

# Chapter 7

## Edible Films and Coatings for Fruits and Vegetables

Guadalupe I. Olivas and Gustavo Barbosa-Cánovas

### 7.1 Introduction

There is a growing trend toward increased consumption of fresh fruits and vegetables. According to the USDA, fresh fruit consumption in the United States in 2000 was 28% above average annual fruit consumption of the 1970s, and fresh vegetable consumption was 26% above average annual vegetable consumption for the same period (USDA 2001–2002).

Higher consumption of fruits and vegetables has been associated with growing interest in a healthier diet, and is expected to increase over time. International organizations (World Health Organization/WHO 2002; Food and Agriculture Organization/FAO 2003) have been urging nations everywhere to promote consumption of fruits and vegetables, as a diet high in such foods has been found to be associated with decreased incidences of birth defects, mental and physical retardation, weakened immune systems, blindness, cardio-vascular diseases, and some forms of cancer and diabetes (Ford and Mookdad 2001; Genkinger et al. 2004; Hung et al. 2004; FAO 2003). WHO (2002) has estimated that low fruit and vegetable intake is among the top ten risk factors contributing to mortality (2.7 million deaths each year). They also reported that 19% of gastrointestinal cancer, 31% of ischemic heart disease, and 11% of stroke occurrences are caused by low intake of fruits and vegetables.

Consumers today have higher expectations than ever before, insisting their food be more nutritious and safer to eat, with wider variety and longer shelf life. In the case of produce, maintaining high quality food for long periods of time is difficult, since fruits and vegetables are composed of living tissue which undergoes major

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G.I. Olivas (✉)

Centro de Investigación en Alimentación y Desarrollo (CIAD), Av. Río Conchos  
S/N, Cuauhtémoc, Chihuahua 31570, Mexico  
e-mail: golivas@ciad.mx

G. Barbosa-Cánovas

Center for Nonthermal Processing of Food, Washington State University,  
Pullman, WA 99164-6120, USA  
Barbosa@wsu.edu

changes in chemical and physical states due to synthetic and degradative biochemical processes. Nutritional, flavor, textural, and pigmentation changes can all affect quality of produce (Kays and Paull 2004).

Maintaining quality of fruits and vegetables becomes even more difficult when produce has been minimally processed. Thus, fresh-cut or minimally-processed fruits and vegetables have become very important issues among food scientists and technologists in recent years. Initially, fresh cut produce was only offered to restaurants or supplied to the food service industry, where commodities were then sold to consumers within a short time; thus, there was no need to maintain quality of food for long periods. Now fresh cut fruits and vegetables have expanded to supermarkets in response to consumer demand.

As with intact fresh produce, consumers likewise expect minimally processed food commodities to be nutritious, attractive, and ready-to-eat, as well as to exhibit high quality and long shelf life, with no differences in flavor and texture from the original counterpart. These expectations are difficult to meet, since minimally processed commodities undergo rapid deterioration, wherein increased respiration rate and ethylene production, and consumption of sugars, lipids and organic acids accelerate ripening process. These changes cause senescence and, thus loss of texture and water, as well as undesirable changes in flavor and color (Kays 1991).

Use of edible films and coatings has been studied as a good alternative for preservation of intact and fresh-cut fruits and vegetables, since such films can create semi-permeable barriers to gases and water vapor, maintaining quality of the product. Edible films and coatings have also been studied as potential carriers of additives to help preserve, or even improve quality of produce. Application of edible coatings consists of applying a thin layer of edible material to the food's surface, while generation of edible films involves casting a film of edible material to cover the commodity. However, in studies on edible films and coatings, the two terms are generally considered the same, and results are often reported interchangeably (Gordon 2005).

Overall, the purpose of using edible films and coatings for fruits and vegetables is to retard transfer of gas, vapor and volatiles, thus providing food with a modified atmosphere that decreases respiration and senescence, reduces aroma loss, retains moisture and delays color changes throughout storage.

## **7.2 Postharvest Physiology**

Since fruits and vegetables consist of living tissue, subsequent physiological and biochemical changes which cause detrimental changes in quality and shelf life of produce are common after harvesting. Respiration, transpiration and ethylene production are main factors contributing to deterioration of fruits and vegetables (DeEll et al. 2003). After harvest fresh, produce can also experience biotic and abiotic stresses, which can modify their characteristics prior to consumption. Extent to which quality and shelf life of produce is actually affected will also depend on factors, such as cultivar, variety and stage of maturity.

## ***7.2.1 Postharvest Physiology of Intact Fruits and Vegetables***

### **7.2.1.1 Ethylene Production**

Ethylene is a hormone produced when vegetable or fruit undergoes stress. Ethylene triggers ripening and senescence, and is partially responsible for changes in flavor, color and texture of fruits and vegetables (Kays and Paull 2004). On the other hand, removal of ethylene will slow ripening and senescence. Controlled atmosphere (CA) or modified atmosphere (MA) storage of produce can reduce ethylene production/action, preserving quality of fruits and vegetables for longer periods.

### **7.2.1.2 Water Loss**

One important factor, which is necessary to preserve quality of fruits and vegetables, is avoidance of water loss. Moisture is lost during transpiration when water is converted from liquid to gas. Before harvest, the fruit or vegetable preserves the amount of water stored inside by replacing or taking back water lost (due to transpiration) through roots. When produce is harvested, it loses its source of water, so recuperation from water loss is not possible. When water is lost, turgor of produce decreases, as does firmness. Water stress also causes metabolic alterations changes in enzyme activation causing accelerated senescence, reduced flavor and aroma, decline in nutritional value, and increased susceptibility to chilling injury and pathogen invasion. Maximum acceptable water loss allowed before the commodity is considered unmarketable varies; apples and oranges can tolerate 5% water loss, while celery and cabbage can tolerate 10% (Kays and Paull 2004).

### **7.2.1.3 Respiration**

Enzymatic reactions occur in fruits and vegetables during respiration where oxygen is consumed, carbon dioxide is produced, and heat and energy are released. Respiration is required to keep produce alive and to support any developmental changes. Respiration rate itself is influenced by temperature, humidity and gas composition. When oxygen composition is lowered, respiration decreases and hence, senescence does as well. However when oxygen concentration falls below threshold level anaerobic respiration occurs, which in turn causes ethanol production, off-flavor formation and loss of harvested produce (Kays and Paull 2004).

## ***7.2.2 Postharvest Physiology of Minimally Processed Fruits and Vegetables***

Problems mentioned above increase with partial or total loss of skin in minimally processed fruits and vegetables. Skin protects produce against water loss and pathogen

invasion and provides partial barrier to gases. Slicing, chopping, and peeling, etc., of fruits and vegetables can cause injury not only to cells immediately exposed by the action, but also to unexposed cells deep within the tissue, increasing extent of damage (Saltveit 1997).

### **7.2.2.1 Ethylene Production**

Generally, there is noticeable increase in ethylene production when produce tissue is wounded, inducing deep physiological changes such as ripening in climacteric fruits (Abeles et al. 1992). For example, in green tissues, ethylene triggers chlorophyll degradation, whereas in carrots, high concentration of ethylene triggers increase in phenolics and isocoumarin, giving a bitter taste to the vegetable (Poenicke et al. 1977; Sarkar and Phan 1979). Rate of ethylene production experienced in minimally-processed fruits and vegetables will depend on produce type and maturity stage at which it is cut (Toivonen and DeEll 2002). For instance, in fresh kiwifruit, tomatoes and strawberries, all three undergo increase in ethylene production when cut (Watada et al. 1990), whereas pears do not (Gorny et al. 2000; Rosen and Kader 1989).

### **7.2.2.2 Water Loss**

Cutting, slicing, and peeling, etc., of fruits and vegetables, will increase water transpiration rate due to exposure of tissue following removal of natural epidermal layer, and will also increase surface area of exposure (Toivonen and DeEll 2002). Water loss through transpiration cannot be replaced and is problematic, since loss of small amounts of water will severely impact produce quality. With water loss, turgor of produce drops, as well as turgidity and firmness. As mentioned, water stress also causes metabolic alterations, changes in enzyme activation, causing accelerated rate of senescence, reduced flavor and aroma, decreased nutritional value, and increased susceptibility to chilling injury and pathogen invasion (Sams 1999).

