Paper no.: 12 Paper Title: Food Packaging Technology Module-21: Packaging of Fresh Fruits and Vegetables

13.1 Introduction

The demand for fresh fruits and vegetables is continuously increasing but their preservation is still a challenge for food industry as they have ability to respire. Apart from common physico-chemical and microbiological degradations there can be degradations from respiration, transpiration and ripening. Such reactions are influenced by processing, storage and distribution condition which deteriorates initial quality of fruits and vegetables. Temperature and processing can help in preservation if properly controlled. Lower temperature reduces the rate of reaction and packaging may avoid dehydration as well as vapour saturation.

13.2 Changes in the quality of fruits and vegetables

Several changes take place in the quality of fruits and vegetables such as changes in sensory quality, microbiological quality and nutritional value. Sensory attributes are time-dependent and refer to flavor, body and texture as well as color and appearance, which evolve with maturation and aging. Microbiological quality of fresh fruits and vegetables is of great importance from a safety point of view. Spoilage microorganisms are involved in produce degradation but generally do not directly affect human health except fungi mycotoxin. Although fruits have generally been considered safe from pathogens, some might be found sporadically in vegetables. Sanitation methods are employed but are not totally effective as microorganisms can locate in subsurface structures of produce and survive biocidal washes.

The nutritional value of fresh fruits and vegetables is also part of their quality and depends on the variety of the produce and its maturity. The initial content of phytonutrients in fresh produce is important, but their bioavailability depends on the extent of release of phytonutrients during digestion and subsequent absorption.

13.2.1 Respiration and Ripening

Fruits and vegetables are live product and obtain all the nutrients for their growth from the parent plant. When detached from it, they draw on their own reserves to achieve aerobic respiration and maintain their cellular integrity. During respiration, stored carbohydrates are broken down into glucose, which is oxidized into CO_2 , water and energy via several enzymic steps. As soon as these substrates become unavailable, other carbonated resources, such as constitutive protein or membrane lipids, are used, leading to the death of the product. Thus, the potential shelf life of fruits and vegetables is closely related to their respiration rate, expressed as the quantity of O_2 consumed (or CO_2 released) per time and per mass of produce.

The respiration rate is specific to a particular fruit or vegetable, in terms of species and varieties, but may differ depending on its maturity, mainly in climacteric fruits. Fruits are classified as climacteric (peaches, apples, kiwis, etc.) or non-climacteric (citrus fruits, small red fruits, etc.) according to their ability to synthesize the growth hormone

ethylene in an autocatalytic way or not, respectively. For climacteric fruits, an increase in respiration is associated with an increase in ethylene: when the respiration rate reaches a maximum value, which is called respiration crisis, ethylene production also reaches its maximum, which is called climacteric crisis. During the biosynthesis of ethylene, the product ripens and several biochemical and structural changes occur, such as softening due to the degradation of pectin or internal browning caused by the enzymic oxidation of phenolic compounds.

Minimal processing such as peeling, slicing, and destoning cause mechanical stresses that result in an increase in respiration activity from 2 - 8 fold and stimulate ethylene production from 5 - 20 fold. By increasing the wounded surface area, mechanical stresses also result in enzymic alterations in fresh commodities such as enzymic browning or pectin degradation, and increased proliferation of microbial spoilage.

13.2.2 Dehydration

In association with aerobic respiration, water vapor is produced and natural dehydration occurs, caused by diffusion of water vapor from the high-concentration compartments in fresh product to the low concentration in the surrounding environment. Marketing of items that have suffered significant water loss becomes difficult. As fruits and vegetables contain over 90% water, a loss of 5% or more water is visually noticeable, lowering the grade of the produce and resulting in a decrease in its commercial value. Major effects of water loss are a reduction in weight and a wilted appearance; there is also a reduction in nutritional value as the amount of water-soluble components decreases when water is released, a loss in aroma and flavor, and an enhanced sensitivity to chilling injuries. In the case of climacteric fruits, water loss can accelerate the climacteric crisis as observed in avocados. Although excessive dehydration is not recommended whatever the product, moderate dehydration may be beneficial to some vegetables such as bulbs or common mushrooms.

