**Zone 3**	**Zone 4**	**Zone 6**	**Zone 7**			
	180 °C	180 °C	160 °C	160 °C	170 °C	150 °C			

The Scanning Electron Microscopy (SEM) analysis of the PP, PP/HNT-CA_0.25%, and PP/HNT-CA_1% films was performed using Zeiss LEO Supra 35VP. The films were mounted onto cross-view SEM stubs using double-sided carbon adhesive tape and were coated with Au-Pd. A secondary electron detector was used to obtain high resolution at 3 kV.

Mechanical properties of PP/HNT-CA nanocomposite films were tested using a Zwick Roell Z100 universal testing machine (UTM), which has a load cell of 200 N, 22 mm grip distance, and a crosshead speed of 12.5 mm/min according to ASTM D1708-10. Each specimen was tested at least five times.

2.2.6. The activity of PP/HNT-CA nanocomposite films on the shelf life of bananas

Grand Naine bananas were harvested from the greenhouses in Antalya, Turkey and transferred to the laboratory within 24 h. Bananas were exposed to 100 ppm ethylene gas in an airtight container for 24 h to mimic the commercial ethylene treatment applied to bananas in ripening rooms. PP, PP/HNT-CA_0.25%, PP/HNT-CA_1% bags with a size of 35 × 35 cm were prepared using a thermal bag sealer. Bags were perforated using a paper punch resulting in 24 holes of 0.6 cm diameter in each bag. Five bananas of the same size, color, and weight, from the same comb, were inserted into each bag and the bag was sealed with a rubber band. Three sets were prepared for each control PP and nanocomposite films along with 3 sets of unpackaged bananas as no film-controls. All sets were stored at room temperature for 7 d. Bananas were photographed every day to monitor any change in their appearance and color during the storage process.

Weight loss, which is one of the parameters used to examine the quality of bananas, was evaluated. Bananas in all sets were weighed on the first day before packaging and on the seventh day, after being taken out of the bags. Average percent weight loss of bananas in each bag was reported.

The firmness of bananas was examined using A TA.XTplusC Texture Analyzer (Stable Micro Systems) equipped with a three-point bend rig probe (A/3PB). The analyzer was calibrated with 2 kg load cell and the measurement was performed in compression mode at a pre-test speed of 2 mm/s, test speed of 1 mm/s, post-test speed of 2 mm/s, and a trigger force of 5 N. The pre- probe distance was arranged at 30 mm, and the post-return probe distance was arranged at 30 mm. The peeled bananas were placed on two supportive lengths and the position on the supportive length of the bananas was adjusted to be exactly perpendicular to the probe motion plane. The firmness of bananas in each set was reported as the average firmness of 5 bananas.

Color measurements of the banana peel were performed using the manual colorimeter PCE-CSM 1 (PCE Instruments UK Ltd). L*, a*, and h^o color values were examined to interpret the quality of the bananas. Due to the inhomogeneous color distribution of the peels, the surface of the banana was divided into three regions as upper, middle, and lower, and 15 color scans were made from each. Color measurements were made on the first day of the experiment and on the seventh day. An average of 45 data points taken from each banana was calculated and for each set an average color score of 5 bananas in each bag was reported.

2.2.7. Statistical analysis

The one-way ANOVA test was used on the experimental results, which are included in the examination of at least three samples, that identified the significant statistical differences between the results. The mean results differences were examined by $p<0.05$ using Origin Pro software v.8.5. (OriginLab Corporation, USA).

2.3 Results and Discussion

To obtain an ethylene production inhibition agent release system, HNTs were impregnated with CA via solvent-assisted impregnation with vacuum application (Figure 1a). The impregnation of HNTs with the CA was proved using TGA via the difference of the total weight loss of neat HNTs and HNT-CA nanohybrids in the temperature range of 20 to 1000 ºC (Figure 1b). HNT-CA nanohybrids were demonstrated to contain 25.3 wt. % CA. The slight deviation from the theoretical CA content of 30 wt. % was potentially due to the volatility of the CA causing it to be lost on vacuum application. Vacuum-assisted impregnation allows the internal cavity of HNTs to be filled beyond their capacity, causing not only filling of the lumen but also all pores due to capillary effect[205,206]. Thus, cinnamaldehyde impregnated HNTs were not expected to absorb ethylene gas as opposed to neat HNTs, which are well known to present ethylene adsorption properties.

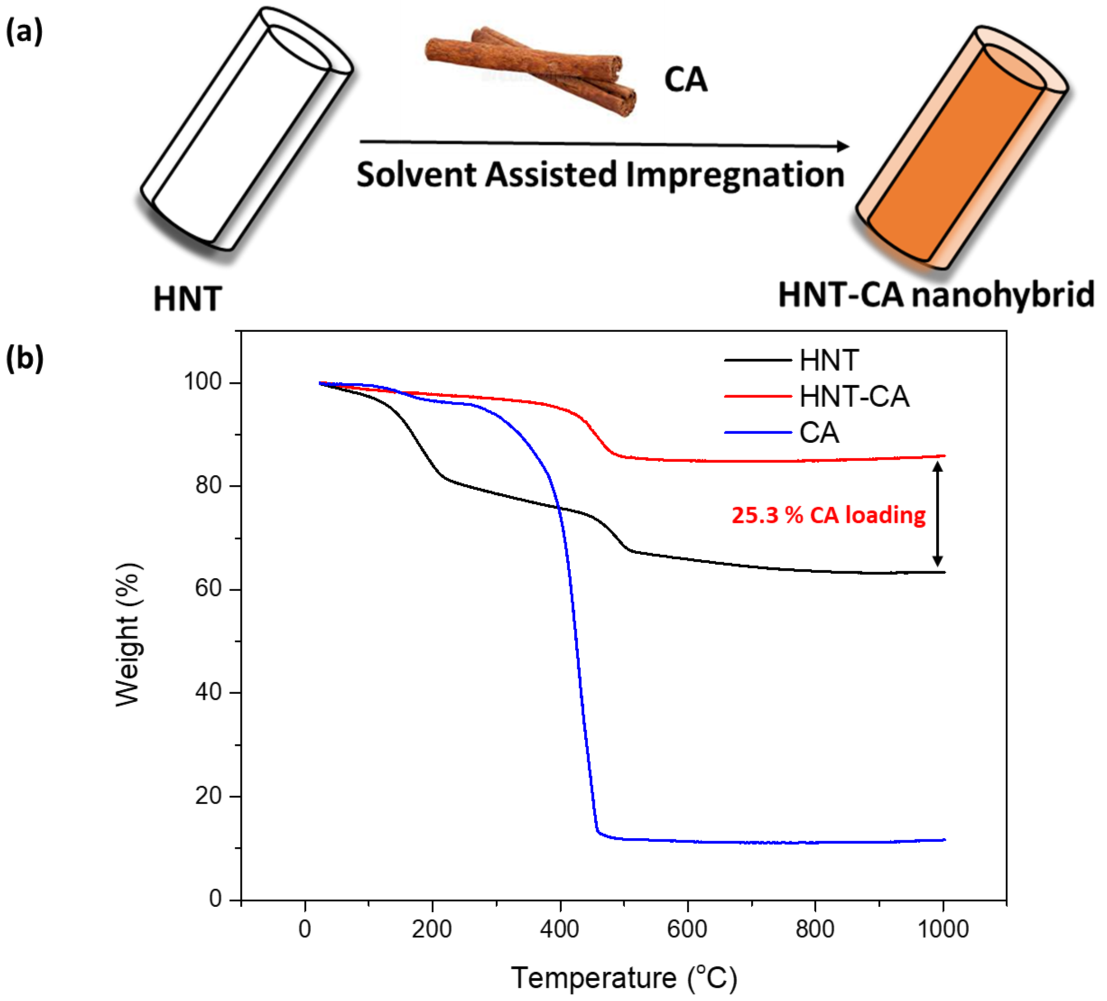

Figure 1. Schematic illustration of impregnation of HNTs with CA (a), TGA of HNT and HNT-CA nanohybrids (b).

HNTs have already been demonstrated to be used as ethylene scavenging additives inside nanocomposite films that can increase the shelf-life of bananas [99,207]. Here, however, HNTs were used as carriers for an ethylene production inhibition agent, therefore, the release of CA from HNTs must be demonstrated to confirm that the shelf-life improvement affect is caused by the CA essential oil and not the HNTs themselves. The release profile of the CA was investigated using DSC. Figure 2a demonstrates the phase transitions of neat HNTs, CA, and the HNT-CA nanohybrids that were used to monitor the release of CA from the HNT-CA nanohybrids. The evaporation point of pure CA at 197.5 ºC was shifted to higher temperatures for the HNT-CA nanohybrids and were recorded at 216.9 °C proving that the CA was actually impregnated in HNTs. Figure 2b demonstrates the release profile of the CA from the HNT-CA nanohybrids for 180 d. The results showed that, at the end of the first 10 d, 62 % of all CA was released from the HNTs, and 70 % of the total CA was released at the end of 40 d. It has been observed that 10 % of the CA has remained in the HNT for a long time and was slowly released. Because of their unique tubular structure, HNTs inhibited the release of the encapsulated CA resulting in a sustained release system that can slowly release the CA over a long time. This result demonstrated that the HNT-CA nanohybrids will have a long shelf life and will be active for at least 180 d.

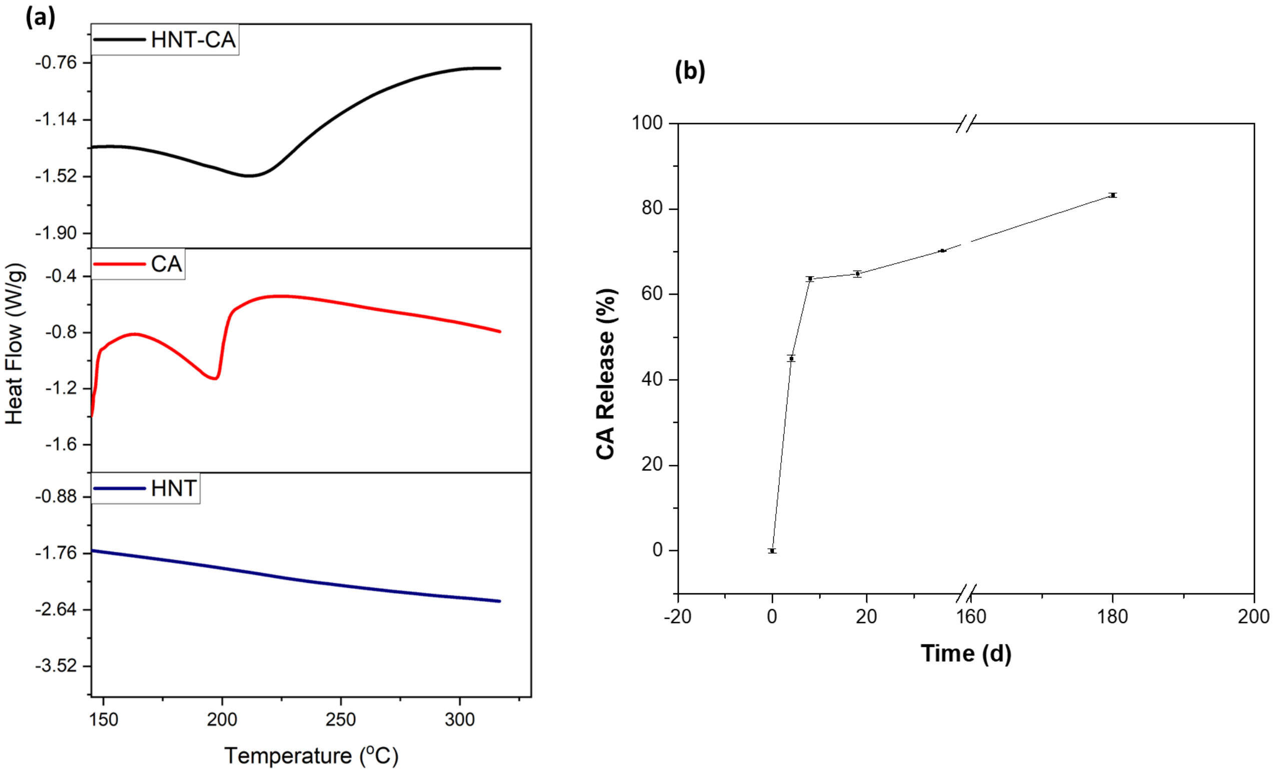

Figure 2. DSC diagram of raw HNTs, CA, and HNT-CA nanohybrids (a), release profile of CA from HNT-CA nanohybrids (b).