### **7.2.2.3 Respiration**

Wounding of fruits and vegetables also causes increase in respiration, thereby increasing production of carbon dioxide and consumption of oxygen, further causing decrease in stored reserves. This increase will also depend on commodity type, storage temperature and degree of wounding (Ahvenainen 1996). For instance, slicing a mature green tomato can increase respiration up to 40% at 8°C, compared with intact fruit (Mencarelli et al. 1989). However minimally-processed apples do not show increased respiration (Lakakul et al. 1999). When minimally-processed produce is packaged under modified atmosphere with very low oxygen concentration, anaerobic respiration will occur, with consequent formation of off-flavors, ethanol,

ketones and aldehydes. Increase in respiration depends on the commodity, as some fruits and vegetables do not show increase in these compounds (e.g., bananas), while others such as tomatoes do (Toivonen and DeEll 2002; Mencarelli et al. 1989).

#### **7.2.2.4 Browning**

Enzymatic browning is one of the main problems encountered in maintaining quality of fresh-cut fruits and vegetables. When a fruit or vegetable is cut, reaction occurs that is catalyzed by the enzyme polyphenol oxidase, wherein phenolic compounds react with atmosphere oxygen in the presence of copper, causing formation of dark compounds (Ahvenainen 1996). Enzymatic browning is the main problem occurring in fruits such as apples, pears, bananas and peaches, as well as in vegetables such as potatoes and lettuce (Sapers 1993).

#### **7.2.2.5 Microbial Contamination**

When fruit or vegetable tissue is wounded, surface moisture and cytoplasmic remains of ruptured cells with high concentrations of sugars and proteins will be present, which are ideal conditions for microbial growth (Saltveit 1997). This microbial growth could cause food borne illnesses and food spoilage (Nguyen and Carlin 1994). Minimally-processed fruits and vegetables are susceptible to invasion by microorganisms, such as *Pseudomonas spp.*, *Erwinia herbicola*, *Flavobacterium*, *Xanthomona*, *Eterobacter Agglomerans*, *Leuconostoc mesenteroides*, *Lactobacillus spp.*, molds, and yeasts (Zagory 1999). It is important to be aware that a modified atmosphere can cause growth of and toxin production by *C. Botulinum* on fruits with pH higher than 4.8, so provision should be made to coat tropical fruits in particular to avoid *C. Botulinum* growth (Olivas and Barbosa-Cánovas 2005).

### **7.3 History of Edible Films and Coatings for Fruits and Vegetables**

Edible films and coatings have been extensively studied for the last 20 years, and much has been published on their use for fresh and minimally-processed fruits and vegetables (Tables 7.1 and 7.2). Reviews found in literature on the topic of edible coatings for whole fruits and vegetables (Platenius 1939; Claypool 1940; Hardenburg 1967; Curtis 1988; Park and Chinnan 1990; Hagenmaier and Shaw 1992; Banks et al. 1993; Baldwin 1994; Park 1999) and minimally-processed fruits and vegetables (Wong et al. 1994; Baldwin et al. 1995a, b; Nisperos and Baldwin 1996; Olivas and Barbosa-Cánovas 2005; Lin and Zhao 2007) have addressed the issue indicating different perspectives.

**Table 7.1** Edible coatings on minimally processed fruits and vegetables

Fruits	Coatings and concentrations	Additives and concentrations	Variables evaluated	Results	References
Apple slices	Apple puree-alginate	CaCl <sub>2</sub> , <i>N</i> -acetylcysteine, oregano oil, lemongrass oil, vanillin	C, EtOH, Et, F, ST, MG	Coatings extended the shelf life of fresh-cut apple	Rojas-Graü et al. (2007)
Apple and papaya cylinders	Alginate or gellan	Glycerol, CaCl <sub>2</sub> , B. lactis, sunflower oil	WVP, WS, B. lactis	Gellan coatings avoided WL better than alginate coatings. Alginate- and gellan-based edible coatings carried successfully viable probiotics on papaya and apple cylinders	Tapia et al. (2007)
Apple slices (Gala)	CaCl <sub>2</sub> + Alginate or alginate/acetylated monoglyceride-linoleic acid or alginate butter-linoleic acid	Potassium sorbate, alpha-monostearate	WL, C, F, MG, TA, SS, FV	All coatings preserved F, and C. WL was delayed, mainly with Alg-monoglyceride-linoleic acid coating. Higher amounts of Butanol, hexanal, 1-hexanol, trans-2-hexenal on coated samples at end of storage.	Olivas et al. (2007)
Mango slices	Chitosan	-	ST, WL, C	The coating retarded WL and drop in sensory quality, increasing the SS content, TA and AA content and inhibiting MG.	Chien et al. (2007b)
Shelled Pecans	CMC	PG, Sorbitol, lecithin, $\alpha$ -tocopherol, BHA, BHT, citric acid	ST, R, C	Imparted shine, F was not preserved, R was delayed.	Baldwin and Wood (2006)
Apple slices	WPC + Beeswax	AA, cysteine Cys, or 4-hexylresorcinol	WL, C, BI, ST	WPC-AA and WPC-BW coatings reduced B. WL was not prevented by coatings use.	Pérez-Gago et al. (2006)
Apple slices	WPI, WPC or HMPC + Beeswax or carnauba	Glycerol, stearic acid	WL, BI	WL was not avoided. WPI and WPC were more efficient at preserving C compared with HMPC.	Pérez-Gago et al. (2005a)

Persimmon pieces	WPC-Beeswax or WPC-Beeswax + AA	Glycerol	WL, F, C,	WPC-BW-Ascorbate coatings reduced B, WL, and F loss in fresh-cut persimmons	Pérez-Gago et al. (2005a)
Apple slices	WPI-beeswax	Glycerol, stearic acid	WL, C, ST	Lower BI than uncoated apples. WL was not reduced by use of coating	Pérez-Gago et al. (2003b)
Pear wedges	Methylcellulose (MC) and MC-stearic acid (SA)	AA, potassium sorbate, CaCl <sub>2</sub>	WL, F, MG, C, TA, SS, FV	Coating retarded B. WL was delayed on pears coated with MC-SA. Pear wedges coated with MC-SA formulation contained higher amounts of hexyl acetate	Olivas et al. (2003)
Baby carrots	Xanthan gum	Calcium lactate calcium gluconate, vitamin E	C, ST, Vitamin E, $\beta$ -carotene, Calcium	Calcium and vitamin E increased on coated carrots. Edible coatings improved C	Mei et al. (2002)

WPI whey protein isolate; F firmness; WL weight loss; TA titratable acidity; SS soluble solids; RR respiration rate; AA ascorbic acid; C color; MG microbial growth; IGC internal gas composition; FV flavor volatiles; DS decay symptoms; ST sensory test; EtOH ethanol; G gloss; Wh whitening; S sugars; Et ethylene; BI browning index; B browning; PG propylene glycol; BHA butylated hydroxyanisole; BHT butylated hydroxytoluene; R rancidity; WS water solubility

**Table 7.2** Edible coatings on intact fruits and vegetables

Fruits	Coatings	Additives	Variables evaluated	Results	References
Mandarin	Low molecular weight chitosan (LMWC) or High molecular weight chitosan (HMWC)	-	WL, F, TA, AA, Fungal decay	LMWC coating improved firmness, titratable acidity, ascorbic acidity, and water content. Mandarin coated with LMWC exhibited greater antifungal resistance than TBZ	Chien et al. (2007a)
Strawberry	Starch	Sorbitol	C, F, WL, SS, MG C, F, WL, SS, MG C, F, WL, SS, MG	Opaque coating	Ribeiro et al. (2007)
	Carrageenan	Glycerol + CaCl <sub>2</sub> Tween 80		Preserved better firmness	
	Chitosan	Tween 80 + CaCl <sub>2</sub>		Delayed WL Delayed water loss	
Cherry	Aloe vera gel and water 1:3	-	RR, WL, C, F, MG	Delay in WL, F loss	Martínez-Romero et al., (2006)
Strawberry	Chitosan	Tween 80, oleic acid	SSD, WVR, TA, pH, SS, anthocyanin, Fungal decay, RR, MP, ST	Anthocyanin content decreased throughout storage in coated samples. Coatings had no significant effects on TA, pH and SS content. Coated fruits had decrease in aroma and flavor, especially when the ratio oleic acid:chitosan was high	Vargas et al. (2006)
Strawberry	Calcium gluconate or chitosan or chitosan + Calcium gluconate		Fungal decay, WL, F, C, pH, TA, SS	Coatings decreased surface damage and delayed fungal decay. Chitosan coatings retained F and delayed changes in external C	Hernandez-Munoz et al. (2006)
Cherry	LBG + Beeswax or shellac	Polysorbate 80, glycerol, NH <sub>3</sub>	F, C, WL, ST, EtOH	C decay was not prevented by the coating. WL and F loss was delayed	Rojas-Argudo et al. 2005
Strawberry	Cactus-mucilage	Glycerol	F, C, ST	Coating increased shelf life of strawberry	Del-Valle et al. (2005)



