EFFECT OF COATING MATERIALS ON SHELF-LIFE OF COLD STRAWBERRY AND APRICOT FRUITS

BY

HANAN ABO EL-FOTOUH MOHAMMED ALI
B.Sc. Agric. Food Technology, Ain Shams University, 1999
M.Sc. Agric. Sci. (Food Science), Fac. Agric., Cairo Univ., 2006

THESIS
Submitted in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

Agricultural Sciences
(Food Science)

Department of Food Science
Faculty of Agriculture
Cairo University
EGYPT

2015
ABSTRACT:
This study was carried out to produce an edible coating with the ability to prolong shelf life of fruits and vegetables manufactured from carbohydrates or proteins. Six thickening agents [methylcellulose (MC), starch (ST), gelatin (GE), carrageenan (CR), gellan (GL) and carboxymethyl cellulose (CM)], three antimicrobial agents such as chitosan (CH), cinnamon oil (CO) and potassium sorbate (KS) and antioxidant agents such as citric acid (CA) and ascorbic acid (AA) were chosen to produce coating solutions to be applied on strawberry and apricot fruits, also such solutions were dried to obtain edible films. The physical properties [water vapor permeability (WVP) and solubility in water] and mechanical properties [tensile strength (TS) and elongation (E°)] of the edible films were determined. Three coating materials (MC, GE and ST) with the incorporation of the antimicrobial agents and the antioxidant agents were selected on the basis of their physical properties and were applied on the surface of strawberry and apricot fruits and then were stored at 4°C for 20 and 28 days, respectively.

The effect of these coating formulae on the microbiological activity, physical, chemical properties and sensory characteristics of coated fruits were determined through the storage period. Results showed that addition of CH or CO to the film solutions used for the production of films led to the lowest values of water vapor permeability and solubility in water while, it led to an increment in the values of tensile strength and elongation of these films. Results indicated that storage period led to a significant rise of the microbiological activity and significant decline in physical, chemical properties and sensorial characteristics for coated and uncoated fruits, but the coating treatments had a positive impact on these properties.

Results revealed that methylcellulose coating material incorporated with CH followed by CO then KS particularly the MC+CH+AA was the superior treatment for strawberry fruits to prolong its shelf life and to maintain its microbiological activity, physical, chemical properties and sensorial characteristics at the end of storage period. On the other hand, apricot fruits treated with gelatin coating material incorporated with CH followed by CO or KS especially GE+CH was the outstanding treatment to prolong its shelf life and to maintain its microbiological activity, physical, chemical properties and sensorial characteristics at the end of storage period.
Key words: Edible coating, Shelf life, Tensile Strength, Methylcellulose, Gelatin, Starch, Chitosan, Cinnamon Oil, Potassium Sorbate, Citric Acid, Ascorbic Acid, Strawberry Fruits, Apricot Fruits.

Introduction:
Several techniques have been done to extend the useful marketing distances and holding periods for fresh horticultural commodities after harvest. In spite of the progress made, over a quarter of all harvested fresh fruits and vegetables were lost due to spoilage. This represents a large economic waste even in developed countries with more devastating consequences in many tropical regions of the world. Tropical fruits and vegetables present a more serious problem due to the fact that most of them are also chilling sensitive. Therefore, temperatures below 10 °C cannot be used effectively to extend their storage life (Maftoonazad and Ramaswamy, 2005).

Chemically synthesized polymeric films are widely used for packaging in food industry. They are easily and inexpensively produced from uniform raw materials and are flexible as well as durable. A serious disadvantage of these films is that they are not biodegradable. The growth of environmental concerns over nonbiodegradable petrochemical-based plastics has raised interest in the use of biodegradable alternatives originating from renewable sources (Petersen et al., 1999).

The basic composition of edible coating for fresh-cut fruits may include hydrocolloids and lipids. These hydrocolloids (proteins and carbohydrates) tend to form hydrophilic networks, usually being a good barrier to oxygen and carbon dioxide, but a poor barrier to water. Some polysaccharides that have been successfully used to coat fresh-cut fruits include carrageenan, maltodextrin, methylcellulose, carboxymethyl cellulose, pectin, alginate, chitosan, starch, and microcrystalline cellulose (Bico et al., 2009).

Functional, nutritional, organoleptic and mechanical properties of coatings can be improved by the use of additives like antibrowning agents, preservatives, firming agents, plasticizers, nutraceuticals, volatile precursors,
flavours and colours (Baldwin et al., 1996). Glycerol and polyethylene glycol are the most often used plasticizers for cut fruits. These substances have the ability to modify the mechanical properties of the coatings by moving polymer chains apart and reducing the rigidity of the structures (Wong et al., 1994).