Ethylene production inhibition properties of the HNT-CA nanohybrids were investigated with an experimental setup, where apples were used as ethylene producers in an airtight chamber connected to an ethylene analyzer. Figure 3 demonstrated that when HNT-CA nanohybrids were placed in the chamber, the ethylene production from the same apples were reduced by 20 %. Under the same conditions the presence of neat HNTs did not decrease the ethylene concentration. Although neat HNTs are well known to present ethylene absorption properties, they did not decrease the ethylene concentration within this experimental setup, potentially due to the presence of apples acting as continuous ethylene producers, and the ethylene absorption rate being slower than the ethylene production rate. On the other hand, under the same experimental conditions, the presence of HNT-CA nanohybrids significantly reduced the ethylene concentration relative to the environment without HNTs or HNT-CA nanohybrids. As CA impregnated HNTs are not expected to absorb ethylene gas, the lower ethylene concentration in the presence of HNT-CA nanohybrids can only be explained with the ethylene production inhibition effect of the released CA. It can be clearly stated that the CA released from the HNTs slowed down the ethylene production in apples, and that HNT-CA nanohybrids can be used to provide an inhibition action of the ethylene production of fruits and vegetables.

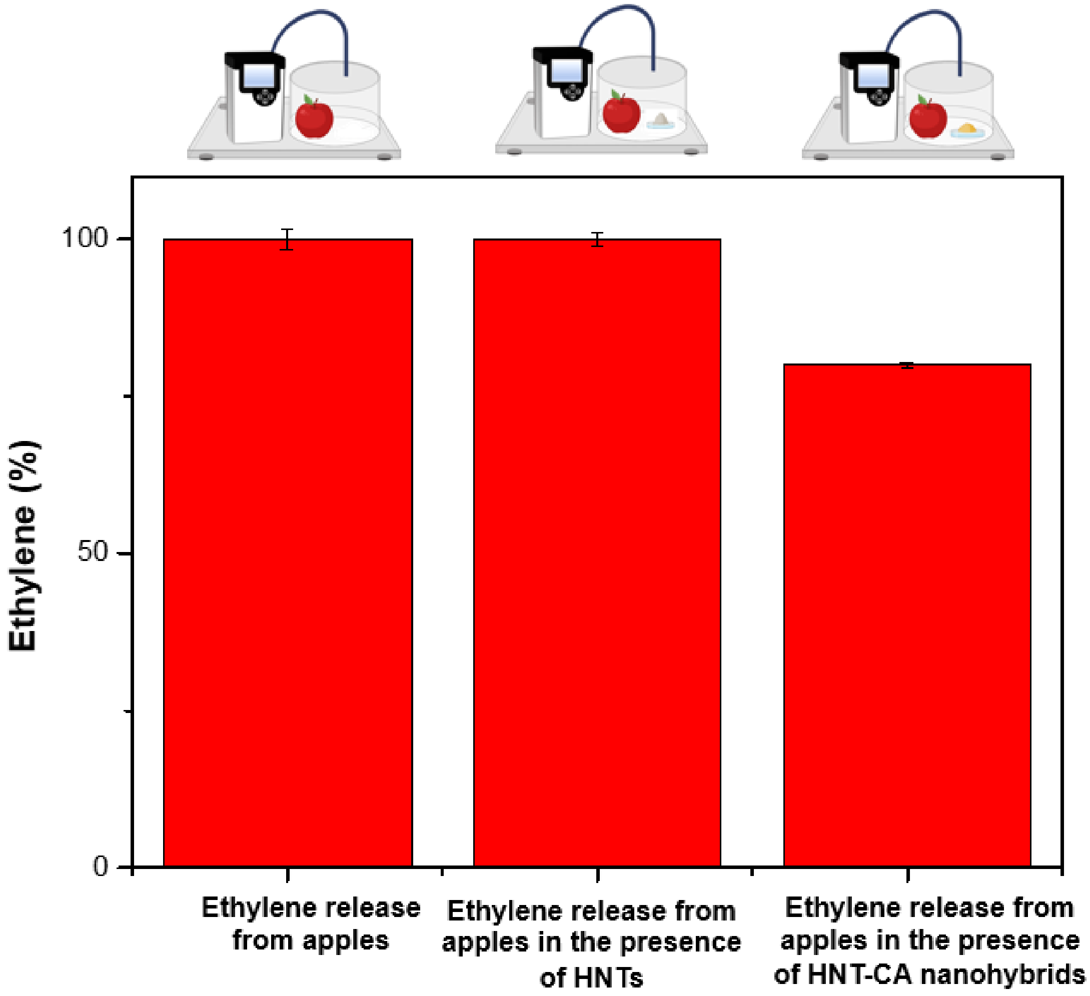

Figure 3. Ethylene production inhibition performance of HNT-CA nanohybrids**.**

Inhibition of the production of the ethylene gas by the HNT-CA nanohybrids was further confirmed on bananas by monitoring the shelf life of ethylene-treated bananas. Two sets of green bananas were placed into airtight boxes, one containing HNT-CA nanohybrids and the other one empty and stored at room temperature for 7 d. Each day, bananas were taken out of the boxes and photographed to monitor their ripening in the absence and presence of the HNT-CA nanohybrids

(Figure 4). The bananas, which were placed in the box containing HNT-CA nanohybrids significantly presented a slower ripening period, as they remained greener, free of brown stops then the bananas, which were placed in the empty box, after 7 d. This result indicated that the CA was released from the HNT-CA nanohybrids and inhibited the ethylene production level of bananas, so, HNT-CA nanohybrids can be used as ethylene production inhibition agents to improve the quality of bananas during storage.

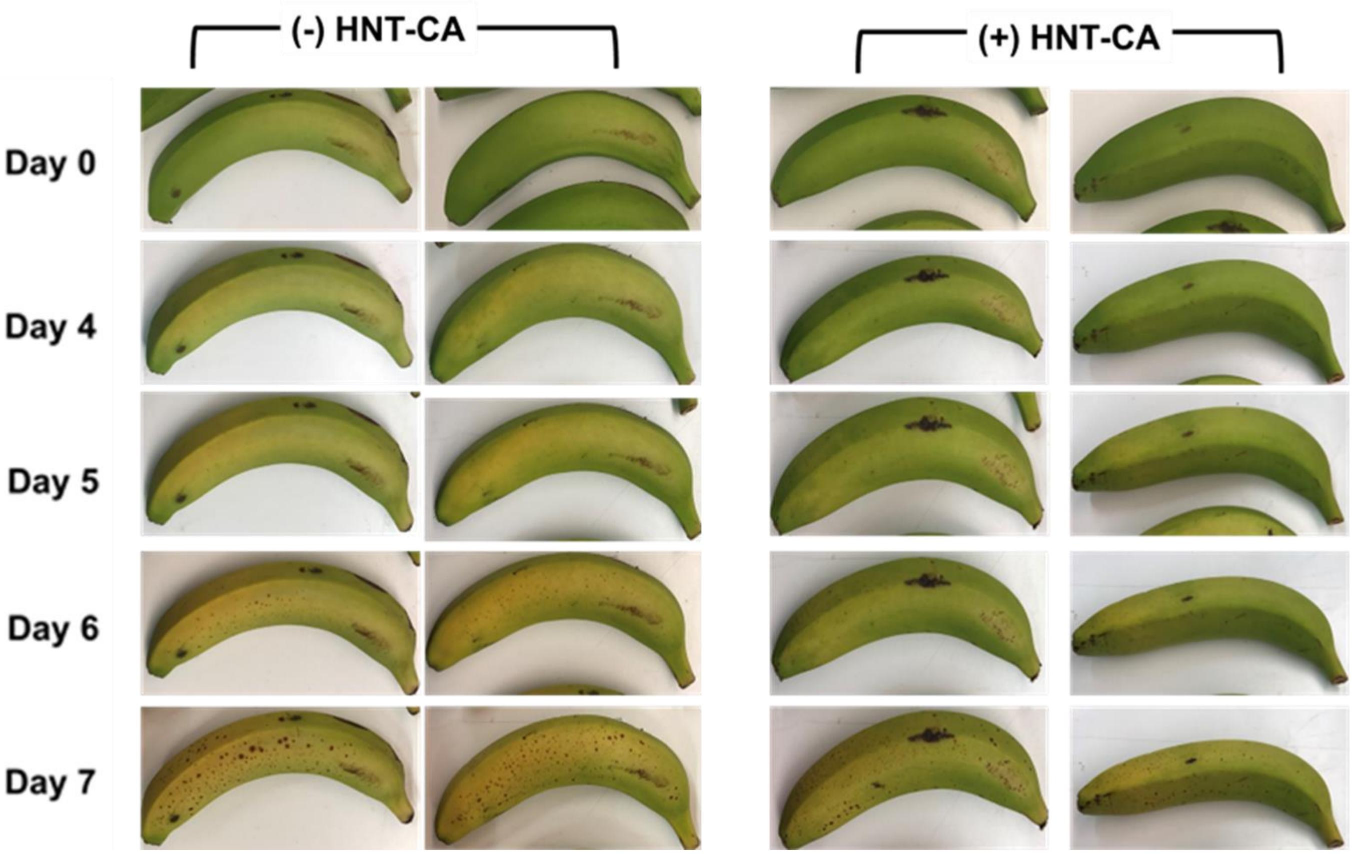

Figure 4. Ripening of bananas in the absence and presence of HNT-CA nanohybrids.

In order to incorporate HNT-CA ethylene production inhibition agents into active food packaging films that can improve the shelf life of bananas and prevent banana waste and spoilage, HNT-CA nanohybrids were embedded into PP matrix and PP/HNT-CA nanocomposite films were produced. A PP/HNT-CA masterbatch containing 15 wt. % HNT-CA was prepared using a twin-screw extruder, which was then used to prepare bioriented PP nanocomposite films in a pilot scale film production line. 30 µm thick PP-MWNT_0.25% and PP-MWNT_1% nanocomposite films with 9.4 % and 31 % haze transmittance, respectively, which appeared to be brownish in color were obtained (Figure 5a). SEM was used to examine the morphology and agglomeration behavior of HNT-CA nanohybrids inside the polymer matrix (Figure 5b). Damage occurred in the matrix due to the inhomogeneous distribution and agglomerations of HNT-CA nanohybrids in PP/HNT-CA films containing 1 wt. % HNT-CA and therefore defects were observed in the film. On the other hand, it was observed that the distribution of HNT-CA nanohybrids was homogeneous in PP/HNT-CA films containing 0.25 wt. % HNT-CA, and almost no agglomerations were seen. Agglomeration of HNTs in the polymer matrix at higher HNT concentrations was demonstrated before[99]. In addition, there have been some studies to understand the agglomeration behavior that creates damage on the matrix and its effect on mechanical properties. In general, HNTs have been used as a reinforcing agent because of its unique tubular structure[208] and have been demonstrated to have a positive impact on the mechanical properties of the materials when used at optimized ratios. Similarly, in this study, the incorporation of the CA impregnated HNTs into PP films was demonstrated to slightly improve the mechanical properties (Figure 5c). Young's Modulus, tensile strength and elongation at break values have increased as the HNT-CA concentration in the PP/HNT-CA films increased and mechanically robust nanocomposite films, which can be used as food packaging materials, were obtained.

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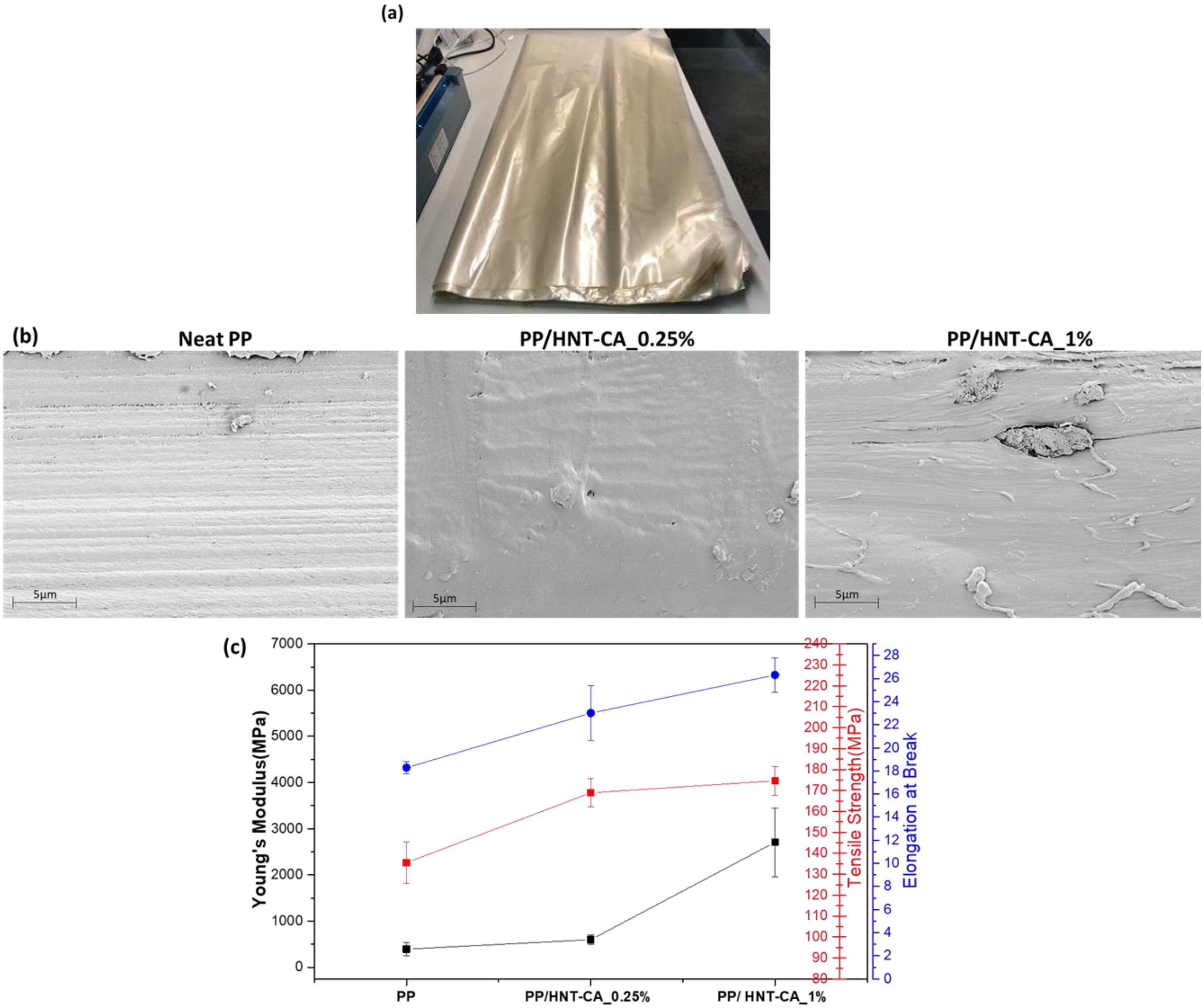

Figure 5. Photograph of the PP/HNT-CA_1% nanocomposite film (a), cross-section SEM images of neat PP, PP/HNT-CA_0.25 %, and PP/HNT-CA_1 % nanocomposite films (b), mechanical properties of the nanocomposite films (c).