13.2.3 Effect of temperature

It is well known that temperature is one of the major factors affecting shelf life of fresh product and needs to be positively controlled during handling and marketing of such commodities. Respiration of raw fruits and vegetables increases 2-3 folds for every 10°C rise in temperature within the range of temperature usually encountered in the distribution and marketing chain (4–30°C). In the case of fresh-cut produce, this factor may increase by 3-8 folds. By decreasing temperature, the rate of enzymic reactions and respiration is reduced. For climacteric fruits, postharvest storage at low temperatures might be necessary to allow ripening, such as for some pears or might accelerate their ability to produce ethylene, such as for kiwifruit. Although refrigeration appears to be the most appropriate method for fresh produce preservation, it is not always easy to achieve in retail distribution. In addition, it does not suit all commodities as observed by the development of chilling injuries (e.g., core flush or soft scald observed in most exotic fruits) that are often combined with a rise in respiration rate.

13.2.4 Effect of composition of gas

Another factor affecting respiration and consequently the overall quality of fresh produce is gas composition. Usually, lowering the O_2 level is really effective in reducing respiration, but anoxia (a switch to anaerobic catabolism and growth of anaerobic flora that produce undesirable off-flavors and off-odors) should be avoided. High CO_2 levels (more than 10%) might also reduce the respiration of several commodities such as onions, strawberries, or cucumbers and can limit the production of ethylene as observed in kiwifruit or inhibit its production, as observed in tomatoes. High CO_2 levels induce a bacteriostatic effect on aerobic bacteria but might lead to the development of anaerobic flora.

Injuries might occur when a fresh product is exposed to a level of CO_2 above its tolerance limit: formation of brown spots on lettuce or yellowing of mushrooms are common visual degradations caused by a high CO_2 content. Together with CO_2 , 1-methylcyclopropene (1-MCP) is also considered as a competitive inhibitor of ethylene action and can be used to delay ethylene production and the respiration crisis. As the optimal combination of O_2 and CO_2 greatly depends on the respiratory activity of the product (values range from less than 35 up to 300 mg O_2 kg⁻¹ h⁻¹) and its sensitivity to CO_2 , there is no unique atmosphere composition that could be applied to all fresh commodities. Critical concentrations of O_2 and CO_2 exist for each fruit or vegetable. Packaging materials must be properly chosen for each product; otherwise the headspace atmosphere may be inefficient or detrimental.

13.3 MODIFIED ATMOSPHERIC PACKAGING (MAP)

In 1930s, controlled atmospheres were used in storage rooms during shipment and transportation to preserve the freshness of fruits. The gas machinery allowed the maintenance of low O_2 and moderate to high CO_2 levels. It can be and is increasingly extended to other gases (e.g., argon and xenon) or vapors (water vapor, ethylene, aroma compounds, etc.). In passive MAP, gas and vapor exchanges occur between the produce and its surroundings as well as through the packaging material. If there is microbial contamination, respiration pathways of microorganisms (aerobic or anaerobic) are also involved in gas exchanges. Initially the headspace composition is air and then, after a transient period, it reaches a steady state when gas and vapor permeation through the material balances gas and vapor consumption and production from the produce. This steady state atmosphere must be as close as possible to the optimal recommended atmosphere; otherwise it might be detrimental to the quality of the commodity.

Hence, it is essential to select a film with suitable gas and vapor permeabilities. It should be stressed that most synthetic polymer films exhibit too low a permeability to gases and vapors and most often need to be perforated (micro-holes) to allow sufficient gas exchange. Whatever the packaging material used, the produce can be exposed to unsuitable gas compositions during the transient period, thus preventing the positive

effects of the steady state atmosphere. e.g. in mushroom packages, the transient CO₂ peak induced browning.

Active MAP has been developed to overcome this drawback and suppress or reduce the transient period. Gas flushing with an inert gas mixture is used to quickly reach a desired ratio of O_2 and CO_2 and suppress the transient period of passive MAP so that the initial headspace composition is different from normal air. Active MAP can also be achieved by the release or absorption of gases or vapors from or by active agents in combination with gas/vapor permeation. This opens up new possibilities for packaging such as the controlled release of antimicrobial agents in case of temperature abuse and/or the removal of unsuitable substances such as ethylene when produced. Such systems are commercially available for MAP of fresh produce.