The greatest losses in food are due to microbiological alterations. Many chemical and physical processes have been developed to preserve food quality. Among these processes, adequate packaging (a fundamental factor in the conservation and marketing phases). Thus, packaging plays a prominent role in maintaining food quality (Debeaufort et al., 1998).

In most fresh or processed foods, microbial contamination occurs at a higher intensity on the food surface, thus requiring an effective microbial growth control (Padgett et al., 1998).

Traditionally, antimicrobial agents are added directly to the foods, but their activity may be inhibited by many substances in the food itself, diminishing their efficiency. In such cases, the use of antimicrobial films or coatings can be more efficient than adding antimicrobial agents directly to the food since these may selectively and gradually migrate from the package onto the surface of the food, thereby high concentrations being maintained when most necessary (Ouattara et al., 2000).

Consumers require fresh and minimally processed foods that are exempt from chemically synthesized substances, and search for those enriched with natural substances that bring health benefits and maintain nutritional and sensory characteristics (Falguera et al., 2011). Therefore, in recent times the efforts of researchers have been focused on searching for new naturally occurring substances that act as possible alternative sources of antioxidants and antimicrobials (Ponce et al., 2008).

Recently, edible coatings have also been tested as effective carriers of many functional ingredients to increase the concentration of those compounds in the fresh product to provide additional health properties. Antimicrobial agents (i.e. chitosan), antioxidants (i.e. vitamin E), calcium and essential oils (i.e. turmeric acid) among others have been successfully applied to different ready-to-eat fruit (Mei et al., 2002).
Natural antimicrobials have been identified in herbs and spices and several studies have reported on the preservative action of spices or their essential oils. Among these natural antimicrobials are eugenol from cloves, thymol from thyme and oregano, carvacrol from oregano, vanillin from vanilla, allicin from garlic, cinnamicaldehyde from cinnamon, and allyl isothiocyanate from mustard (López-Malo et al., 2007).

Berraera- Necha et al. (2008) reported that the essential oils of cinnamon (Cinnamomum zeylanicum) and clove (Syzygium aromaticum) inhibited the conidial germination and reduced growth of C. gloeosporioides. Infection by postharvest pathogenic fungi was also reduced by these oils. Because essential oils like these have low mammalian toxicity, are biodegradable and non-persistent in the environment the possibility of developing essential oils for use in control postharvest diseases may be an attractive alternative.

Oxygen is also involved in many degradation reactions in foods, such as fat and oil rancidity, microorganism growth, enzymatic browning and vitamin loss. On the other hand, the permeability to oxygen and carbon dioxide is essential for living tissues, such as fresh fruits and vegetables, for respiration. So, moderate barrier coatings are more appropriate. If a coating with the appropriate permeability is chosen, a controlled respiratory exchange can be established and thus the preservation of fresh fruits and vegetables can be prolonged. It is expected that oxygen permeability of edible films can be controlled by using some antioxidants as additives in the film composition. Ascorbic acid or citric acid can be used for this purpose (Ayranci and Tunc, 2004).

Strawberries (Fragaria x ananassa) are a highly perishable fruit with a short postharvest life mainly due to fungal decay. The shelf-life of fresh strawberries at low temperatures (0–4°C) is usually around 5 days (Vargas et al., 2006).

Strawberries are delicate and perishable fruits, susceptible to mechanical damage, physiological deterioration, water loss and decay (Sanz et al., 1999). Strawberries have a very short post-harvest life, and losses can reach 40% during storage (Satin, 1996). Reduction in turgidity as a result of
water loss causes shriveling and faster depletion of nutrients and organoleptic properties, and is a major cause of fruit deterioration (Nunes et al., 1998). In Chile, cold storage of strawberries is not very common and this fruit is usually stored in markets at room temperature between harvest and consumption. For this reason, product losses are very high. With the use of edible coatings and cold storage, spoilage could be minimized (Del-Valle et al., 2005).

Apricot (*Prunus armenica L.*) is one of the most popular fruits cultivated in Egypt. Since its season is rather short, considerable quantities are freshly consumed while the rest are processed into natural or standardized juice, dried sheets or fruits, canned apricots, jams, and concentrated juice (El-Nemr et al., 1995).

Therefore this investigation was carried out to cover the following topics:

1- Production of edible films with six different thickening agents, three different antimicrobial agents and two different antibrowning agents.

2- Evaluation of physical and mechanical properties of edible films.

3- Application of edible coatings on fresh strawberry and apricot fruits using three different thickening agents and three different antimicrobial agents and two different antibrowning agents.