The effect of the nanocomposite films on the shelf life of bananas was evaluated. The green life of bananas is defined as the time it takes the harvested green bananas begin to ripen.[209] The shelf life of bananas, on the other hand, defines the time from the initiation of the ripening of in ripening rooms with ethylene treatment[210], until the bananas are completely ripe and lose their marketability. Since the study focused on increasing the shelf life of bananas, bananas packaged with the films to be tested were monitored right after they were treated with ethylene. Bananas packaged in perforated bags prepared from the nanocomposite films were stored at room temperature for 7 d, and on the 7th day, weight loss, firmness, and color values of bananas were determined in comparison to the initial quality parameters of bananas.

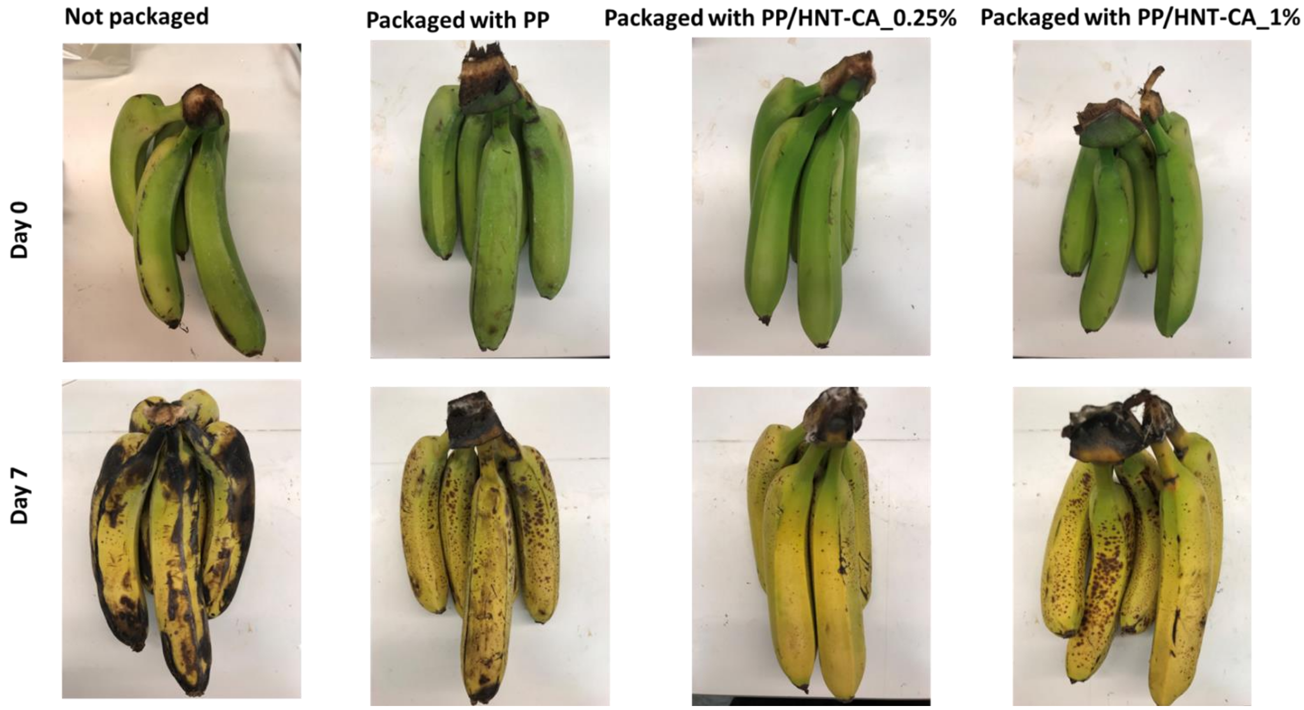

Figure 6. Photographs of not-packaged bananas, bananas packaged with PP, PP/HNT-CA_0.25%, and PP/HNT-CA_1% at day 0 and day 7.

Figure 6 represents the appearance of the bananas packaged with the control and nanocomposite films along with the unpackaged bananas at 7 d. The quality of bananas stored without packaging and bananas packaged with control neat PP film appeared to be low due to a high number of brown spots and dark regions. On the other hand, bananas that were packaged with the PP/HNT-CA_1% and PP/HNT-CA_0.25% nanocomposite films demonstrated a significantly fresher appearance at 7 d. Especially, bananas packaged with PP/HNT-CA_0.25% nanocomposite films presented a greener tinted color relative to control bananas and were free of brown spots. PP/HNT-CA_0.25% nanocomposite films showed a better performance for increasing the quality of bananas than the PP/HNT-CA_1% nanocomposite films, as well. Potentially, at higher nanohybrid content in the nanocomposite film, agglomeration occurred, and this has caused a lower release rate of CA from the matrix. Moreover, higher nanoparticle content might have damaged the matrix and the defects in the films might have decreased the barrier function of the packaging.

The positive effect of the PP/HNT-CA_1% and PP/HNT-CA_0.25% nanocomposite films on banana quality have also been proven by the weight loss and flesh firmness of bananas (Figure 7). While bananas stored without packaging and bananas packaged with the neat PP film presented a weight loss of 40 % and 14 %, respectively, at 7 d, the bananas lost less than 8 % in weight, when they were stored in the PP/HNT-CA bags (Figure 7a). Apparently, the respiration rate of the bananas decreased in the presence of the CA released from the PP/HNT_CA films, further confirming that the ripening was slowed down. The firmness test results performed on day 7 are shown in figure 7b. It was concluded that the bananas stored in PP/HNT-CA_0.25% and PP/HNT-CA_1% bags were significantly firmer than bananas stored in neat PP bags. When the ANOVA test was performed, it was stated that there was no difference between the firmness values of the bananas in the PP/HNT-CA_0.25% and PP/HNT-CA_1% packages. In conclusion, it can be stated that the nanocomposite films containing HNT-CA nanohybrid affected the ripening process of bananas, where the CA released from the films has inhibited the ethylene release from the bananas, allowing them to remain firmer.

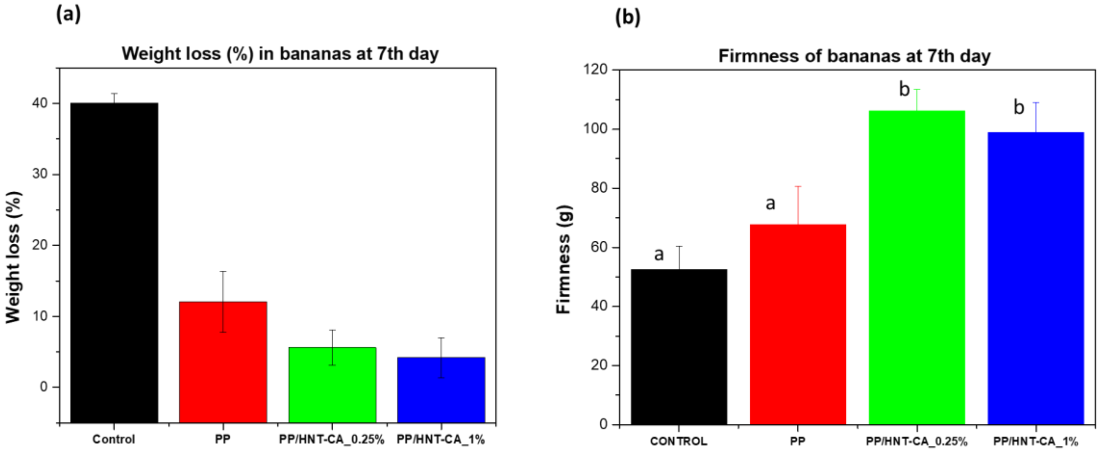

Figure 7. Weight loss (%) of bananas at 7 days (a), firmness of bananas at 7 days (b).

Change of peel color of bananas from green to yellow as a result of chlorophyll degradation is an important indicator of ripening. Bananas stored in the HNT-CA nanohybrid-containing nanocomposite films were investigated in terms of their color values to evaluate their ripening process in relation to control bananas. The color measurements of the bananas which were taken out of the bags on the 7th day were made using a colorimeter (Figure 8). According to the literature, the L*, b* and h° values decrease for bananas during the ripening period[211,212]. Bananas that were stored inside the PP/HNT-CA_1% and PP/HNT-CA_0.25% bags, demonstrated significantly higher L*, b* and h° values compared to the unpackaged bananas and bananas packaged with the neat PP films, indicating a slower ripening. The CA released from the nanocomposite films has inhibited the ethylene release from bananas, thus slowed down the ripening, which has increased the shelf life of bananas.

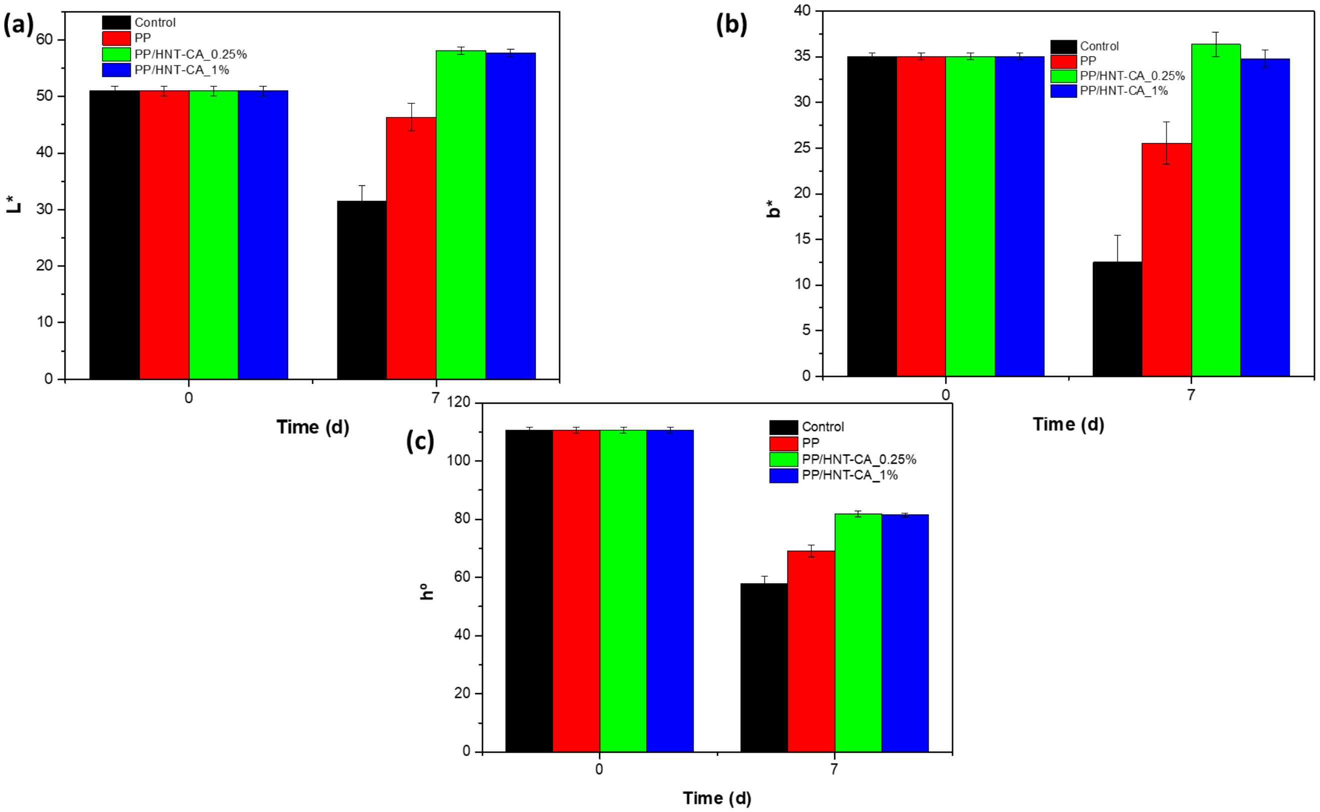

Figure 8. *Effect of the nanocomposite films on the L* (a), b* (b) and h° (c) values of bananas*

2.4 Conclusions

The potential of the CA essential oil as an ethylene production inhibiting agent and its incorporation into food packaging films to increase the shelf life of bananas has been studied. By using HNTs as nano-containers, a CA essential oil sustained release system was designed, and were embedded in the PP matrix at different ratios to investigate the effectiveness of the resulting films on increasing the self-life of bananas. PP-HNT-CA nanocomposite films were demonstrated to decrease the rate of the ripening of bananas, as demonstrated by the firmness, weight loss and color changes. While bananas, which were packaged with PP films and those that were stored without packaging, presented more dark regions and brown spots, higher weight loss and more softening at 7 days, bananas packaged with the nanocomposite films presented quality parameters indicating higher freshness. The nanocomposite films incorporated with HNT-CA nanohybrids have strong potential as ripening-retarding food packaging films, which can help prevent the economic losses due to spoilage of bananas.