Guava	Dextrans	Glycerol	FV, C	Coatings showed poor water retention on fruits stored at room temperature. Best efficiency of dextrans was at 4°C, by increasing guava quality (size, color, aroma, water content)	Quezada-Gallo et al. (2005)
Grapes	Aloe vera gel	-	WL, C, F, SS, TA, ST, RR, MG, Et	A. vera gel delayed postharvest quality losses, extending storability from 7 days at 1°C to 3.5 days. Coating reduced MG	Valverde et al. (2005)
Apricots and green peppers	MC + Stearic acid	PEG, PEG + CA, PEG + AA	WL, Vitamin C	Coatings delayed WL of fresh apricots and green peppers. Coatings containing AA or CA lowered vitamin C loss	Ayrancy and Tunc (2004)
Cherry	Sodium caseinate or milk protein concentrate	Glycerol and Bees wax or stearic-palmitic acid blend	SS, TA, pH, WL	Coatings reduced WL of the fruits. Edible coatings had a beneficial effect on sensory quality of cherries	Certel et al. (2004)
Cherry	Semperfresh™ 10 and 20 g/L	-	F, WL, TA, SS, SC, AA, C	Effective in reducing WL, and preserving F, AA, TA and C. Shelf life increased by 21% at 30°C and 26% at 0°	Yaman and Bayo (2002)
Apple	Shellac, candelilla, shellac-carnauba	-	-	Shellac caused anaerobic respiration on Braeburn and Granny Smith apples. This research recommends shellac for "Delicious," carnauba-shellac for "Braeburn" and "Fuji" apples	Bai et al. (2003a)
Apple	Zein	Propylene glycol	F, G, Wh, TA, FV, S, IGC, Et, ST	Good overall apple quality comparable to a commercial shellac coating	Bai et al. (2003b)
Plum	HPMC + Beeswax or shellac	Stearic acid, glycerol	WL, F, Et, EtOH	WL of coated plums decreased as lipid content increased. F was not affected by coating after short-term storage at 20°C. In prolonged storage, coatings significantly reduced F loss and internal breakdown	Pérez-Gago et al. (2003a)

(continued)

Table 7.2 (continued)

Fruits	Coatings	Additives	Variables evaluated	Results	References
Grapes	Chitosan	NaOH to modify pH to 5.6.	Inhibition of <i>Botrytis cinerea</i>	They observed that inhibitory effect originated from combination of coating and antifungal effects and stimulation of defense responses	Romanazzi et al. (2002)
Pear	Carabauba wax	-		Decrease in pear friction discoloration and internal O <sub>2</sub> concentration	Amarante et al. (2001)
Pear	Carabauba wax	-		Modification of O <sub>2</sub> instead of CO <sub>2</sub> was the means of delaying ripening	Amarante et al. (2001)
Kiwifruit	Soy protein + pullulan + stearic acid	Glycerol	Peroxidase, pectin, TA, RR, Et	Coating retarded softening of kiwifruit	Xu et al. (2001)
Mango	Cellulose, Nature Seal® 2020 hydroxypropyl-cellulose Carabauba, Tropical Fruit Coating 213 (TFC)	Preservative, acidulant and emulsifier Fatty acid soaps	IGC, WL, FV, SS, TA, DS, ST, F	Both coatings created modified atmospheres, reduced decay, and improved appearance. Polysaccharide coating delayed ripening and increased concentrations of flavor volatiles. Carabauba coating reduced WL	Baldwin et al. (1999)

*F* firmness; *WL* weight loss; *TA* titratable acidity; *SS* soluble solids; *RR* respiration rate; *CA* citric acid; *AA* ascorbic acid; *C* color; *MG* microbial growth; *IGC* internal gas composition; *FV* flavor volatiles; *DS* decay symptoms; *ST* sensory test; *EtOH* ethanol; *G* gloss; *Wh* whitening; *S* sugars; *Et* ethylene; *LGB* Locust bean gum; *SSD* surface solid density; *WVR* water vapor resistance; *MP* mechanical properties; *TBZ* thiabendazole

Application of edible coatings to preserve quality of fruits and vegetables is not new. Hardenburg (1967) comments that their use dates back to the XII century, where oranges and lemons were coated with wax in China to preserve the fruits longer. In the U.S., the first patent on use of edible coatings dates back to 1916, where a method preserving whole fruits with molten wax was patented by Hoffman (Hoffman 1916). In 1972, Bryan patented a method to preserve grapefruit halves with edible coating composed of low methoxyl pectin and locust bean gum dispersed in grapefruit juice.

## 7.4 Technical Development of Edible Films and Coatings

The main purpose of employing edible films and coatings is to provide a semi-permeable barrier against gases and vapor; however, there are other purposes (e.g., to carry additives such as texture enhancers, antimicrobials, antioxidants, etc.; Table 7.3). In general, edible films and coatings represent an interesting option for intact and minimally-processed fruits and vegetables, since a barrier can be formed that protects the produce and decreases rate of physiological postharvest deterioration.

Successful application of edible films or coatings as barriers for fruits and vegetables mainly depends on developing film or coating that can provide appropriate internal gas composition for a specific fruit/vegetable (Park 1999). Some factors/questions need to be addressed when developing a film or coating: (1) how properties of coating solution will affect the product, (2) how coating will change with time, (3) how coating will interact with the product that might lead to flavor/off-flavor generation, and (4) how storage conditions will affect coating. Other considerations include importance of thickness, color, and flavor of coating, since these parameters can change final quality of the coated product.

Thus, to develop the appropriate film or coating, full understanding of the physiology of the fruit/vegetable being coated is needed, as well as a clear idea of the function of the film or coating relative to the product. Different purposes of films and coatings developed for fruits and vegetables are more fully detailed in the next section.

**Table 7.3** List of additives incorporated into edible films and coatings for fruits and vegetables

Additives	Examples
Antibrowning compounds	Ascorbic acid
Antimicrobial agents	Potassium sorbate
Texture enhancers	Calcium chloride
Nutrients	Vitamin (E)
Aroma precursors	Linoleic acid
Probiotics	<i>B. lactis</i>
Flavors and colorants	Apple puree

## **7.4.1 *Edible Films and Coatings for Preservation of Fruits and Vegetables***

### **7.4.1.1 Water Loss**

Edible films/coatings decrease water vapor transmission rate by forming a barrier on the fruit or vegetable surface. This barrier prevents texture decay, since water is essential for preservation of cell turgor (Garcia and Barret 2002). Metabolic alterations that can cause accelerated rate of senescence due to water loss can also be avoided with their use. Ability of films and coatings to function as barriers to water vapor relies on external conditions, which include (1) temperature and relative humidity, (2) characteristics of commodity such as type of product, variety, maturity and water activity, and (3) characteristics of film such as composition, concentration of solids, viscosity, chemical structure, polymer morphology, degree of cross-linking, solvents used in casting the film, and type of plasticizer used (Olivas and Barbosa-Cánovas 2005). In case of minimally-processed fruits, there is usually very high water activity present at the surface, making it difficult to develop a coating that delays water loss, since capacity of films to work as barriers to water vapor decreases as water activity increases in the commodity (or relative humidity of the environment) (Hagenmaier and Shaw 1990). However a number of coatings have been developed that can delay water loss in some minimally processed fruits and vegetables (Table 7.1).