4- Determination of physico-chemical, microbiological and sensory changes of edible coated strawberry and apricot fruits during storage.

**CONTENTS:**

**INTRODUCTION**

**REVIEW OF LITERATURE**

1. Definition of edible films and coatings
2. Types of edible films and coatings
   a. Starch
   b. Carrageenan
   c. Gellan
d. Gelatin
e. Methylcellulose
f. Carboxymethyl cellulose

3. Improvement of edible films properties
   a. Glycerol
   b. Antimicrobial agents
      1. Chitosan
      2. Potassium sorbate
      3. Cinnamon oil
   c. Antioxidant agents
      1. Ascorbic acid
      2. Citric acid

4. Factors affecting mechanical properties of the edible films
5. Factors affecting physical properties of the edible films
   a. Water solubility
   b. Water vapor permeability

6. Application of edible coating on fresh fruit
   a. Effect of edible coating on microbial count of fruits
   b. Effect of edible coating on chemical and physical properties of fruits
      1. Effect of edible coating on physical properties of fruits
         a. Color
         b. Respiration rate
         c. Firmness
         d. Weight loss
         e. Decay ratio
      2. Effect of edible coating on chemical properties of fruits
         a. Titratable acidity
         b. Sugars content
         c. Fruits pigments content
            1. Anthocyanin content
            2. Carotenoids
         d. Ascorbic acid
         c. Effect of edible coating on sensory properties of fruits

MATERIALS AND METHODS
RESULTS AND DISCUSSION
1. Factors affecting physical and mechanical properties of the edible films
   a. Physical and mechanical properties of starch films
      1. Physical properties
         a. Water vapor permeability
         b. Solubility
      2. Mechanical properties
         a. Tensile strength and elongation
   b. Physical and mechanical properties of carrageenan films
      1. Physical properties
         a. Water vapor permeability
         b. Solubility
      2. Mechanical properties
         a. Tensile strength and elongation
   c. Physical and mechanical properties of gellan films
      1. Physical properties
         a. Water vapor permeability
         b. Solubility
      2. Mechanical properties
         a. Tensile strength and elongation
   d. Physical and mechanical properties of gelatin films
      1. Physical properties
         a. Water vapor permeability
         b. Solubility
      2. Mechanical properties
         a. Tensile strength and elongation
   e. Physical and mechanical properties of methylcellulose films
      1. Physical properties
         a. Water vapor permeability
         b. Solubility
      2. Mechanical properties
         a. Tensile strength and elongation
   f. Physical and mechanical properties of carboxymethyl cellulose films
      1. Physical properties
         a. Water vapor permeability
         b. Solubility
2. Mechanical properties
   a. Tensile strength and elongation

2. Application of edible coating on fresh fruits
   a. Effect of edible coating materials on microbial count of fruits
      1. Effect of edible coating materials containing chitosan on microbial count of fruits
      2. Effect of edible coating materials containing cinnamon oil on microbial count of fruits
      3. Effect of edible coating materials containing potassium sorbate on microbial count of fruits
   b. Effect of edible coating on physical and chemical properties of fruits
      1. Effect of edible coating on physical properties of fruits
         a. Effect of edible coating on color of fruits
            1. Effect of edible coating materials containing chitosan on color of fruits
            2. Effect of edible coating materials containing cinnamon oil on color of fruits
            3. Effect of edible coating materials containing potassium sorbate on color of fruits
         b. Effect of edible coating materials on respiration rate of fruits
            1. Effect of edible coating materials containing chitosan on respiration rate of fruits
            2. Effect of edible coating materials containing cinnamon oil on respiration rate of fruits
            3. Effect of edible coating materials containing potassium sorbate on respiration rate of fruits
         c. Effect of edible coating materials on firmness of fruits
            1. Effect of edible coating materials containing chitosan on firmness of fruits
            2. Effect of edible coating materials containing cinnamon oil on firmness of fruits
            3. Effect of edible coating materials containing potassium sorbate on firmness of fruits
      d. Effect of edible coating materials on weight loss of fruits
         1. Effect of edible coating materials containing chitosan on weight loss of fruits
2. Effect of edible coating materials containing cinnamon oil on weight loss of fruits
3. Effect of edible coating materials containing potassium sorbate on weight loss of fruits
e. Effect of edible coating materials on decay ratio of fruits
   1. Effect of edible coating materials containing chitosan on decay ratio of fruits
   2. Effect of edible coating materials containing cinnamon oil on decay ratio of fruits
   3. Effect of edible coating materials containing potassium sorbate on decay ratio of fruits
2. Effect of edible coating on chemical properties of fruits
   a. Effect of edible coating on titratable acidity of fruits
      1. Effect of edible coating materials containing chitosan on titratable acidity of fruits
      2. Effect of edible coating materials containing cinnamon oil on titratable acidity of fruits
      3. Effect of edible coating materials containing potassium sorbate on titratable acidity of fruits
   b. Effect of edible coating on total sugars of fruits
      1. Effect of edible coating materials containing chitosan on total sugars of fruits
      2. Effect of edible coating materials containing cinnamon oil on total sugars of fruits
      3. Effect of edible coating materials containing potassium sorbate on total sugars of fruits
   c. Effect of edible coating materials on pigments content of fruits
      1. Effect of edible coating materials containing chitosan on pigments content of fruits
      2. Effect of edible coating materials containing cinnamon oil on pigments content of fruits
      3. Effect of edible coating materials containing potassium sorbate on pigments content of fruits
d. Effect of edible coating on ascorbic acid content of fruits
1. Effect of edible coating materials containing chitosan on ascorbic acid of fruits
2. Effect of edible coating materials containing cinnamon oil on ascorbic acid of fruits
3. Effect of edible coating materials containing potassium sorbate on ascorbic acid of fruits