CHAPTER 3. A Novel Flexible Waterborne Polyurethane Nanocomposite Foam incorporated with Halloysite Nanotubes as Fresh-keeping Pads for Fruits and Vegetables

3.1 Introduction

The deterioration of fresh fruits before reaching the consumer is one of the most important issues which needs an effective solution in the food supply chain. The most important reasons for the spoilage of fruits are high levels of ethylene gas and excess moisture. Ethylene gas, a natural plant hormone, is released by climacteric fruits during the growing and ripening stages. But these climacteric foods may encounter high ethylene exposure during the post-harvesting stages such as storage and transportation, which might lead to over-ripening and deterioration. To increase the shelf-life of fruits by decreasing the ethylene concentration, substances that can inhibit or delay ethylene biosynthesis and release have been reported [180–183]. With recent advances, food packaging materials containing active agents that can prevent food spoilage by decreasing the ethylene concentration in the packaging headspace have been reported. Ethylene-absorbing particles such as zeolite and clay nanoparticles[99,102,185] and ethylene oxidizing agents such as potassium permanganate, palladium, and titanium dioxide [185–187] have been successfully integrated into food packaging films. While these solutions have been shown to be effective in increasing the shelf life of fruits, the amount of the ethylene absorbing or ethylene oxidizing agents incorporated into these films is limited, due to stringent film properties such as transparency and mechanical strength, that need to be retained, and thus the direct incorporation of large amounts of active agents into packaging films is not usually practical. While ethylene oxidizing agents have been extensively studied and used as packaging inserts, ethylene absorbing food packaging materials with high surface area and absorption capacity, that can be used as packaging inserts in any type of food packaging have not been previously reported.

While moisture is needed in a packaging environment to prevent water loss and related senescence in fresh produce, excess levels of moisture in the packaging headspace, that exists naturally due to the respiration and transpiration of the fresh produce is also an important problem for the deterioration in the supply chain[213,214]. High humidity conditions during storage and transportation stages lead to increase in bacterial growth, accelerating the aging of fruits with a loss of the quality. Moisture regulation is crucial for the food packaging systems not only to inhibit microbial growth, but also for the improvement of the shelf-life of products[215]. Moisture absorbers can be used as a regulator of the relative humidity in the packaging headspace to optimize the storage conditions required to preserve the freshness of the fresh produce. A wide range of moisture absorbers has been studied in different types such as sachets[216,217], films[218,219], and trays[215,220–222]. Foam-type materials made of synthetic or natural polymers, or their composites have been utilized in the form of meat exudate absorbers that can prevent meat spoilage[223], thermal insulators that can control temperature variations[224], or antimicrobial agent releasing materials to control microbial growth on food samples[225]. While foam-type materials have strong potential as light-weight moisture scavenging materials due to their porous structures, they have not been investigated as moisture absorbing active food packaging materials that can be inserted into already used packaging systems.

Halloysite Nanotubes (HNT) are natural, non-toxic clay-based nanoparticles that have a hollow tubular nanostructure, which have been highly utilized in nanotechnology applications as reinforcing agents for polymeric materials[113,114], nanocarriers[108,109] or controlled release systems[226]. HNTs have also been demonstrated to present high ethylene absorption properties and incorporated into food packaging films to increase the shelf life of ethylene-sensitive food products[99,101,207,227]. In this study, HNTs were incorporated into a three-dimensional carrier matrix in the form of a foam that allows gas passage, which can easily, practically and safely included as ethylene absorbent inserts in all kinds of food packages. As the carrier matrix for HNTs, a waterborne polyurethane (WPU) product with ionic and hydrophilic character was synthesized, which was expected to present moisture absorption properties, in addition to serving as a porous scaffold for the HNTs obtained by a foaming process from the aqueous dispersion. While there are a limited number of studies reporting WPU foams in the literature[228,229], utilization of WPU foams as food packaging materials has not been demonstrated previously. The incorporation of HNTs into WPU foams was studied for their utilization as easy-to-make, safe, industrially applicable fresh keeping packaging materials that improve the shelf life of fresh fruits when inserted into packaging environments during transportation and storage.

3.2 Experimental

3.2.1. Chemicals

Polyester polyol of ethylene glycol/adipic acid/butane diol (Mn = 2000 g/mol, Desmophen 1652) and hexamethylene diisocyanate (HDI) were acquired from Covestro AG. Ethylene diamine (EDA), and acetone (99.5%) were purchased from Sigma-Aldrich. Sodium 2-[(2-aminoethyl)amino]ethanesulphonate (Vestamin A95, AEAS) was provided by Evonik. Borchi Gel

A LA as a thickener for waterborne dispersions was provided by Borchers. Betain 45 and ammonium stearate (AS) were provided by Denge Kimya Int. Trade Co. Ltd. HNTs were provided by ESAN, Eczacıbaşı.

3.2.2 Synthesis of WPU Dispersion

The acetone method was used to prepare the waterborne polyurethane (WPU) dispersion[230]. The diisocyanate monomer (HDI, 14.7 g) and polyol (Desmophen 1652, 95.5g) were charged into a four-necked, 1-L glass round-bottomed-flask equipped with a heating mantle, overhead stirrer, condenser, and a thermocouple, and allowed to polymerize at 80 °C until the theoretical NCO value was reached to obtain an isocyanate terminated prepolymer. Isocyanate content of the reaction mixture was determined by the standard di-butyl amine back-titration method (ASTM D2572-97). The reaction mixture was then cooled to 50 °C and the prepolymer was dissolved in 200 g acetone to reach 40 wt% solids content. The chain extension step was carried out by adding 0.8 g EDA and 7.3 g AEAS (50% in water) mixture dropwise into the prepolymer solution at 50°C. The resulting polyurethane polymer was then dispersed in water by the slow addition of 150 g distilled water into the flask while cooling the mixture to 40°C. Finally, acetone was completely removed from the reaction mixture by vacuum distillation at 45°C, 50 mbar. The waterborne polyurethane dispersion product with a solid content of approximately 35 wt% and pH value of 7.0 – 7.2 was collected by filtering through a 50-micron filtration media.

3.2.3. Preparation of HNT-WPU foams

25 g of the WPU dispersion with 35 wt % solid content was mixed with 4.25 g of 20 % v/v aqueous AS solution, 0.25 g Betain 45 and 0.5 g Borchi Gel A LA and agitated for 10 min until a foamy liquid mixture was obtained using a kitchen blender (700 W). 5 g HNTs, which were previously dried at 100 °C for 24 h in a vacuum oven, was mixed into the foamed mixture using an overhead mechanical stirrer for 5 min. The final foamy liquid mixture was cast into 7 × 15 × 3 cm Teflon molds and dried overnight at 70 °C to obtain WPU-HNT foams. The control WPU foam was prepared using the same procedure without the addition of HNTs.

3.2.4. Characterization of nanocomposite foams

The Scanning Electron Microscope (SEM) images of nanocomposite foams were obtained using Zeiss LEO Supra 35VP SEM. Foam samples cut into cross sections were placed onto SEM stubs via double-sided carbon adhesive tape and coated with Au-Pd. The images were obtained with the secondary electron detector at 3kV. The average pore sizes of samples were calculated using ImageJ software. The size distribution of the pores was determined from 200 data points for each sample.

The HNT content inside the nanocomposite foam was analyzed using the Shimadzu Corp. DTG-60H (TGA-DTA). Samples were heated from 25 °C to 1000 °C with a rate of 10 °C/min under an inert nitrogen atmosphere. The HNT content was calculated by the remaining weight of the HNT-WPU foams at 1000°C.

The compression strength of the foams was determined using TA.XTplusC Texture Analyzer (Stable Micro Systems). Firstly, the force calibration of the analyzer was completed with a 2 kg load cell and the height calibration was automatically confirmed. The cylinder probe (P/36) was used in the compression mode to investigate compression strength of foams with 2 mm/s pre-test speed, 0.5 mm/s test speed, 5 mm/s post-test speed, and 5 g trigger force with 20 %, 45 %, and 60 % compressions. The distance between the baseline and probe was adjusted to 30 mm before and after the tests. The max value at the compression peak on the stress vs. strain (%) graph was reported as the compression strength of the samples [231].

Densities of the foams were calculated using Quantachrome Ultrapyc 1200e Automatic Gas Pycnometer (Quantachrome Corporation). All measurements were run ten times at room temperature under an inert helium atmosphere.

The moisture uptake (%) of the foams was examined at 100 % humidity conditions. Before running the analysis, the samples were dried at 70 °C for one day. The samples were placed in a 20 L air-tight chamber at 100 % relative humidity and stored for 14 days. The moisture uptake was determined by calculating the difference between the pre- and post-experiment weights of the samples (Eq. 3). For each foam sample, three separate measurements were taken, and mean and standard error values were reported using Eq. 3;

$$M = \frac{Wf\text{-}\mathrm{W}i}{Wi} x100 \qquad \text{(Eq. 3)}$$

where M is the % moisture uptake, W_f is the final weight of the foam after 14 days, and W_i is the initial weight of the foam.

The ethylene scavenging capacity of nanocomposite foams was determined by monitoring the the ethylene concentration in an airtight container, in the presence and absence of the WPU-HNT_33% foams. The foams to be tested were dried inside an oven at 70 °C overnight to remove absorbed gases before each test. One 7 × 15 × 3 cm foam was placed in a 1 L one-neck round bottom flask fitted with a septum, that was connected to a F-950 Three Gas Analyzer (Felix Instruments, USA) with the detection capability in the range of 0-200ppm. 90 ppm ethylene was injected into the container and ethylene gas measurements were carried out at 15 min, 1 h, 2 h, 3 h and 72 h. Measurements were performed 3 times for each data point and an average ethylene concentration was reported. As a control, the ethylene concentrations in the glass container that did not contain any foams were monitored under the same conditions.

The ethylene concentrations were also monitored in continuous mode for 6 h after 50 ppm ethylene gas was injected into a 2 L airtight plastic container equipped with a fan. In the continuous mode of the ethylene analyzer, gas composition in the container was continuously circulated through the gas analyzer. The ethylene absorption efficiency of the foam sample was determined using Eq. 4;

$$Ethylene\ Absorption\ (\%) = \frac{Initial\ ethylene\ concentration - Final\ ethylene\ concentration}{Final\ \ ethylene\ concentration} x100 \qquad \text{(Eq. 4)}$$

3.2.5. The effect of nanocomposite foams on the shelf life of bananas

Grand Naine bananas were harvested from the greenhouses in Antalya, Turkey and transferred to the laboratory within 24 h. Bananas were exposed to 100 ppm ethylene gas for 24 h inside an airtight container to mimic the commercial ethylene treatment. To investigate the effect of nanocomposite foams on bananas, five bananas of the same size, color, and weight, which were in the same bundle, were placed into 35 x 35 cm polyethylene bags. WPU and WPU-HNT_33% foams were placed into the bags and packaged bananas were stored for 6 days at room temperature without opening the tied bags. After day 6, each day bags were opened, bananas were photographed, and placed back into the bags containing the foams. The weight loss of bananas was determined by calculating the ratio of the weight of bananas on day 8, to the initial weight of the bananas on day 0.

A TA.XTplusC Texture Analyzer (Stable Micro Systems) was utilized to analyze the firmness of bananas. Before the experiment, the force calibration was completed with a 2 kg load cell, and the distance calibration was adjusted according to the position of the baseline and probe. The three-point bend rig (A/3PB) probe was utilized with the compression mode to analyze the firmness of the bananas. The test parameters were specified as pre-test speed 2 mm/s, test speed 1 mm/s, post-test speed 2 mm/s, and 5 N (5 g) trigger force. Pre- and post-probe distances were arranged at 30 mm. Before analyzing the bananas' firmness, bananas were peeled. Peeled bananas were placed on lengths of support set perpendicular to the plane of movement of the probe, with the probe in the middle of the banana. Firmness values were reported by taking the average of the firmness data obtained from 5 different bananas.