### **7.4.1.2 Texture**

When coating or film is applied to a commodity, a modified atmosphere is developed. Reduction of internal oxygen and increase of carbon dioxide in the commodity will in some cases delay softening (Kader 1986). Intact apples retained firmness when stored under modified atmosphere (Knee 1980). Edible coatings can also preserve texture of fruits and vegetables by acting as a partial barrier to water and serving as carriers of texture enhancers. Loss in texture has been delayed with application of edible coating to whole avocados (Maftoonazad et al. 2007). Olivas et al. (2007); likewise preserved texture of cut-apples when coated with alginate films containing calcium chloride.

### **7.4.1.3 Respiration**

Edible films or coatings can reduce respiration and, hence increase shelf life of a commodity. In selection of a coating, several considerations should be addressed to avoid extremely low oxygen concentration inside the commodity. Low oxygen concentration in the product could lead to anaerobic respiration, which can result

in deterioration of product due to production of off-flavors and accelerated senescence (Kays and Paull 2004). Some studies (Tables 7.1 and 7.2) show how edible films/coatings have favorably delayed respiration, and in some cases caused anaerobic respiration.

#### **7.4.1.4 Ethylene**

A well selected edible coating will produce a modified atmosphere inside the fruit, reducing levels of internal oxygen. If oxygen concentration inside the commodity drops below 8%, there will be a decrease in ethylene production (Kader 1986), and the commodity's quality will be preserved longer.

#### **7.4.1.5 Color**

One of the most important attributes of fruits and vegetables is color (Kays 1999). For some minimally-processed fruits and vegetables, browning is a big problem that can be controlled by use of films or coatings as carriers of anti-browning agents. The most common antioxidant used on fruits and vegetables is ascorbic acid; however other compounds have been successfully used such as cysteine, 4-hexylresorcinol, citric acid and calcium chloride (Olivas et al. 2007; Pérez-Gago et al. 2006). Baldwin et al. (1996) coated apple slices and potato cores with Nature Seal™ and found that ascorbic acid delayed browning more effectively when applied in edible coating than in aqueous solution. Depending on coating formulation, appearance of fruit can be affected positively or negatively by selected coating. For instance, candelilla wax gives a natural, noncoated appearance to apples, whereas shellac or carnauba coating (when in contact with water) will give whitish color to apples (Bai et al. 2003a).

#### **7.4.1.6 Flavor**

Perhaps the most important attribute of fruits and vegetables is flavor. Consumers may buy the commodity based on its appearance when first purchased, but if the flavor is not acceptable, they will avoid buying the product a second time. Flavor can be preserved or modified with edible films or coatings by two different means: (1) as a barrier to aroma volatiles, and (2) as a carrier of flavors. Baldwin et al. (1999), for instance, found that a polysaccharide coating worked as a barrier to aroma volatiles on whole mango. Edible coatings can also modify internal atmosphere of the commodity, causing low oxygen and high carbon dioxide concentration. This is not beneficial to flavor, since it could lead to a decrease in production of characteristic flavor compounds (Ke et al. 1994; Fellman et al. 2003). Some

works have even suggested the possibility that edible coatings on cut fruits can supply fruits with volatile precursors (Olivas et al. 2003, 2007). Pear wedges coated with a methylcellulose–stearic acid formulation contained higher amounts of hexyl acetate throughout storage, probably due to synthesis in wounded tissue from the stearic acid contained in the coating (Olivas et al. 2003). Higher production of hexanol was observed in apples coated with alginate–linoleic acid. According to Paillard (1979), hexanol can be produced from fatty acids such as linoleic acid.

#### 7.4.1.7 Microbial Contamination

In case of minimally-processed fruits and vegetables, where natural protection (skin) has been eliminated, opportunity for microorganisms to invade and grow on the surface of the fruit is present. Incorporating antimicrobial compounds into edible films or coatings will preserve quality of fresh-cut fruits and vegetables. Since antimicrobials are needed just on the surface of the product, their application as part of a coating will help minimize antimicrobial usage (Vojdani and Torres 1990). Retention of antimicrobial on coated produce surface will depend on coating attributes (composition, hydrophilic characteristics and manufacturing procedure) and commodity type (pH and water activity), as well as storage conditions (temperature and duration) (Cagri et al. 2004). Antimicrobials most commonly used include potassium sorbate, sodium benzoate, sorbic acid, benzoic acid and propionic acid; other natural antimicrobials such as lemongrass, oregano oil and vanillin have also been used (Rojas-Graü et al. 2007).

#### 7.4.1.8 Nutritional Quality

Edible films and coatings can affect nutritional quality of fruits and vegetables. On one hand, they can be used as carriers of nutrients. On the other hand, they can produce abiotic stress, which could modify metabolism of the commodity, affecting production of nutrients. Some works have determined effects of coatings on nutritional quality, and on phenolics and other phytochemicals. Viña et al. (2007) coated Brussels sprouts with starch and analyzed effect of coating on amount of ascorbic acid and total flavonoids retained in the vegetable after storage. Han et al. (2004) found higher amounts of vitamin E and calcium on strawberries coated with chitosan, containing calcium and vitamin E in the formulation, due to diffusion of these nutrients into the fruit. Romanazi et al. (2002) observed an increase in phenylalanine ammonia-lyase activity, a key enzyme for synthesis of phenolic compounds, on grapes coated with chitosan. Edible coatings have also been used as carriers of probiotics. *Bacillus lactis* was maintained for 10 days on fresh-cut fruits under refrigeration, when applied on alginate- and gellan-based edible coatings (Tapia et al. 2007).

## 7.5 Properties of Edible Films and Coatings

### 7.5.1 *Edible Films and Coatings as Partial Barriers to Water Vapor and Gases*

Edible coating or film mainly works as a partial barrier to water vapor and gases by decreasing transmission rate of a given partial pressure difference between internal and external atmospheres. This partial barrier is conducive to a modified internal atmosphere low in oxygen and high in carbon dioxide, suppresses respiration rate and reduces transpiration losses. Scientific literature provides vast amounts of information on barrier properties of edible films; however, comparisons between different films are sometimes difficult or impossible due to use of different types of equipment and dissimilar test conditions during measurements (Tuil et al. 2000). Choosing a proper coating is complex, because it depends on specific respiration and transpiration rates of the commodity and outside environmental conditions. When applying a coating to a fruit, whole or cut, permeability to gases is modified due to the barrier formed by coating. This could lead to anaerobic respiration.

Respiration and ripening of fruits and vegetables involve gas exchange with the environment. Carbon dioxide, oxygen, water and other metabolic byproducts, such as ethylene and other volatile compounds, are main substances exchanged during storage. Surface coatings modify gas exchange rate between environment and fresh produce, and thus control transpiration, respiration and other metabolic processes that lead to loss of quality. The mechanics and main factors involved in mass transfer processes through fruit skin and coated fruits follow.

Fruits and vegetables exchange gases with their storage environment through a phenomenon known as gas diffusion. Gas diffusion is a passive transport phenomenon in which Gibbs free energy is minimized through mass transfer from a region with high concentration of a given chemical species to a region with lower concentration of the same chemical species. During this spontaneous process, the interface between the two mentioned regions (natural skin or an artificial coating) may present some opposition to the mass transfer process, affecting mass transfer rate. Unless the interface in a system completely hinders mass transfer, diffusion carries on until equilibrium is reached (i.e., when a concentration gradient ceases to exist). Interphases causing extremely high opposition to a specific compound are referred to as “impermeable”. Unidimensional steady state mass transfer, as the one witnessed in fresh produce stored under specific conditions, may be mathematically described by Fick’s first law of diffusion, which states that mass flux per unit area of a given chemical species ( $J$ ) is proportional to its concentration gradient ( $\partial\phi/\partial x$ ).

$$J = D \frac{\partial\phi}{\partial x} \quad (7.1)$$

Magnitude of the proportionality constant ( $D$ ), known as diffusivity, theoretically depends on temperature ( $T$ ), viscosity ( $\eta$ ) of medium in which diffusion is taking place, and on size of diffusing particles ( $r$ ), according to the Stokes–Einstein relation,

$$D = \frac{k_B T}{6\pi\eta r} \quad (7.2)$$

where  $k_B$  is the Boltzmann constant ( $1.380 \times 10^{-23}$  J/K). In practice, however  $D$  values for specific situations may depart from this theoretical value due to structural peculiarities or chemical affinity effects, making empirical correction necessary.