c. Effect of edible coating on sensory characteristics of fruits
1. Effect of edible coating materials containing chitosan on sensory characteristics of fruits
2. Effect of edible coating materials containing cinnamon oil on sensory characteristics of fruits
3. Effect of edible coating materials containing potassium sorbate on sensory characteristics of fruits

SUMMARY
REFERENCES
ARABIC SUMMARY

SUMMARY:

This study was carried out to evaluate the availability of the production of coating materials for fresh fruits, manufactured from carbohydrates and proteins. Six thickening agents [methylcellulose (MC), starch (ST), gelatin (GE), carrageenan (CR), gellan (GL) and carboxy methylcellulose (CM)], three antimicrobial agents such as chitosan (CH), cinnamon oil (CO) and potassium sorbate (KS) and antioxidant agents such as citric acid (CA) and ascorbic acid (AA) were separately used to produce coating solutions and edible films. The physical properties [water vapor permeability (WVP) and solubility in water] and mechanical properties [tensile strength (TS) and elongation (E°)] of the edible films were determined. Three coating materials (methylcellulose, gelatin and starch) with the incorporation of the antimicrobial agents and the antioxidant agents were selected on the basis of their physical properties. They were applied on the surface of strawberry and apricot fruits and then were stored at 4°C for
20 and 28 days, respectively. The effect of these coating formulae on the microbiological activity, physical, chemical properties and sensory characteristics of coated fruits were determined throughout the storage period.

The obtained results could be summarized as follows:

1. The films produced using thickening agents (MC, GE, ST, CR, GL and CM) recorded different values of water vapor permeability and solubility in water reaching \(7.01 \times 10^{-6}\) and 9.86%, \(6.81 \times 10^{-5}\) and 16.98%, \(9.80 \times 10^{-5}\) and 12.37%, \(1.09 \times 10^{-3}\) and 20.91%, \(5.69 \times 10^{-3}\) and 32.57% and \(7.18 \times 10^{-3}\) and 18.64%, respectively. Three thickening agents (MC, GE and ST) have been selected on the basis of their low water vapor permeability and solubility in water compared with other thickening agents and were applied on the surface of strawberry and apricot fruits and then were stored at 4°C for 20 and 28 days, respectively.

2. The addition of CH or CO to the film solutions used for the production of films led to lower values of water vapor permeability and solubility in water while, addition of KS elevated these values compared to other films. Moreover, incorporation of AA to the film solutions decreased water vapor permeability and solubility in water values of final films compared with CA addition.

3. The incorporation of CH or CO into the film solutions used for the production of films led to an increase in the values of tensile strength and elongation of these films, while adding KS produced films with low tensile strength and elongation. Likewise, CA addition decreased tensile strength and elongation of the films while, adding AA increased tensile strength and elongation of the films. High values of these properties are required quality for packaging materials to be able to withstand pressure during trading and be able to protect the product.

4. Storage period led to the significant rise of the total bacterial count, yeasts and molds and psychrophilic bacteria counts for coated and uncoated fruits, but the microbiological activity in coated fruits was significantly lower than in uncoated ones. It was also noted that strawberry fruits coated with coating formulae containing MC recorded
the lowest count followed by coatings containing GE then ST especially when incorporated to CH followed by KS then CO while, coating formulae containing GE with the same additives had the same effect on apricot fruits. Moreover, strawberry fruits treated with MC+CH recorded the lowest total bacterial count, yeasts and molds and psychrophilic bacteria count reaching 6.2, 5.2 and 2.4X10² CFU / g, respectively, while in the case of apricot fruits treatment with GE+CH is the best 1.1x10³, 1.0x10³ and 8.5X10² CFU / g, respectively at the end of storage period.