3.2.6. The effect of nanocomposite foams on the shelf life of tomatoes

Tomatoes were purchased from a local farmers market and transferred to the laboratory within 48 h of harvest. 6 tomatoes of the same color, weight and size were placed in 20 x 30 cm plastic boxes containing a WPU or WPU-HNT_33% foam. Tomatoes were stored in sealed boxes for 14 days at room temperature. After 14 days, the weight loss and firmness measurements of the tomatoes were completed. The weight loss of tomatoes was calculated by calculating the percent change in the initial weight of the tomatoes. The firmness of the tomatoes was analyzed with A TA.XTplusC Texture Analyzer (Stable Micro Systems). The force and distance calibration of the analyzer were completed before the experiment. The needle type of probe (P/2N) was utilized with pre-test 2 mm/s, test speed 2 mm/s and post-speed 2 mm/s, and 5 N (5 g) trigger force. In order to correctly analyze the firmness of the tomatoes, tomatoes were peeled at the bottom carefully with a sharp knife and 8 flesh firmness measurements were taken on each tomato. Mean and standard error values of 6 different tomatoes in each box was reported. Following the firmness measurements, tomatoes were placed back to the packaging with and without the foams and stored 7 days at room temperatures, at the end of which they photographed.

3.3. Results and Discussion

WPU-HNT nanocomposite foams were prepared by the incorporation of HNTs into foamed WPU dispersions. The WPU dispersion was mixed with an aqueous AS solution as a surfactant, betaine as a foaming agent and stabilizer, and Borchi GEL A LA as a thickener, and mechanically blended resulting in a foamy dispersion with three-fold volume increase. HNTs were mixed into the foamed dispersion at 20, 33, 45, and 50 wt % HNT contents followed by casting in a mold and removal of water by drying, resulting in off-white, flexible and light foams (Figure 9). Control WPU foams that did not contain HNTs appeared to be white in color and lighter than the WPU-HNT foams. While the incorporation of HNTs into the WPU foam at 25 and 33 wt. % resulted in flexible foams, nanocomposites containing 45 and 50 wt. % HNTs presented not flexible structures, which appeared to be like pads as opposed to foams (Figure S1).

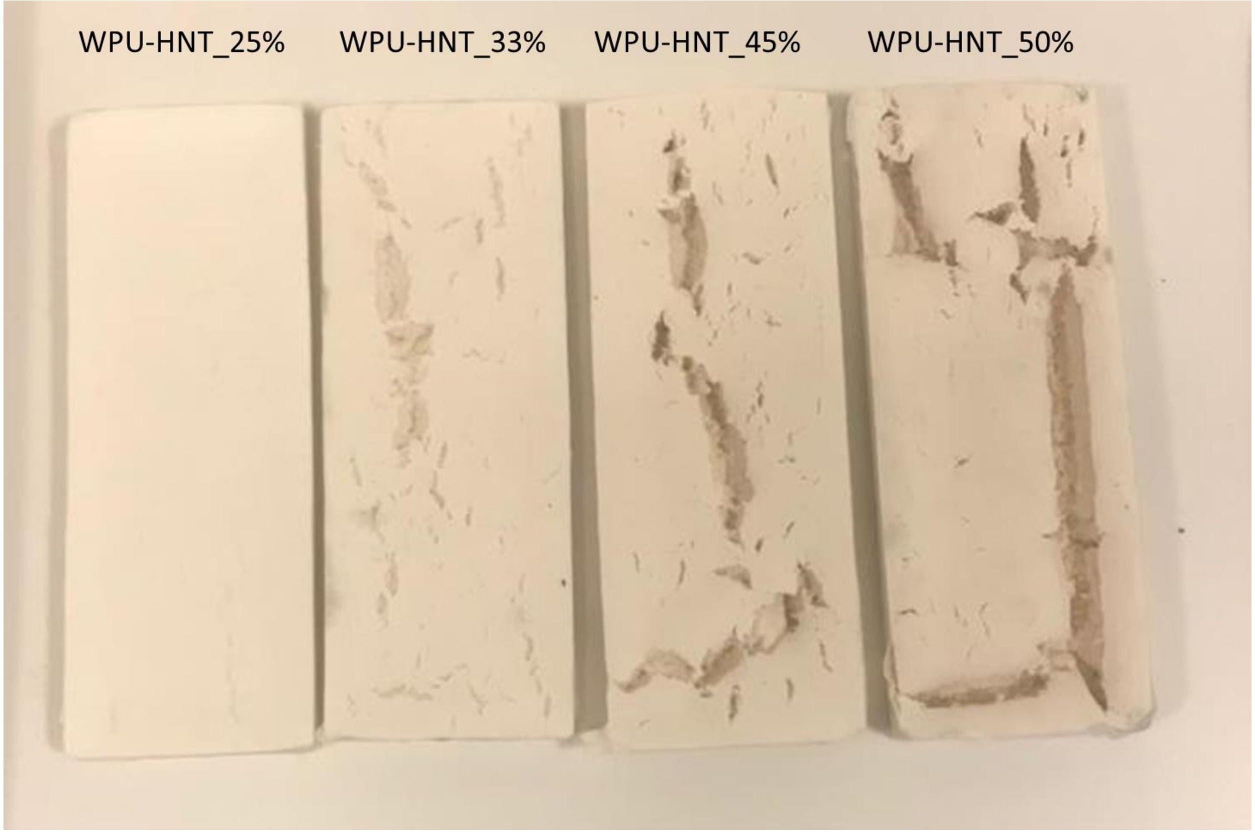

Figure S1. Appearance of WPU-HNT foams at 25, 33, 45, 50 wt. % HNT content.

Therefore, further studies were performed with WPU-HNT_33% foams which contained the highest amount of HNTs among the formulations that allow the formation of a foam structure.

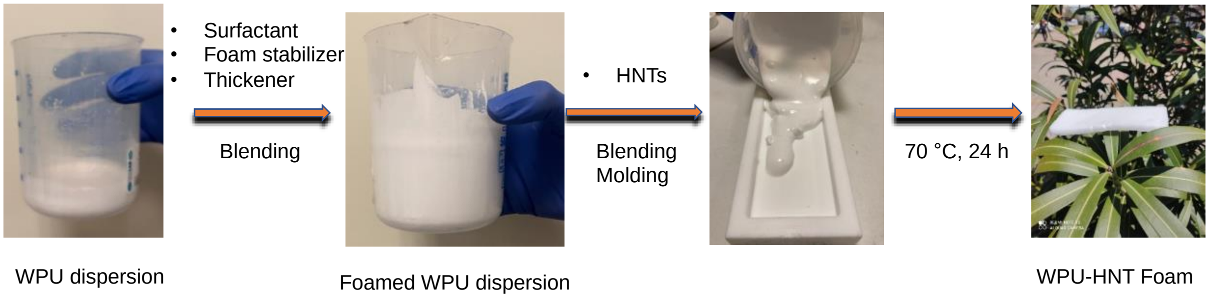

Figure 9. Preparation of WPU-HNT foams.

The morphology of the WPU and WPU-HNT_33% foams was visualized by imaging the cross-sections of the samples with SEM (Figure 10a). Both the WPU and the WPU-HNT samples demonstrated micron-sized pores confirming the formation of open-cell foam structures. The average pore sizes of both foams, on the other hand, appeared to be significantly different. While the average pore size of the WPU foam was measured to be 315.7 µm, the WPU-HNT foam which contained 33 wt. % HNTs presented a lower average pore size which was measured to be 151.5 µm (Figure 10b). The presence of HNTs, which were homogeneously distributed along the WPU matrix (Figure 10c) resulted in smaller pores of the foam. Potentially, the nanotubular HNTs with high aspect ratios and large surface areas acted as nucleating agents, which increases the contact between the particles, polymer matrix and the gas lowering the free energy for bubble formation, resulting in larger cell sizes[232].

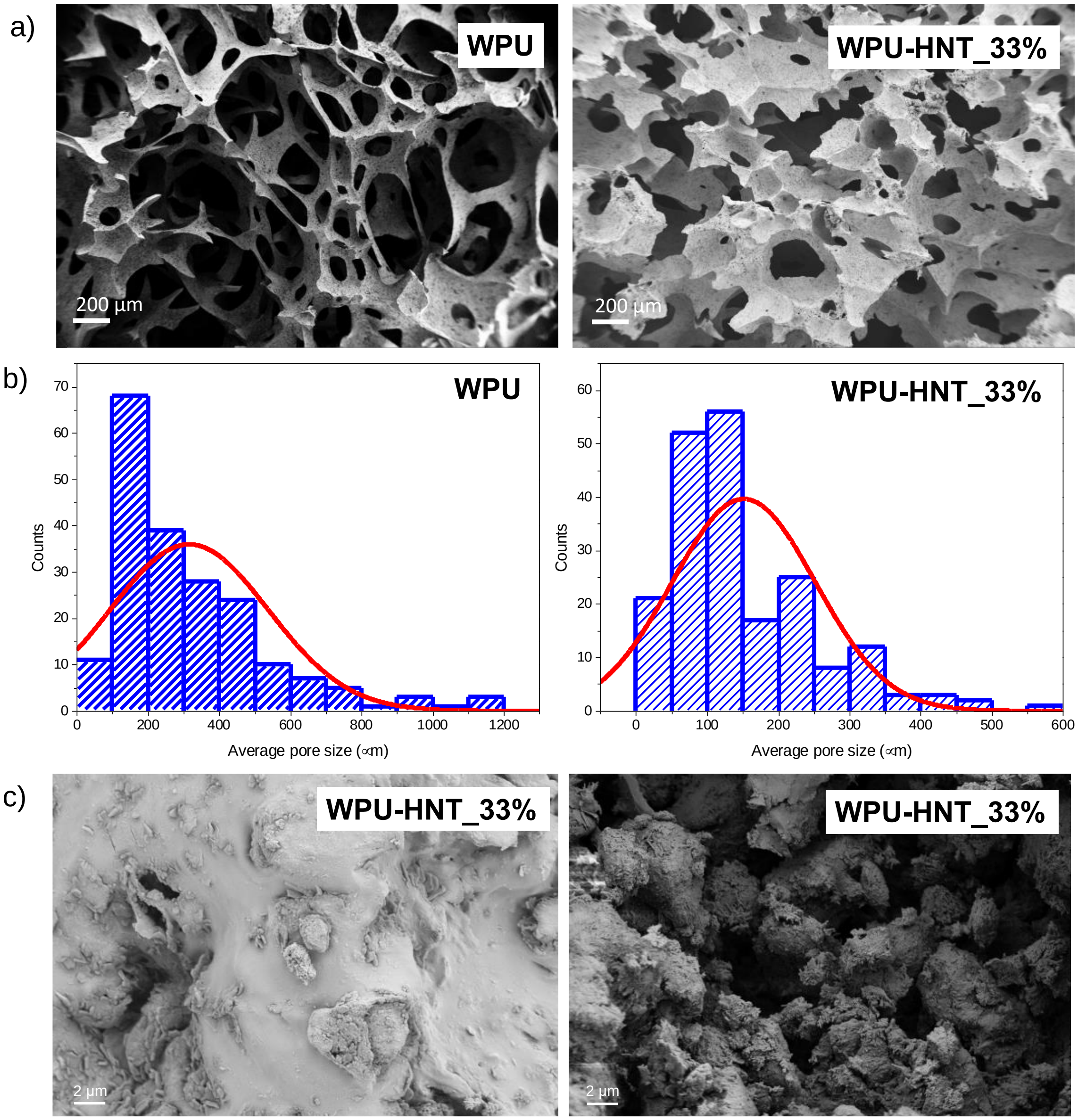

Figure 10. a) SEM images of WPU (left) and WPU-HNT_33% (right) foams, b) pore size distributions of WPU (left) and WPU-HNT (right) foams, c) SEM images of the WPU-HNT_33% foams demonstrating the distribution of HNTs within the foam.

There is a strong correlation between the function of the foam-type materials and their density because density is one of the main variables that affect the physical properties of the material, such as lightness, morphology, barrier properties and mechanical properties [233–235]. The density not only affects the physical properties, but it also indirectly has an impact on the efficiency of the material on its application [233,236]. The impact of the incorporation of HNTs into the WPU foam on the density of the resulting nanocomposite foams was demonstrated in Figure 11. There is an increase on the density of the WPU foams after the addition of 33 wt. % HNTs. The incorporation of HNTs during the foam processing has increased the density of the WPU foam as a result of the enhanced nucleation effect, which has increased the cell sizes and reduced the pore sizes[235,237], which coincides with the data obtained from the morphology analysis by SEM.