In order to have a mathematical expression to model and describe gas diffusion (normal to the surface) through biological membranes, Eq. (7.1) may be solved by separating the variables and integrating from point  $x_1$ , where concentration  $c_1$  of a given chemical species is found to be point  $x_2$ , and where concentration  $c_2$  of the same chemical species exists, yielding:

$$J = D \frac{(c_1 - c_2)}{(x_2 - x_1)} \quad (7.3)$$

Typically  $(x_2 - x_1)$  represents thickness of the membrane, and since the chemical species being diffused through the membrane is a gas, Eq. (7.3) may be substituted by Eq. (7.4):

$$J = DS \frac{\rho_1 - \rho_2}{\text{thickness}} \quad (7.4)$$

where gas concentrations and concentration gradient are expressed as a function of the partial pressure of diffusing gas on both sides of the membrane ( $\rho_1$  and  $\rho_2$ ), using Henry's law:

$$c = S\rho \quad (7.5)$$

where concentration ( $c$ ) of a gas is proportional to its partial pressure ( $\rho$ ), depending on a proportionality constant known as solubility ( $S$ ). Diffusivity multiplied by solubility of a specific gas through a specific membrane is known as permeability coefficient  $P$ , changing Eq. (7.4) to its final form as:

$$J = P \frac{\rho_1 - \rho_2}{\text{thickness}} \quad (7.6)$$

### 7.5.2 Edible Films and Coatings for Active Packaging

Besides working as partial barriers to vapor and gases, edible films and coatings can serve as carriers of ingredients to help preserve quality and improve nutritional value of fruits and vegetables. When coating is used for more than providing a barrier to external conditions, it is called active coating (Rooney 1995). Antimicrobial agents, texture enhancers and anti-browning compounds can be added to preserve quality of a commodity longer. Incorporation of some nutrients to the coating can increase nutritional value of the commodity. Aroma precursors can also be incorporated into a coating to increase flavor production (Olivas et al. 2003).



### **7.5.3 Factors Affecting the Properties of Films and Coatings**

Properties of films (or coatings) are affected by characteristics of the film, commodity, and environment, such as coating solution composition, viscosity of coating solution, coating thickness, type of product, plant variety, fruit/vegetable maturity, previous fruit treatment, fruit surface coverage (how coating adheres to surface of fruit) and external atmosphere (Hagenmaier and Shaw 1992; Banks et al. 1993; Cisneros-Zevallos and Krochta 2002). A clear understanding of how these factors affect performance of a film will aid in developing a proper coating for a specific product. Some of these factors are discussed next.

#### **7.5.3.1 Coating Composition**

Composition of film or coating affects its permeability. Chemical structure, concentration, chemical nature, physical state, method of preparation, crystallinity, polarity, orientation, presence of additives and use of compound blends will all affect performance of a film (Miller and Krochta 1997; Morillon et al. 2002). A coating containing hydrophilic compounds is not a very good barrier to water vapor, while hydrophobic substances perform well as barriers to moisture migration, since lipid-based edible coatings have low affinity for water due to their apolar nature (Morillon et al. 2002). Length of the hydrocarbon chain affects WVP (water vapor permeability) of lipid compounds. Higher the carbon number, lower the WVP, as the apolar part of the molecule generally increases with increasing number of carbons (McHugh and Krochta 1994). However, if number of carbons is higher than 18, this behavior reverses, presumably due to heterogeneous nature of coating produced (Koelsch and Labuza 1992). Lipids with higher affinity to water when used in coatings will have greater permeability to water vapor. Factors such as lipid concentration, physical state, degree of nonsaturation and chemical structure also affect WVP of lipid coatings. Morillon et al. addressed these important issues in a review published in 2002.

#### **7.5.3.2 Coating Thickness**

Cisneros-Zevallos and Krochta (2003b) published a work in which physical principles of dip-plate coatings were applied to fruit coatings. They demonstrated that internal modified atmosphere of a coated commodity depends on coating thickness, while at the same time coating thickness depends on viscosity, concentration, density and drainage time of coating solution. Debeaufort et al. (1993) found that water vapor transfer rate and permeability decreased when thickness of a triglyceride coating increased from 0 to 60  $\mu\text{m}$ .

#### **7.5.3.3 Aging of Films**

It is important to bear in mind that a coating will change over time along with its properties. Edible coatings, depending on their formulation, are subject to chemical

and physical changes that can cause degradation of polymer chains, migration of low molecular weight additives, water absorption, etc. If there is migration of plasticizer, mechanical properties of film will be affected (Anker et al. 2001).

#### **7.5.3.4 Type of Commodity**

Quality of coated fruits can vary greatly, since each fruit, even those of the same variety, is different in skin resistance, gas diffusion, fruit respiration rate, etc. Also, the effect of individual applications of coatings will vary between fruits, affecting coating thickness and proportion of pores blocked by coating material (Banks et al. 1993). Coatings developed for one variety of fruit may not be appropriate for another. Bai et al. (2003a) studied coatings for apples and found that shellac is the best coating for Delicious apples; however, this coating caused anaerobiosis on Braeburn and Granny Smith apples.

#### **7.5.3.5 Fruit Surface Coverage**

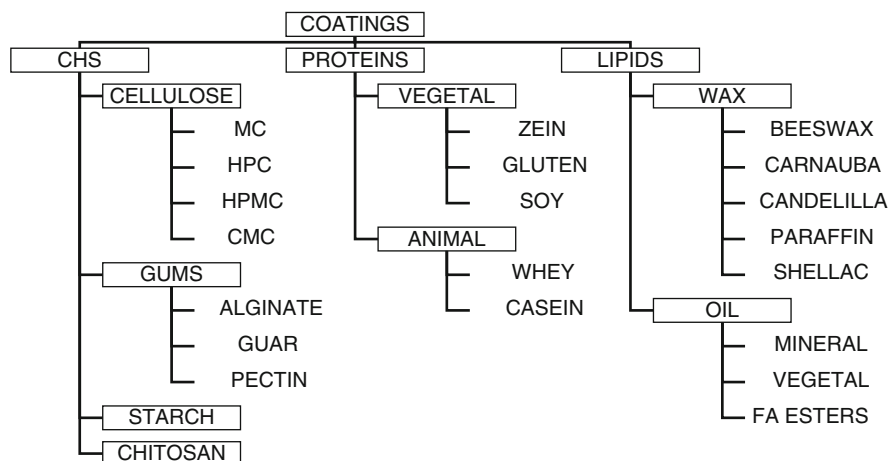
According to Banks et al. (1993), fruit coatings work as barriers to gases by blocking pores on the fruit's surface. In addition, they found that coating of fruit cuticle can affect water vapor diffusion.

#### **7.5.3.6 Storage Conditions**

Film permeability depends on relative humidity (RH) and gas composition of the environment, which can also affect properties of coating. In case of cut fruits, water activity of the coated fruit is also affected, as shown by Cisneros-Zevallos and Krochta (2002). When cut fruit was coated with a hydrophilic film, they found that the surrounding environment's RH greatly affected barrier properties of the film. Temperature also affects properties of edible films or coatings. Kester and Fenema (1989) studied WVP of films at temperatures varying from 15 to 40°C, and observed that WVP decreases when temperature decreases.

## **7.6 Composition of Edible Films and Coatings**

Edible films and coatings are composed of hydrocolloids, which consist of either polysaccharides or proteins, or hydrophobic compounds (e.g., lipids or waxes). Edible films may also be composed of a mixture of hydrocolloids and hydrophobic compounds (composite films or coatings). Figure 7.1 shows the most common compounds used in edible films and coatings.