13.3.1 Passive Modified Atmosphere Packaging

Bi-axially oriented polypropylene (BOPP), low density polyethylene (LDPE), and polyvinyl chloride (PVC) are synthetic polymers used as trays, pouches, or overwraps for packing fresh fruits and vegetables. However, in most cases, they need to be perforated to allow sufficient gas and vapor transfer. Two kinds of perforated materials are available: (a) macroperforated films that slightly protect the produce against dehydration by slowing down water vapor transfers and (b) microperforated films that provide a large range of O₂ permeabilities (from 190 to 42,000 mL O₂ m⁻² 24 hr⁻¹) and can be tailored to the O₂ requirement of most produce. However, they exhibit several physical limitations. CO₂ diffuses through the film at a similar rate to O₂. Therefore, it is impossible to achieve low O_2 (1–5%) without accumulating high CO_2 (15–20%). Thus, these films are applicable only for products that can tolerate high CO₂ without experiencing injury. This is due to the permselectivity of materials, which is the ratio of the CO_2 permeability coefficient to the O_2 permeability coefficient; this ratio is 1 for perforated films. Commonly, in nonperforated synthetic films, the permselectivity is around 4-6. Another drawback is that detrimental changes in the steady state modified atmosphere cannot be avoided if the chill chain is disrupted since the activation energy (Ea) for gas permeation through synthetic films is two-fold lower than the Ea for respiration rates of most of fresh produce. This means that O₂ consumption and CO₂ production by fresh produce are faster than diffusion of both gases through the packaging during temperature abuse. When synthetic films are perforated, the effect of temperature on permeation through pores (air) is much less compared to its effect on permeation through the polymer. As permeation through the pores accounts for most of the total permeation through a perforated film, the activation energies for perforated films are close to zero. Thus, perforated films are not able to compensate for the effect of temperature variations during storage on the respiration rates of fruits and vegetables.

13.3.1.1 Protein-based materials

The development of hydrophilic materials such as protein-based films appears to be of great interest to replace perforated materials in many applications. The film-forming

ability of polymers such as proteins and polysaccharides from renewable resources is known and widely used for a long time, especially in the fruit and vegetable industry. Coating of fruits and vegetables is commonly employed to offer consumers a product with a shiny and glossy appearance; it also contributes to the establishment of internal modified atmospheres and limits physiological decay, dehydration, and microbial spoilage.

Although most of the commercial plastic films are relatively unaffected by relative humidity (RH), gas permeability of protein-based films sharply increases at high RH, such as in fresh fruit and vegetable packaging. For example, at 23°C, CO₂ permeability is 570 times lower for wheat gluten film stored at 0% RH than for LDPE stored under the same conditions, and it is 10 times higher for wheat gluten film stored at 95% RH than for LDPE stored under the same conditions. The same effect was observed with O₂ permeability but to a lesser extent. Consequently, the permselectivity of wheat gluten films is also affected by RH and ranges from 5 in a dry atmosphere to 30 under 95% RH. The increasing RH effect has been attributed to a modification of the wheat gluten network structure and polymeric chain mobility, related to a change from a glassy to a rubbery state. The fact that CO₂ permeability is more affected than O₂ can be related to specific interactions between CO2 and the water-plasticized protein matrix under high RH conditions. Water sorption could provide better accessibility to active sites for CO₂ sorption onto the protein matrix, mainly hydrogen binding with glutamine residue. Thus generated modified atmospheres can be both low in O₂ and CO₂, as described for MAP of common mushrooms.

Temperature also affects gas permeability of protein-based films and this is more pronounced in films stored at high RH as observed for O_2 and CO_2 permeability as well as ethylene permeability of wheat gluten films. When stored at high RH, ethylene permeability of wheat gluten increases 5 times when temperature increases from 23°C to 45°C. Such behavior is of great interest in delaying ripening of climacteric produce during shipping and distribution in cases of temperature abuse. The E_a for CO_2 permeation of these materials at high RH is close to that of CO_2 production for almost all fresh fruits and vegetables. This means that wheat gluten films should be able to self-adjust the CO_2 content in cases of temperature abuse. However, despite low cost and interesting functional properties, wheat-gluten-based films exhibit poor mechanical properties at both low and high RH. Combination with other materials or fillers appears to be the best way to overcome this defect, but problems of compatibility as well as loss of biodegradability have to be taken into consideration.

13.3.1.2 Fiber-based and protein composites

Combinations of wheat gluten proteins with fiber-based materials such as paper and socalled composite materials have already been studied to overcome their poor mechanical properties. Recently, combinations of wheat gluten proteins with nano-fillers such as montmorillonite (MMT) have been demonstrated to be an efficient way to reduce the drawback of moisture sensitivity. Thus, combining wheat gluten proteins with paper and MMT to produce so-called nano-composite materials could make the most of the functional properties of wheat gluten proteins while overcoming their drawbacks of insufficient mechanical properties and moisture sensitivity.