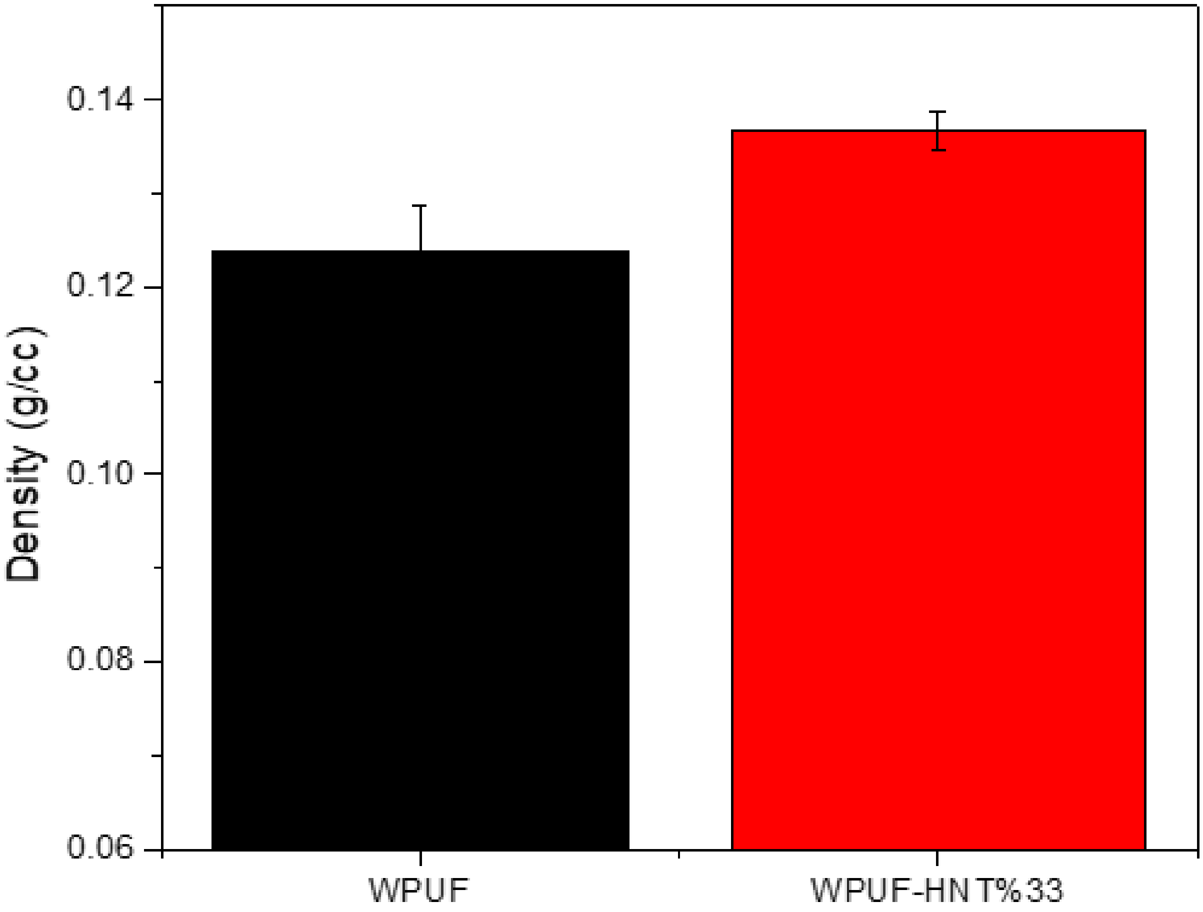

Figure 11. *Densities of WPU and WPU-HNT foams.*

The incorporation of the HNTs into the WPU foams was further confirmed using TGA (Figure 12). The HNT content inside the polymeric foam was calculated as the difference between the weight loss of WPU and WPU-HNT foams from 20 to 1000 °C normalized with the remaining weight of HNTs under the same conditions. The fact that the experimental HNT content, which was calculated to be 31 wt. %, was well correlated with the 33 wt. % theoretical content demonstrated that the HNTs were compatible with the WPU dispersion and they were successfully embedded inside the polymer matrix.

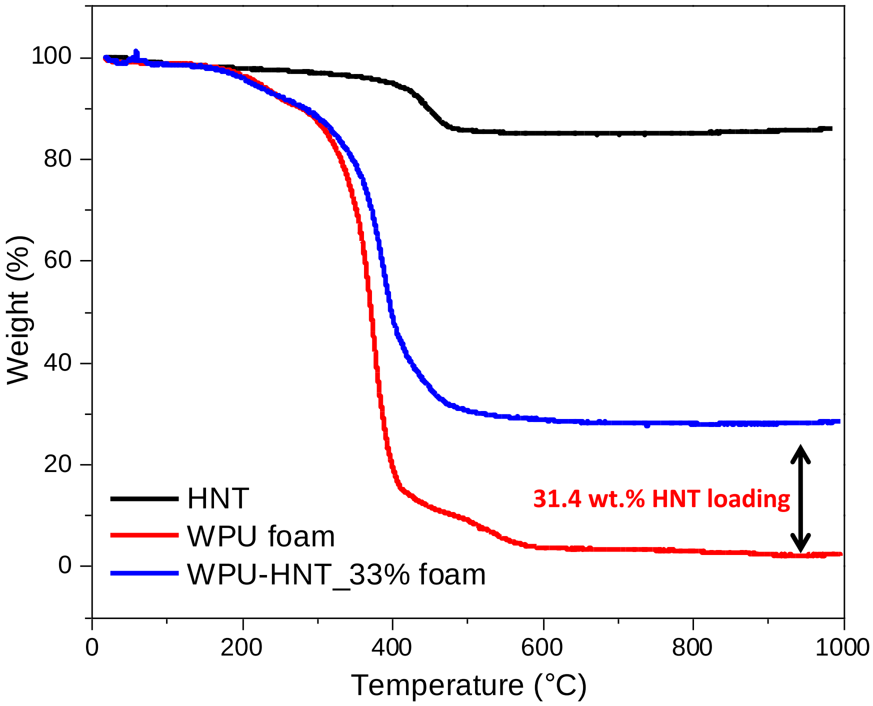

Figure 12. TGA of HNTs, WPU foam and WPU-HNT foam.

Whether HNTs integrated into WPU foams as ethylene adsorbing agents exert a synergistic affect and also improve the durability of the foams, was studied. The compression strength of the WPU-HNT_33% foams at different strain rates was measured to be significantly higher than the compression strength of the neat WPU foam (Figure 13, Figure S2).

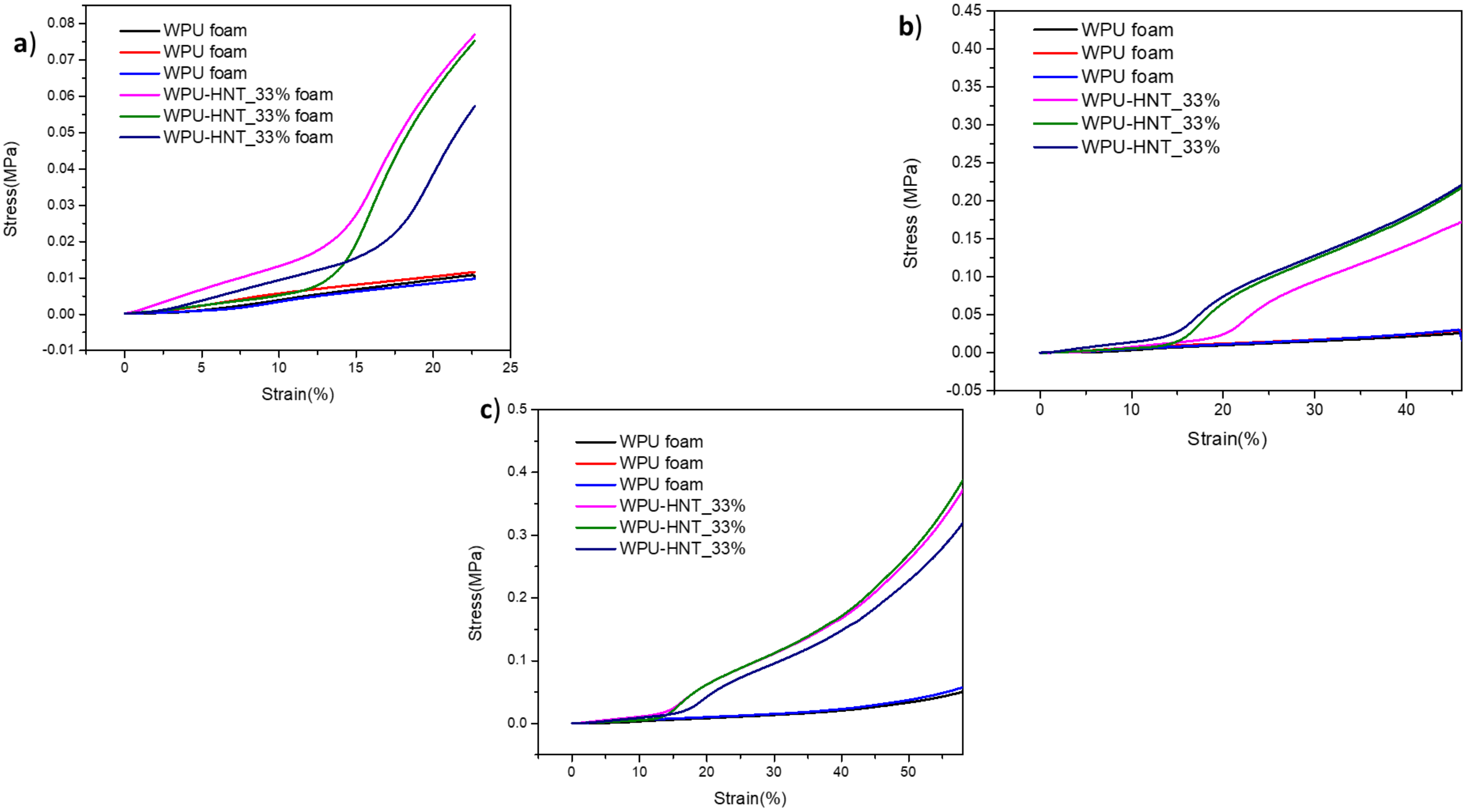

Figure S2. Stress-strain curves of WPU and WPU-HNT_33% foams at 20 % (a), 45 % (b), and c) 60 % (c) strain.

In addition, while the compression strength of the WPU foam did not significantly change at increasing strain rates, the compression strength of the WPU-HNT_33% foams increased linearly, potentially due to their smaller pore sizes and higher densities. Stress-strain analysis of the foams demonstrated that the presence of the HNTs inside the WPU matrix significantly increased the mechanical stability of the nanocomposite foam. This result is consistent with the data reported in the literature, which have demonstrated the utilization of HNTs as reinforcing agents to improve the mechanical properties of nanocomposite materials [99,238,239].

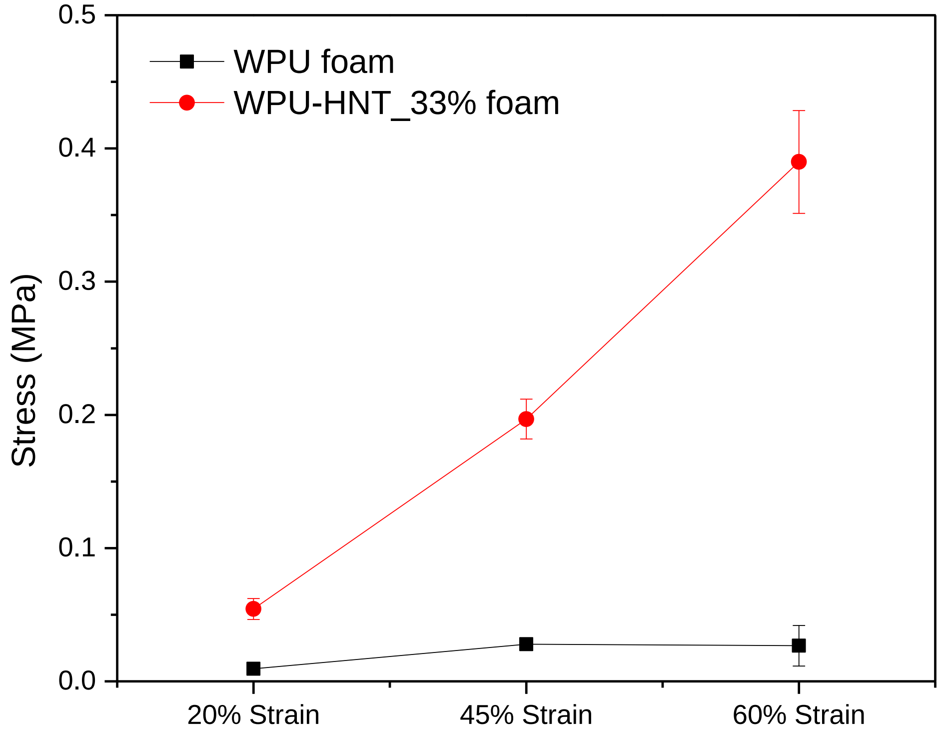

Figure 13. Compression strength of WPU and WPU-HNT_33% foams at 20, 45 and 60 % strain.