**Fig. 7.1** Main components of edible films and coatings for intact and minimally processed fruits and vegetables (CHS carbohydrates; FA fatty acids; MC methylcellulose; HPMC hydroxypropyl-methylcellulose; HPC hydroxypropylcellulose, CMC carboxymethylcellulose)

## 7.6.1 Carbohydrates

### 7.6.1.1 Chitosan

The compound chitosan comes from marine invertebrates and is a derivate of chitin, which after cellulose, is the most abundant polysaccharide resource on earth (Tuil et al. 2000). Chitosan is a high-molecular-weight cationic polysaccharide composed of (1 → 4)-linked 2-acetamido-2-deoxy-β-D-glucopyranosyl and 2-amino-2-deoxy-β-D-glucopyranosyl units (Sebti et al. 2005), and produces transparent films. Chitosan is not water-soluble, so a coating solution comprised of weak organic acid (acetic acid) must be used. Chitosan has been shown to be a natural food preservative, though the antimicrobial mechanism involved is not well elucidated. It is believed that positively charged chitosan molecules interact with negatively charged microbial cell membranes, causing change in microbial cell permeability that leads to leakage of cell constituents (No et al. 2007).

Chitosan films or coatings can increase shelf life and preserve quality of fruits and vegetables by decreasing respiration rates, inhibiting microbial development and delaying ripening. They have been used on fruits and vegetables with good results, showing antimicrobial activity against *Bacillus cereus*, *Brochothrix thermosphacta*, *Lactobacillus curvatus*, *Lactobacillus sakei*, *Listeria monocytogenes*, *Pediococcus acidilactici*, *Photobacterium phosphoreum*, *Pseudomona fluorescens*, *Candida lambica*, *Cryptococcus humiculus*, and *Botrytis cinerea* (Devlieghere et al. 2004; Romanazzi et al. 2002). Chitosan is considered ideal coating for fruits and vegetables, mainly because it can form a good film on the commodity's surface and can control microbial growth (Muzzarelli 1986; No et al. 2007).

Even though the high hydrophilic character of chitosan films (Sebti et al. 2005) could adversely affect their properties and use as coatings for fresh-cut fruits and vegetables, they have been used nevertheless on cut fruits such as peeled litchi (Dong et al. 2004) and fresh-cut Chinese water chestnuts (Pen and Jiang 2003) with good results.

Chitosan coatings have also been used on grapes to control incidence of *Botrytis cinerea*. It was observed by Romanazzi et al. (2002) that besides having a direct effect against *B. cinerea*, chitosan caused an increase in phenylalanine ammonia-lyase activity (a key enzyme for synthesis of phenolic compounds, usually characterized by antifungal activity). They concluded that the inhibitory effect of chitosan originates from a combination of its antifungal properties and ability to stimulate defense responses in the host. Similar results were observed for strawberries where *Botrytis cinerea* and *Rhizopus stolonifer* were inoculated and then coated with 1% chitosan; decay decreased and lower synthesis of anthocyanin was observed, compared to strawberries treated with fungicide. El-Ghaouth et al. (1997) applied chitosan coatings on strawberry, bell pepper and cucumber, observing reduced lesion development due to *Botrytis cinerea* and *Rhizopus stolonifer*, as well as delayed ripening. Others found (El-Ghaouth et al. 1992) that chitosan-coated tomatoes showed reduction in respiration rate and ethylene production, were firmer with less decay, and had less red pigmentation, compared to noncoated tomatoes. Litchi has also been coated with chitosan, where there was delay in reduction of anthocyanin content and increase of PPO activity (Zhang and Quantick 1997; Jiang et al. 2005).

Composite coatings containing chitosan are likewise a good option for fruits and vegetables. Chitosan coatings containing oleic acid had good water retention properties on coated strawberries (Vargas et al. 2006), while apples coated with *N,O*-carboxymethyl chitosan films and placed in cold storage could be maintained in fresh condition for more than 6 months (Davies et al. 1989).

Chitosan has been approved for use as a food additive in Japan and Korea. In the U.S., Generally Recognized as Safe (GRAS) notices were submitted (by a “notifier”) to the FDA in 2001 and 2005 to evaluate chitosan (from shrimp) and its suitability for use; however (at notifier’s request) the FDA ceased evaluation of both notices (No et al. 2007; US FDA/CFR 2006).

### 7.6.1.2 Starch

Starch is an abundant, inexpensive polysaccharide obtained from cereals, legumes, and tubers, and is extensively utilized in the food industry. Starch is a polysaccharide consisting of  $\alpha$ -(1  $\rightarrow$  4) D-glucopyranosyl units with D-glucopyranosyl chains linked by  $\alpha$ -(1  $\rightarrow$  6) glycosidic bonds. It is composed of two macromolecules, amylose, essentially linear, and amylopectin, highly branched. Ratio of amylose and amylopectin varies with source. Regular or standard wheat, corn, and potato starches generally contain lower amounts of amylose than those of most legumes (Hoover and Sosulsky 1991; BeMiller and Whistler 1996). Films formed with starch are often very brittle and have poor mechanical properties (Peressini et al. 2003). These films are formed by drying of a gelatinized dispersion, as hydrogen bonds form

between hydroxyl groups (Lourdin et al. 1995). Since these interactions are weak, mechanical properties of starch-based films are of poor quality. To overcome this problem, it is necessary to blend starch with other compounds or chemically modify the starch (Tuil et al. 2000).

Proportion of amylose and amylopectin within starch will affect film-forming properties. A higher proportion of amylose will improve mechanical properties of the film (Han et al. 2006), as the branch-on-branch structure of amylopectin interferes with intermolecular association and disrupts film formation (Peressini et al. 2003). Rice and pea starch films (30 and 40% amylose, respectively, by weight) containing glycerol as plasticizer (starch:plasticizer ratio of 2:1) were found to have low oxygen permeability and good elastic properties, with pea films showing highest elasticity and WVP (Mehyar and Han 2004). Han et al. (2006) reported higher oxygen permeability and lower elongation (one order of magnitude) for pea starch films (~40% amylose) with glycerol as plasticizer (starch:plasticizer ratio 3:2). Nevertheless, these starch films still showed low oxygen permeability compared to other films, while WVP of starch films was observed to be comparable to that of protein films.

García et al. (1998) compared quality of strawberries coated with starch from different sources (corn starch – 25% amylose; potato starch – 23% amylose; high-amylose corn starch – 50% amylose; high-amylose corn starch – 65% amylose), and found a significant effect of amylose on color, weight loss and firmness of coated strawberries. Strawberries coated with 50% and 65% high-amylose starches best retained their quality attributes compared to other treatments.

Since starch films are hydrophilic, their properties will change with fluctuations in RH; for example, their barrier properties decrease with increasing RH. Starch is therefore not the best option when working with minimally-processed high-water activity commodities. Bai et al. (2002) coated apples with starch solutions and observed high gloss at the beginning of storage. However, they observed a large decrease in gloss during storage, though firmness, internal oxygen and carbon dioxide concentrations of starch-coated apples had values similar to shellac-coated apples (a coating used commercially).

### 7.6.1.3 Cellulose

Cellulose, the most abundant natural polymer on earth, is composed of linear segments (1 → 4)-linked β-D-glucopyranosyl units. Although very inexpensive, cellulose is difficult to use as coating, because of its water-insolubility and highly associated crystalline structure. However, some cellulose derivatives produced commercially such as carboxymethylcellulose (CMC), methylcellulose (MC), hydroxypropylcellulose (HPC), and hydroxypropylmethylcellulose (HPMC), can overcome limitations associated with native cellulose. Due to the cellulose linear structure, these derivatives tend to form good films, though film properties will depend on cellulose structure and molecular weight (Park et al. 1993; Ayranci et al. 1997). Ayranci et al. (1997) found that WVP of HPMC films decreased with increasing molecular weight of HPMC. However, Park et al. (1993) observed the opposite result for MC

and HPC films, wherein WVP of these films increased with increasing molecular weight of HPC and MC. Comparison between MC, HPC, and CMC coatings, applied to shelled pecan nuts, showed CMC to be the best coating material for this application (Baldwin and Wood 2006). CMC coating imparted sheen and delayed rancidity; however firmness was not preserved. WVP of HPMC and MC films was also observed to decrease with increasing polymer molecular weight (Ayranci et al. 1997). Further, MC has been used to preserve green color and firmness of avocados and lower their respiration rates during storage (Maftoonazad and Ramaswamy 2005). Coating apricots and green peppers with a composite film of MC and stearic acid effectively reduced water loss; when coated with a film containing citric acid or ascorbic acid, vitamin C loss was also reduced (Ayranci and Tunc 2004).