Paper coated with wheat gluten solution can no longer be considered as porous regarding O₂ and CO₂ permeability; the presence of MMT in the wheat gluten network did not significantly affect permeability. As permeability is known to be governed by two mechanisms (diffusion and sorption), it was assumed that introduction of MMT did not change solubility nor diffusivity of O_2 and CO_2 . It should be pointed out that O_2 and CO_2 permeability of both coated and nano-composite material increased with increasing RH. As this phenomenon was also observed with pure wheat gluten films, it suggests that the wheat-gluten-based coating layer is the key element of gas barrier properties of the studied materials (composite and nano-composite). As a consequence, gas permselectivity was highly affected by RH and rose from 1.9 to 7.9 and 1.5 to 7.5 for coated and nanocomposite materials, respectively. These results show that the unique gas permselectivity properties of proteins are preserved when combined with paper or Urses MMT.

13.3.2 Active Modified Atmosphere Packaging

Another promising application of protein-based materials is their use as antimicrobial packaging. This relies on the ability of biobased polymers such as proteins to carry active compounds and release them in a controlled way, according to a moisture and temperature triggering effect. The use of plant-derived antimicrobial compounds as natural preservatives has received increasing interest in recent years. The efficiency of thyme, clove and oregano essential oils was related to the presence of the phenolic aroma compounds thymol, eugenol and carvacrol, respectively. The inhibitory effect of phenols could be explained by their interaction and accumulation in the cell membrane of microorganisms, correlated with the hydrophobicity of these compounds.

Carvacrol was added to wheat gluten coating solution with or without MMT (2.5% w/w of wheat gluten) to produce nanocomposite or composite papers, respectively. Release of the volatile compound was assessed at 25°C on all materials as a function of time and using a two-step gradient of RH. This RH gradient was used to simulate, first, the average storage conditions of materials (60% RH for 20 days) and, second, the conditions when used for packaging food (100% RH for 15 days) such as fresh or minimally processed fruits and vegetables, generating an atmosphere close to 100% RH inside the package. Almost 100% of carvacrol was lost within 1 day when deposited onto paper, demonstrating the inadequacy of this material to control the release of a volatile active agent. Composite material lost more than 70% of carvacrol within 20 days of storage. This means that only 30% of the active agent would be available to be released to the food during storage. Once placed at 100% RH, this 30% was entirely released within 8 days (from day 22 to 30). In the presence of MMT added to the wheat gluten network (nanocomposite material), only 20% of the carvacrol was released during 20 days of storage at 60% RH. Consequently, 80% of the volatile active agent remained available to be released during the period in which food is packaged. Once placed at 100% RH, this 80% was entirely released within 13 days (from day 22 to 35).

It can be concluded from these results that the release of carvacrol from paper coated with wheat gluten is RH-dependent with or without MMT. It should be noted that only 2.5% of MMT was sufficient to (a) enable paper coated with wheat gluten to retain high amounts of volatile compounds at 60% RH and to (b) enhance the RH triggering effect for the release of the active volatile agent. Such behavior is extremely interesting for both limiting volatile active agent losses before using the material as food packaging and for triggering the active agent release in the presence of the food.

13.4 FUTURE TRENDS

MAP has the potential to prolong shelf life and quality of fresh fruits and vegetables but the development of innovative materials is still required. To be effective, innovation should be conducted according to an integrated approach combining modeling and material science with plant physiology and food quality. Modeling tools could enable the definition of targeted functional requirements for designing materials that should maintain produce quality by using properly chosen mathematical models and input data. There is still a need to provide extensive data on the following:

- Physiological parameters for raw and fresh-cut pro duce and their temperature dependence
- Physiological tolerance of raw and fresh-cut produce and consumer perception toward common gases (O2 and CO2) but also natural preservatives such as aroma compounds and their combination
- Gas and vapor permeability values of materials under conditions of use (temperature and relative humidity)
- Absorption or release ability of active materials (kinetics and maximum absorption/release)

Thus, designing and processing of new MAP will rely on the smart use of materials tailored to the application. It could also be done in an environmentally friendly manner by using natural and biodegradable components that appear well adapted to the physiology of fresh fruits and vegetables. This means that investigations should focus on the buildup of biobased materials and fully understand the underlying mechanisms of the coating and thermomolding processes of such materials (proteins, layered silicate nanoclays, aroma compounds, etc.).