The ability of the WPU-HNT foams to regulate the atmosphere, that is, to absorb the excess moisture inside the food packaging was investigated. The moisture absorption properties of the foams were determined by placing them in a closed system at 100 % relative humidity for 14 days and calculating the time-based weight gains (Figure 14a). The calculated moisture uptake of the WPU foams demonstrated that the weight of the foam was increased by 12 % relative to its initial weight via absorption of water vapor in the environment. The moisture uptake of the WPU-HNT foams, on the other hand, has decreased when 33 wt. % HNT was incorporated. While the WPU-HNT foams still had a significant moisture absorption capacity of 7 %, the presence of the HNTs has slightly decreased the moisture absorption capacity of the WPU foams. The potential reason is that after the addition of the HNTs into the polymer matrix, the density of the sample increased, which in turn decreased the pore size and limited the water vapor entrapping efficiency of the nanocomposite WPU foam [36]. The decreased moisture absorption of the WPU-HNT foams can be also explained with their increased hydrophobicity as demonstrated by the increase in contact angles relative to neat HNT foams (Figure S3). Potentially, the increase of the density and the related decrease in the pore size have led to a higher hydrophobicity of the contact surface of the foam.

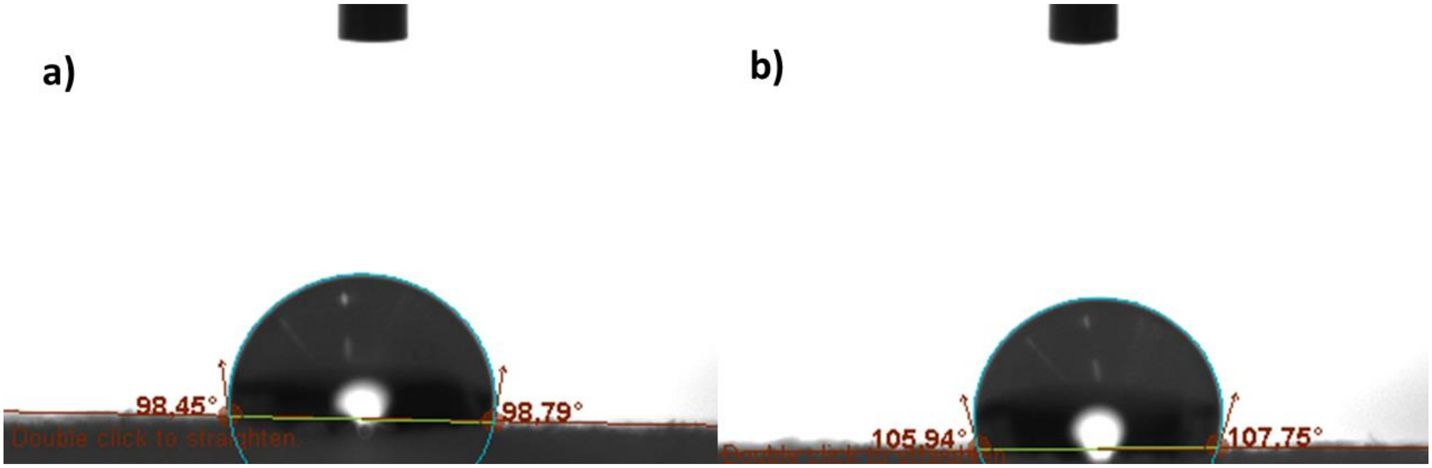

Figure S3. Contact angles of a) WPU and b) WPU-HNT_33% foams.

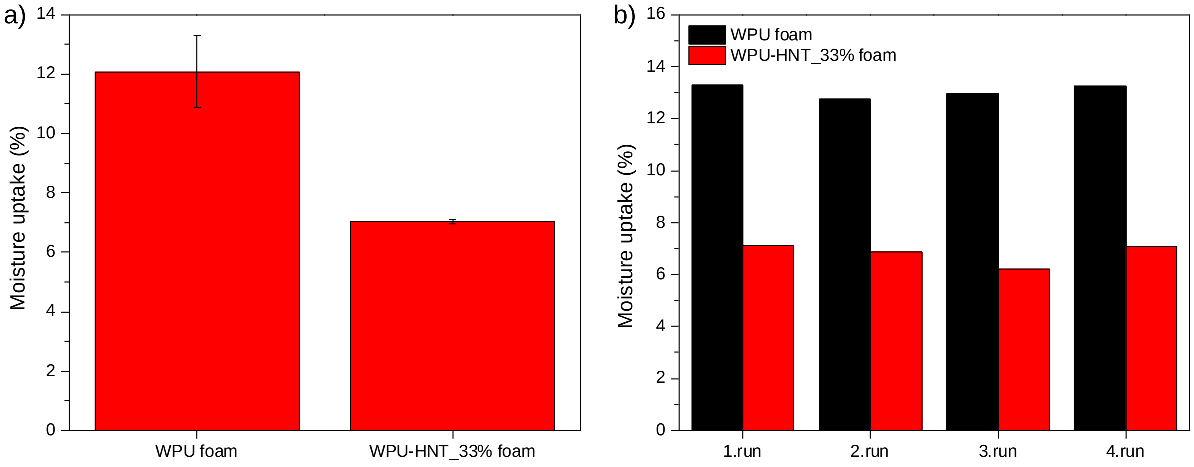

Figure 14. a) Moisture uptake of WPU and WPUF-HNT_33% foams after 14 d at 100 % relative humidity, b) Moisture uptake of WPU and WPUF-HNT_33% foams after 4 cycles of 14 days incubation at 100 % relative humidity followed by drying overnight at 70 °C.

In order to demonstrate the reusability of the WPU-HNT foams as moisture absorbents, the WPU-HNT_33% foam, which has been stored at 100% relative humidity environment for 14 d was placed in an oven overnight to remove absorbed gases and re-tested in terms of its moisture absorbance capacity. Figure 14b demonstrates the moisture uptake of the WPU-HNT_33% foam after four cycles, in which the samples were dried and placed in the same environment again. The fact that the foam presented the same moisture uptake after each cycle demonstrated that the absorbed gases can be removed with a simple drying process and the foam can be easily reused as moisture absorbents.

The ethylene absorption properties of the WPU-HNT foams have been investigated by monitoring the time-based decrease of the ethylene gas concentration in an airtight container in the presence of the foams. (Figure 15). In an airtight container, into which 60 ppm ethylene gas was injected, the reduction in ethylene gas concentration after 6 h was 13 % lower when the WPU-HNT_33% foam was present in the container than when no foam was present (Figure 15a). Under the same conditions the reduction in the ethylene concentration was only 5 % when the WPU foam was present in the container, demonstrating that the HNTs in the WPU-HNT_33% foam absorbed the 8 % of the ethylene gas present in the environment in 6 h, which corresponds to 4 ppm. The gas absorption capacity of WPU and WPU-HNT_33% foam was also determined in the trigger mode of the ethylene analyzer at different intervals during 3 days after injecting 90 ppm of ethylene gas into containers containing these foams (Figure 15b). Data clearly demonstrated that the ethylene gas was quickly absorbed by the WPU-HNT_33% foam. While the ethylene level inside the container without the foam and with the WPU foam was measured around 90 ppm after 15 min, 60 ppm ethylene gas concentration was recorded when the WPU-HNT_33% foam was present in the container. At the end of 3 d, the ethylene absorption efficiency of the WPU-HNT_33% foam was higher than the efficiency of the WPU foam because of the presence of the HNTs. Considering the fact that climacteric foods release ethylene gas at a rate of 1–100 mL kg^{-1} h^{-1} [240], the WPU-HNT foams containing HNTs have the capacity to absorb ethylene gas at the levels usually present in fruit and vegetable packages, thus they have the ability to delay the ripening processes and increase shelf life.

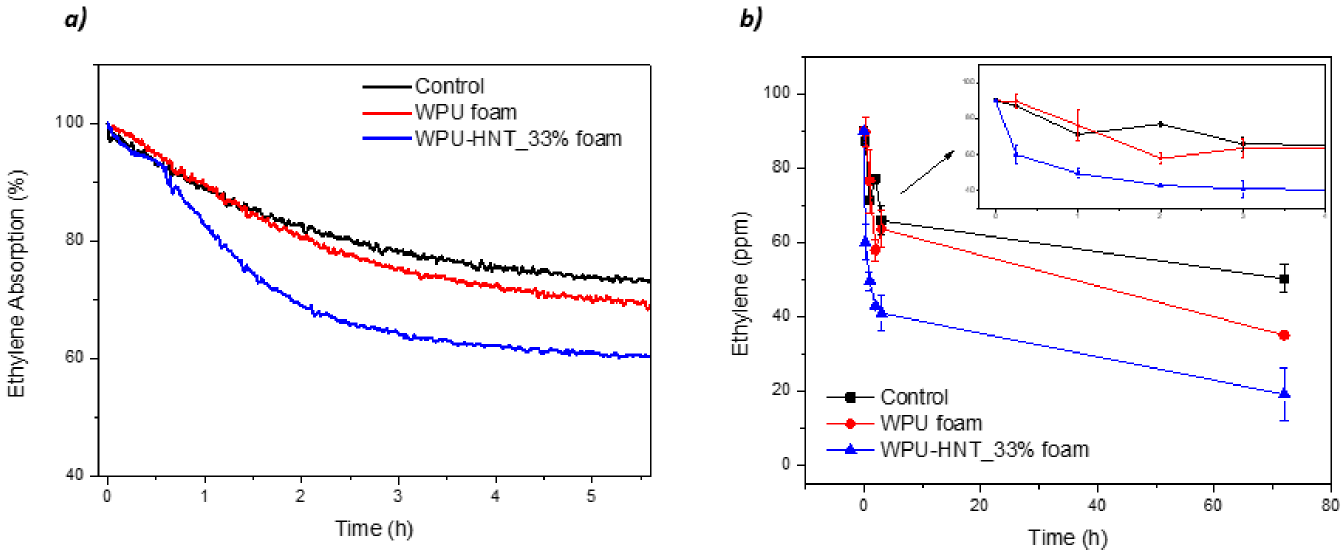

Figure 15. Ethylene absorption of WPU and WPU-HNT_33% foams, a) decrease of ethylene concentration in a container, into which 50 ppm ethylene gas was injected, measured in continuous mode for 6 h, b) decrease of ethylene concentration in a container, into which 90 ppm ethylene gas was injected, measured at different time intervals in trigger mode for 3 d.

To analyze the effectiveness of the WPU-HNT nanocomposite foams in keeping ethylene-sensitive fruits fresh, they were inserted into packages of tomatoes, and the quality of the packaged samples was analyzed in comparison to the same samples packaged without the foams. Sets of tomatoes were placed in airtight plastic boxes, each of which contained WPU, WPU-HNT_25%, WPU-HNT_33%, WPU-HNT_45% or WPU-HNT_50% foams. After being stored for 14 days at 4 °C, tomatoes were tested in terms of their firmness (Figure 16). Tomatoes stored in the presence of any of the foams presented significantly higher firmness values compared to the control tomatoes, which were stored without any foam. Apparently, the moisture absorption properties of the WPU foams allowed the absorption of the excess moisture which normally accelerate the ripening and softening of the tomatoes. The fact that HNT containing WPU foams have kept tomatoes firmer than tomatoes stored with neat WPU foams demonstrated the multifunctional nature of the WPU-HNT foams, which presented ethylene absorbing properties in addition to moisture absorption. Interestingly, the foams that allowed the highest firmness at the end of 14 days of storage contained 33 wt. % HNTs. While moisture absorption properties decrease with HNT content and the ethylene absorption properties are expected to increase with HNT content, the HNT content of 33 wt. %

was demonstrated to be optimal to obtain the highest effectiveness in terms of keeping the tomatoes fresh.

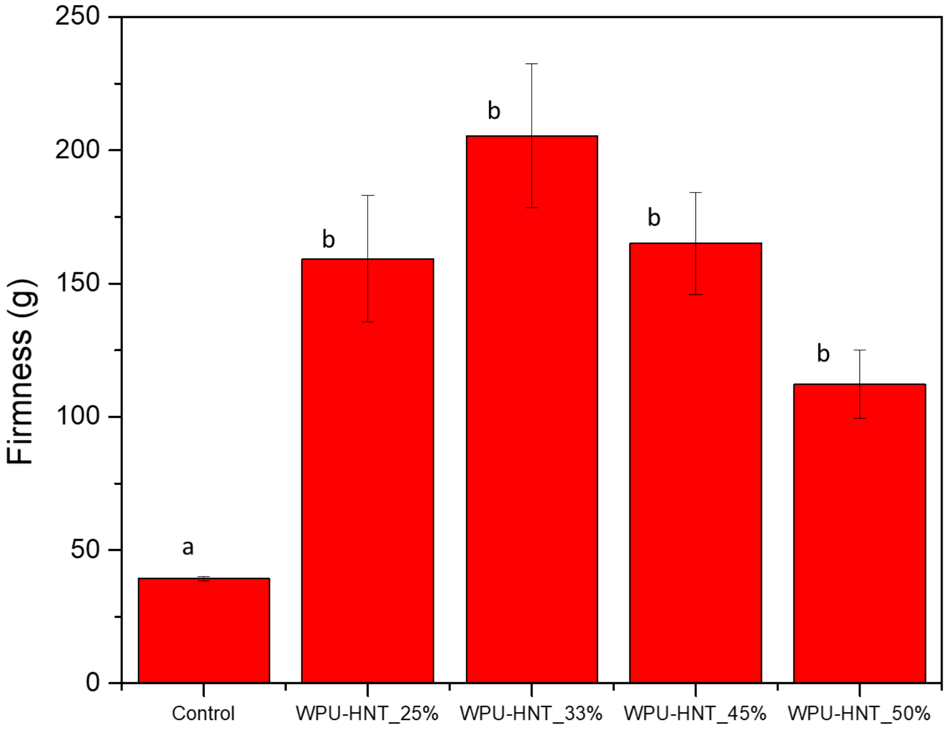

Figure 16. Firmness of tomatoes stored in plastic boxes containing WPU-HNT foams for 14 days.