Carboxymethylcellulose has been widely used as coating for fruits. Some coating formulations containing CMC are already on the market, such as Tal Pro-long™ and Semperfresh™. Tal Pro-long™ (or Pro-long) is composed of sucrose polyesters of fatty acids and the sodium salt of CMC. Semperfresh™ is composed of sucrose esters of fatty acids, sodium salt of CMC, and mono- and diglycerides. These coatings have been shown to retard ripening of fruits (Fig. 7.1). Quality of cherries coated with Semperfresh™ can be preserved for longer periods, reducing weight loss and preserving firmness and skin color. Another cellulose product on the market, Nature Seal™, is composed of cellulose derivatives, but without sucrose fatty acid esters. A combination of Nature Seal™ and soy protein coatings carrying anti-browning agents and preservatives prolonged shelf life of cut apples by 1 week when stored at 4°C (Baldwin et al. 1996).

#### 7.6.1.4 Alginate

Alginate, the sodium salt of alginic acid, is a block copolymer of  $\beta$ -D-mannuronic acid (M) and  $\alpha$ -L-guluronic acid (G), and is isolated from brown seaweed (Sime 1990). Alginate forms strong, translucent, glossy films. Compared to CMC, gelatin, whey protein isolate, potato starch and sodium caseinate films, those of sodium alginate have lowest WVP, oxygen permeability and elongation percentage and highest tensile strength (Wang et al. 2007). Sodium alginate films are soluble in water, acid, and alkali (Wang et al. 2007), making them a good choice for coating whole fruits and vegetables. These films are not as effective for coating minimally-processed fruits and vegetables, though incorporation of calcium cations to decrease solubility of polymers comprising such films would make them a viable option (Olivas et al. 2007).

Composition of alginate (M:G ratio) also affects WVP of films. Alginate-Ca<sup>2+</sup> films with higher concentrations of G have lower WVP than films with higher concentrations of M due to greater ability of G to form intermolecular cross-links via calcium salt-bridges. Although properties of alginate films are influenced by surrounding RH, alginate-Ca<sup>2+</sup> films retain their strength, even at high RH values (Olivas and Barbosa-Cánovas 2008).

Alginate-Ca<sup>2+</sup> coatings have been used successfully to prolong shelf life of fresh-cut Gala apples without causing undesirable anaerobic respiration. These coatings minimized weight loss and browning, and preserved firmness during storage.

## **7.6.2 Proteins**

Proteins can form edible films due to the ability of their side chains to form intermolecular cross-links. Properties of these films depend on the nature of these linkages. In general, protein films are considered to have good gas barrier properties, though their water barrier properties are generally poor (Gennadios et al. 1994), since the latter depend on the RH of the environment and/or water activity of the food. Proteins generally used as coatings for fruits and vegetables are reviewed in paragraphs that follow.

### **7.6.2.1 Zein Coatings**

Zein is a protein composed of prolamines found within corn endosperm, and is soluble in aqueous alcohol. Zein films have strong yellow color relative to HPMC, whey protein concentrate, shellac or whey protein isolate coatings (Trezza and Krochta 2000). Applied to tomatoes, zein coatings will delay color change, weight loss and softening without ethanol production (Park et al. 1994). Zein coatings containing vegetable oils, citric acid and antioxidants have been used to prevent rancidity of nuts and inhibit moisture transfer from fruit pieces in dry mixes (Andres 1984). Park et al. (1996) found that apples coated with zein solutions experienced decrease in respiration rate, whereas zein-coated pears had an increased respiration rate, compared to uncoated controls. Nevertheless, zein coatings delayed weight loss in both apples and pears during storage. A zein coating formulation, containing 10% zein and 10% propylene glycol dissolved in aqueous alcohol, was developed for Gala apples by Bai et al. (2003b). This coating maintained overall fruit quality comparable to commercial shellac coating. Special attention should be taken when coating fruits and vegetables with zein solutions, since, zein coatings can become white in color on contact with water, depending on the coating's concentration (Bai et al. 2003b).

### **7.6.2.2 Gluten and Soy Proteins**

Gluten is the main storage protein in wheat and corn. Gluten films have good oxygen and carbon dioxide barrier properties, but exhibit relatively high WVP (Gennadios and Weller 1990). Mechanical treatment of gluten leads to disulfide bridge formation created by the amino acid, cysteine, which is relatively abundant in gluten. Wheat gluten has been used to preserve quality of fruits and vegetables. Peanuts were coated with a composite coating of soy protein isolate and wheat gluten with the objective of preventing fat deterioration. Soy protein also contains cysteine residues that can form disulphide bridges. Soy protein films are therefore similar to gluten films in mechanical properties. Baldwin et al. (1996) improved properties of Nature Seal™ coating on sliced apples and potatoes by adding soy protein, which reduced coating permeability to oxygen and water vapor.

### 7.6.2.3 Whey

Milk proteins contain 20% whey protein of which  $\beta$ -lactoglobulin is the main protein component. Whey protein is water-soluble, but  $\beta$ -lactoglobulin denatures when heated, exposing internal sulfur groups of cysteine, which then cross-link to form an insoluble film (McHugh and Krochta 1994). Whey protein has been studied extensively as a coating for different foods, including intact and minimally-processed fruits and vegetables. Whey protein was shown to produce a translucent and flexible film with excellent oxygen and aroma barrier properties at low RH (McHugh and Krochta 1994; Miller and Krochta 1997). Though some have found that whey protein films provide a poor moisture barrier, others have reported that incorporation of lipids reduces WVP of whey protein films (McHugh and Krochta 1994; Shellhammer and Krochta 1997; Pérez-Gago and Krochta 2001). Another study indicated that WPI (whey protein isolate) films are good gas barriers, but that they are influenced by the RH of the environment, affecting resistance of coating to oxygen and carbon dioxide permeation. As RH decreased, resistance of the coating to gas transfer increased. At low RH, oxygen decreased and carbon dioxide increased in coated fruits. At RH values ranging from 70 to 80%, anaerobic metabolism was induced due to low oxygen levels (Cisneros-Zevallos and Krochta 2003a).

Whey protein-based coatings were more effective in reducing enzymatic browning of Golden Delicious apple slices than HPMC-based coatings - probably due to the antioxidant effect of amino acids, such as cysteine and/or higher oxygen barrier imparted by the protein. No differences in browning were found between WPI- and WPC- (whey protein concentrate) based films. Lipid inclusion also affected degree of browning (measured with a colorimeter), but these differences were less evident at the end of storage, as assessed by a sensory panel. Results suggest that addition of anti-browning agents to whey protein coatings, combined with proper storage conditions, could significantly extend shelf life of fresh-cut apples (Pérez-Gago et al. 2005a).

### 7.6.3 Lipids

Lipids can be included in formulation of edible coatings or films within a lipid-based film, as a single layer of lipids dispersed in a hydrocolloid network, or as a secondary layer (a lipid layer over a hydrocolloid layer). Coatings containing lipids generally have good moisture barrier properties, since lipids have very low affinity for water (Krochta 1997). The properties lipids confer to films and coatings will depend on the characteristics of the lipid component, such as its physical state, degree of saturation and chain length of fatty acids. Saturated long-chain fatty acids provide coatings with best water vapor barrier properties (among fatty acids), as they produce more densely packed structure and have less mobility than unsaturated short-chain fatty acids (Kamper and Fennema 1984). Lipids which are solid at the desired storage temperature will form coatings with better water vapor barrier



properties than lipids which are liquid under same conditions, mainly because solubility of water vapor in lipids is lower in films having more ordered molecular organization (Kester and Fennema 1989).