Bananas packaged with commercial polyethylene bags containing WPU and WPU-HNT_33%, foams were stored at room temperature. Weight loss and the firmness of the bananas were measured on the 8th day and the effectiveness of the foams were determined by comparing the obtained quality parameters to initial quality parameters of the bananas. The appearance of the bananas on 0, 6, 7 and 8 days of storage was reported to demonstrate the quality of the bananas in terms of formation of brown spots/dark regions and wetting of the peels (Figure 17). The bananas stored without any foams presented very low quality as shown with the brown spots and dark regions that appeared on the banana peel. In addition to that, perspiration of the surface of the bananas was clearly visible on 7 and 8 days of storage. On the other hand, the presence of the foams made a significant difference while retarding the formation of brown spots/dark regions and inhibiting the respiration. More importantly, the quality of the bananas which were stored in the presence of WPU-HNT_33% foams was better than the quality of bananas stored with the WPU foams as can be seen from the lower number of brown spots on the same time of storage. In Figure 18 a and Figure 18 b, the firmness and the weight loss of the packaged bananas on 8 days of storage were demonstrated, respectively. The results proved that the bananas packaged in the presence of WPU and WPU-HNT_33% foams had significantly higher firmness values, compared to the bananas stored without any foams, demonstrating the fresh-keeping properties of these foams. Moreover, the weight loss of bananas during the storage time was lowest when the WPU-HNT_33% foam was present in the packaging environment, which demonstrated that the HNTs contained in this foam presented ethylene absorbing properties resulting in slower ripening processes and less respiration related water vapor release.

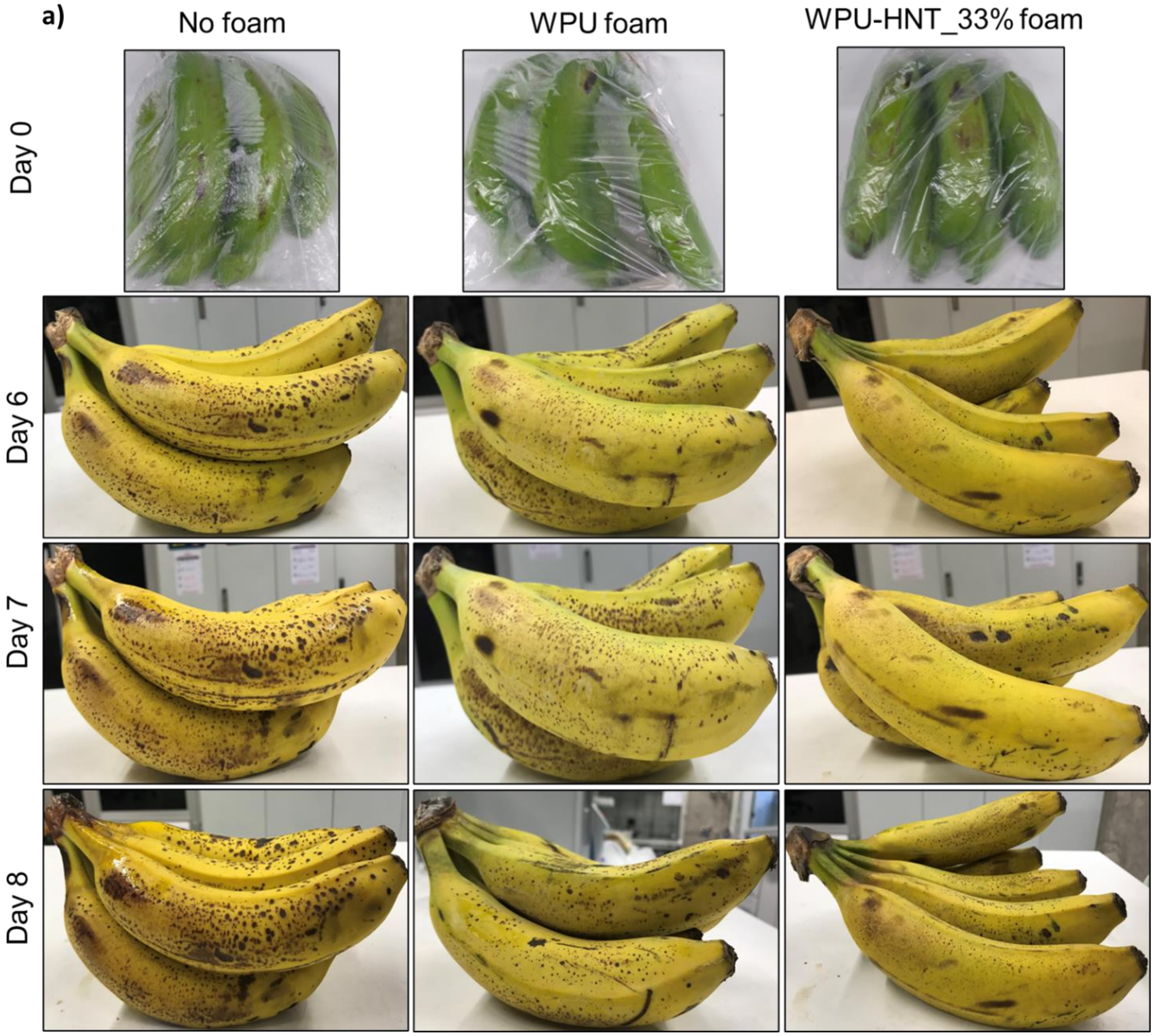

Figure 17. Photographs of bananas without foam, with WPU foam and WPU-HNT33% foam at 0, 6, 7 and 8 days.

The weight increase of the WPU and WPU-HNT_33% foams after the bananas were stored for eight days was also investigated as a way to demonstrate their moisture absorption in the presence of fruits (Figure 18 c). The WPU foams presented a weight increase of 38 %, whereas the weight of the WPU-HNT_33% foam increased by 20 %. This result was in consistency with the moisture uptake data, which showed that the WPU-HNT_33% foam can absorb less moisture than the neat WPU foams.

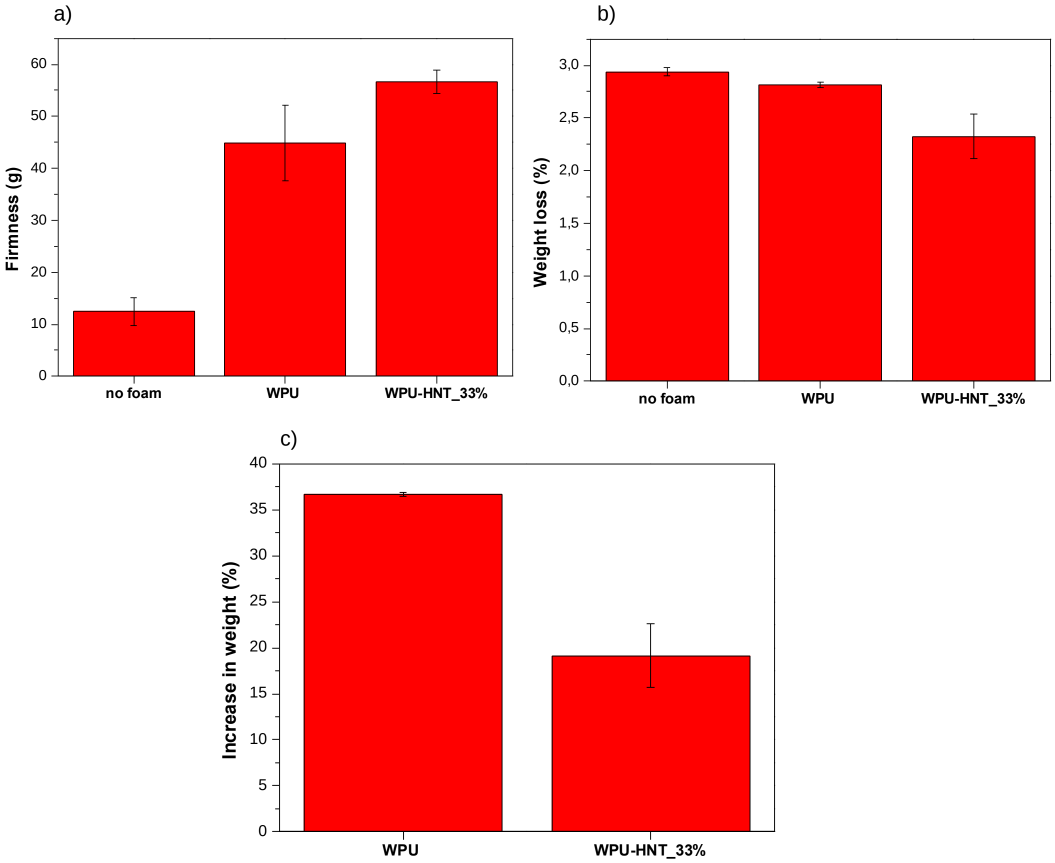

Figure 18. a) firmness of bananas at day 8, b) weight loss (%) of bananas at day 8, c) weight increase (%) of nanocomposite foams at day 8.

The results obtained from the tomato and banana storage experiments have shown that the WPU-HNT_33% foams acted as atmosphere regulators that slow down the ripening of fresh fruits, thus allow them stay fresh for longer time by both absorbing the excess humidity and ethylene gas in the packaging environment.

3.4. Conclusions

The novel HNT containing waterborne polyurethane foams have been studied as atmosphere regulators in the form of food packaging inserts to enhance the shelf life of ethylene-sensitive fruits by absorbing the excess levels of humidity and ethylene gas during storage. HNTs, which are known to present ethylene absorption properties were embedded in a waterborne polyurethane matrix presenting moisture absorption properties, resulting in multifunctional foams that present ethylene absorption and moisture absorption properties. The WPU-HNT foams were demonstrated to increase the shelf life of tomatoes and bananas when inserted into packaging. The WPU-HNT_33% foams have a strong potential as ripening retarding packaging materials that can prevent food loss in fresh fruits during transportation and storage.

CHAPTER 4. CONCLUSIONS

Active food packaging materials have been utilized to inhibit fresh fruit and vegetable deterioration while avoiding food loss based on economic and health problems. There are many parameters that have an effect on food spoilage. Excess amount of humidity and ethylene is some examples of these parameters for food spoilage. A high level of humidity can increase the growth rate of the microorganism that leads deterioration of important nutritional values of food. On the other hand, a high degree of ethylene gas inside the headspace of the packages causes acceleration of the ripening process of food and results in food spoilage. In this thesis, for the prevention of food spoilage dependent on these parameters, two different nanohybrid materials were designed.

In 2. Chapter, an active compound, CA, which has unique properties such as inhibition of ethylene production, was integrated into active food packaging material to prolong the shelf-life of bananas via impregnation of CA into HNTs. A sustained release system was performed while producing a nanohybrid with impregnation of CA into HNTs and was embedded in the PP matrix. The concentration of the active agents inside the PP matrix was studied to analyze the amount of efficiency of CA content on the quality of bananas. The ripening process of banana presence within the PP-HNT-CA nanocomposite film was inhibited in the case of firmness, weight loss, and color changes. The bananas covered with the PP-HNT-CA nanocomposite film have higher quality parameters when compared to bananas covered with PP and bananas not stored with any packaging material at 7 days. As a result, the presence of HNT-CA nanohybrid inside the nanocomposite film can be a good candidate for preventing food spoilage while inhibiting the ethylene production of food.

In 3. Chapter, a novel, flexible waterborne polyurethane foam has been firstly utilized in food application as an atmosphere regulator to increase the shelf-life of the food product while absorbing the excess level of ethylene and humidity. The multifunctional properties of the atmosphere regulators have been observed with the integration of HNT into the polymer matrix. It has been observed that with the direct addition of HNTs, known as ethylene absorbers, into the polymer foam matrix, which has moisture absorption feature, it also exhibits ethylene absorption feature. As a result of experiments on tomatoes and bananas, it has been proven that WPU-HNT foams have positive effects on food quality and shelf life. In line with these results, the produced

WPU-HNT_33% composite foams can be used as packaging materials to prevent food spoilage and have the potential to be a solution to the problems arising from food spoilage.

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