### 7.6.3.1 Carnuba and Shellac Wax

Carnauba is a natural plant wax and is GRAS (generally recognized as safe). It is relatively permeable to gases, and in microemulsion form, is quite shiny. The primary problems with carnauba wax are its loss of gloss during storage and its relatively high gas permeability, which does not effectively delay ripening (Baldwin et al. 1999). However, it is an excellent barrier to water vapor and can be combined with shellac to create a coating of moderate permeability to gases and low permeability to water vapor. Natural Shine™ 8000 (carnauba wax) is used to reduce oxygen transfer into and water vapor out of the fruit, while shellac is used to give a shiny appearance. Johnfresh™ is composed of both carnauba wax and shellac.

Most Delicious apples marketed in the U.S. are coated with shellac or shellac combined with carnauba wax (Bai et al. 2002). Shellac and carnauba wax are often used commercially as a coating for apples and citrus fruits to improve their appearance by adding gloss, to prevent water loss leading to shriveling and loss of marketability, and to maintain quality through delayed ripening and senescence. Unfortunately, both materials are also associated with non-food uses; shellac also has problems with low gas permeability, which can lead to delayed ripening in some fruits (Baldwin et al. 1999) and cause anaerobic conditions. The apple industry is especially concerned that consumers may object to shellac, which does not currently have GRAS status. Shellac has further problems with whitening, or “blushing” as it is referred to in the industry, where water condenses on coated fruit surface after removal from cold storage. Nevertheless, shellac is recognized as one of the shiniest coatings available, and was found to improve appearance of apples. In one study, subsequent sales of red and green apple cultivars, such as Delicious and Granny Smith, respectively, increased due to shellac coatings (Bai et al. 2003a).

### 7.6.3.2 Beeswax

Beeswax can be used as a composite film. Han et al. (2006) added beeswax to pea starch films and found a decrease in WVP and an increase in oxygen permeability with beeswax concentration higher than 30%. Beeswax-pea starch films were homogeneous and translucent. Thickness of pea starch coating significantly increased with addition of beeswax (Han et al. 2006). Beeswax has been used in composite coatings in combination with WPI, WPC, and HMPC to preserve intact fruits such as plums (Pérez-Gago et al. 2003a) and minimally-processed fruits, such as apple slices and persimmon pieces (Pérez-Gago et al. 2005a, b; Pérez-Gago et al. 2006). In most cases, weight loss was not prevented with beeswax, with the exception of coated plums and persimmon pieces (see Tables 7.1 and 7.2).

#### **7.6.4 Other Films and Coatings**

Other compounds have been used to form coatings for fruits and vegetables, such as pullulan, gellan, aloe vera, cactus–mucilage and fruit puree. Aloe vera coatings have been studied for their ability to preserve quality of cherries (Martínez-Romero et al. 2006) and grapes (Valverde et al. 2005). Martínez-Romero et al. (2006) found reduction in the microbial population of coated cherries, while control cherries experienced considerable increase in microbial population; aloe vera coatings also preserved texture and color, and decreased water loss in cherries. Valverde et al. (2005) extended storage life of grapes at 1°C from 7 to 35 days, with reduction in microbial load also observed for coated grapes. A cactus–mucilage film was studied to preserve quality of strawberries (Del-Valle et al. 2005). Coatings containing a mixture of fruit puree and hydrocolloid have likewise been used. Alginate–apple puree was used as coating to preserve quality of apple slices (Rojas-Graü et al. 2007).

#### **7.6.5 Additives in Films and Coatings**

Additives in coatings and films have been used for different purposes. Those already discussed are shown in Table 7.3. Anti-browning compounds, antimicrobial agents, texture enhancers, nutrients, probiotics and flavors are examples of some additives used in coatings. However, plasticizers are the main additives used in films and coatings. Plasticizer is added to the formulation to improve mechanical properties of films and coatings. Without plasticizers, most films and coatings are brittle, and it is difficult to form a homogenous coating. Plasticizer combines with the main component of the film, moving the component's chains apart, and thus reduces rigidity of the structure (Guilbert and Biquet 1996). Plasticizer also attracts water molecules around it, which reduces intermolecular interactions of the main component (Ke and Sun 2001). Major plasticizers used have been polyols such as glycerol, sorbitol and polyethylene glycol (Sothornvit and Krochta 2005), but lately, disaccharides such as sucrose and monosaccharides (e.g., fructose, glucose, and mannose) have been investigated (Zhang and Han 2006). Monosaccharides have proved to be effective as plasticizers (Olivas and Barbosa-Cánovas 2008; Zhang and Han 2006), exhibiting films with lower WVP compared to those containing polyols as plasticizers. Whey protein films that have been plasticized with sucrose have excellent oxygen barrier properties and display high gloss; however, sucrose tends to crystallize with time and lose its properties (Dangaran and Krochta 2007). How plasticizers affect properties of films will depend on factors such as type of plasticizer (molecular size, total number of hydroxyl groups, configuration), its concentration and type of polymer. Plasticizers normally generate a homogenous mixture without phase-separation. However, some works attribute phase separation observed between plasticizer and polymer to an excess of plasticizer or incompatibility between plasticizer and polymer (Aulton et al. 1981; Donhowe and Fennema 1993; Ayranci et al. 1997; Jagchud and Chinnan 1999).

## 7.7 Challenges and Future Trends

Not much work has been done to identify the relationship between the internal atmosphere caused by the coating and velocity of physiological ripening processes, such as respiration, tissue softening, metabolic reactions, production of metabolites and secondary compounds generated during storage. Most work in this area has dealt with changes in quality due to application of coating.

To preserve quality of fruits by means of decreasing oxygen in the internal atmosphere, special care should be taken not to minimize oxygen concentration to a point where anaerobic respiration may occur. Thus, for each fruit, it is necessary to know the optimum oxygen concentration at which rate of consumption is minimized without promoting development of anaerobic respiration.

Although extensive research has been done in the area of edible films and coatings for fresh and minimally-processed fruits and vegetables, most work has been empirical in nature. Many factors should be studied to understand their effects on coating performance for specific types of produce and properties such as:

- Properties of coating solution: composition, concentration, viscosity and density
- Properties of film: mechanical, gas and vapor barrier properties
- Properties of coating: thickness, temperature, and atmospheric conditions
- Properties of the produce (fresh or minimally-processed): respiration rate, water activity, composition, etc

Thus it is necessary to go beyond empirical studies to investigate how these factors/properties will affect the final product and how they can be controlled or modified to enhance quality.

The study of edible coatings for fruits and vegetables deals with a wide range of scientific fields including: chemistry, biochemistry, horticulture, food science and engineering. The final objective should be to develop edible films and coatings that can be marketed commercially. Thus, to place edible coatings on the market, future research will need to concentrate on whole interdisciplinary works that provide comprehensive information that addresses all important issues relative to development of a specific coating for a specific product.

Future research should include:

- Characterization of physicochemical properties of coating solutions (composition, concentration, solubility, viscosity, density, surface tension, etc), including evaluation of how variation in chemical and physical conditions (e.g., pH, temperature, time, etc.) could affect these properties.
- Characterization of films intended for use as coatings, under similar conditions as the commodity being treated. This includes gas and vapor permeability, mechanical and sensorial properties, thickness, solubility, digestibility, etc. Focus should be on understanding possible changes to properties of a film when chemical and physical conditions are modified, simulating likely events a commodity could face during actual handling and storage.
- Study of metabolic reactions occurring within commodities and the extent to which they can be modified with coatings. This includes not only respiration,

but also metabolic reactions conducive to production of biochemicals that could be affected by modified atmosphere, or by the commodity itself while in contact and reacting with chemicals contained in a coating.

- Study of internal gas composition of coated commodities and relationships between internal atmosphere and velocity of physiological ripening processes, such as respiration, metabolic reactions and production of secondary compounds during storage.
- Study of impact of coatings on quality and shelf life of commodities, taking into account all possible conditions they could face during handling and storage.
- Determination of optimal methods of applying coatings most conducive to obtaining high quality product at lowest possible cost.
- Study of consumer acceptability of coatings.
- Study of impact of edible coatings on final cost of commodities.

Studies should focus on commercial viability of edible film and coating technology for fruits and vegetables. There is also a need to study effects of coatings on biochemicals and secondary metabolites.

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