5. The effect of different edible coating on the color properties ($L^*$, $a^*$ and $b^*$) of the fruits next to the storage period was notable where coated fruits recorded significantly the highest values compared with uncoated ones. The addition of AA to the coating formulae had a clear impact on the color of coated fruits recording higher values than the rest of the coated fruits. Moreover, the incorporation of CH into coating formula led to the production of fruits with higher values than fruits treated with formula containing CO, followed by KS, especially when added to formula containing MC in the case of strawberries and formula containing GE in the case of apricot fruits. High $a^*$ values have been observed at the 5th day of storage in strawberries as a result of the continuing synthesis of anthocyanin in all fruits either coated or uncoated. It has been observed that the highest and best values for $L^*$, $a^*$ and $b^*$ were recorded for strawberries coated with MC+CH+AA reaching 25.3, 26.4 and 24.2, respectively. In the case of apricot fruits the best values were recorded for the GE+CH formula reaching 26.1, 18.6 and 40.1, respectively at the end of storage period.

6. The uncoated fruits have higher respiration rate than coated ones during storage at 4°C. It was found that the addition of CH to the various coating formula led to the production of fruits with the lowest respiration rate, followed by formula containing CO then containing KS. Meanwhile, the addition of KS led to the rise of respiration rate of the treated fruits compared with KS free formula. Likewise, CA addition increased respiration rate of the coated fruits while, adding AA decreased it. Strawberries treated with formulae containing MC recorded less
respiration rate, followed by GE then ST, while formulae containing GE produced apricot fruits recorded less respiration rate. Respiration rate was the lowest for strawberries treated with MC+CH +AA reaching 13.26 mlCO₂/kg.hr compared to other formulae at the end of storage period. While, it was the lowest for apricot fruits treated with GE+CH reaching 17.02 mlCO₂/kg.hr at the end of the storage period compared to other formulae.

7. The uncoated fruits recorded the lowest firmness values during the storage period, compared with coated fruits, this return to higher respiration rate and thus increase the activity of enzymes. Strawberry fruits treated with formulae containing MC recorded higher firmness values compared with formulae containing GE or ST, while formulae containing GE produced apricot fruits with higher firmness values. Also, treatments containing CH produced fruits with higher firmness values than fruits treated with formulae containing CO followed by KS. Strawberries treated with MC+CH+AA had the highest firmness values compared to other treatments reaching 12.10 N°, while the treatment by GE+CH was the best treatment of apricot fruits reaching 27.00 N° at the end of the storage period.

8. Weight loss due to loss of water content is a common problem in vegetable and fruit trade in the world wide, and this study has shown that the use of the edible coating can be a solution to this problem. The weight losses were lower in coated fruits when compared to uncoated ones. Addition of CH recorded lower losses than in formulae containing CO, followed by formulae containing KS. In the case of strawberries, treatments containing MC recorded less weight losses while; treatments containing GE produced apricot fruits with less weight losses. Strawberries treated with MC+CH+AA was the best while, treatment with GE+CH was the best for apricot fruits at the end of the storage period where loss rates recorded in the weight reached 22% and 7.5%, respectively at the end storage period.

9. The ratio of decay caused by fungal growth has increased in all fruits during the storage period, but to a lesser extent in coated fruits, especially with formulae containing CH followed by KS then CO. The formulae
containing MC were the best in inhibiting strawberry fruits decay while; formulae containing GE were the best for apricot fruits. It was found that strawberry fruits treated with MC+CH and apricot fruit treated with GE+CH recorded the lowest decay ratio reaching 20% and 45%, respectively at the end of the storage period.

10. A significant decrease in the total acidity in fruits as a result of respiration process has increased during the storage period, but coated fruits were higher in acidity content compared to uncoated ones. Addition of CH to different coating formulae produced fruits with high acidity values compared to other formulae. Strawberries treated with MC+CH+AA formula and apricot fruit treated with GE+CH formula recorded the highest acidity values reaching 7.34% and 12.38%, respectively at the end of the storage period.

11. Sugars decline in fruits are attributed to the respiration process, the higher the respiration rate the lower the sugars content of the fruits, therefore sugars content of coated fruits were significantly higher than in uncoated fruits during storage period. It has been observed that the addition of CH to the coating formulae produced fruits with the highest sugars content compared with other formulae. Also, strawberry fruits coated with formulae containing MC and apricot fruits coated with formulae containing GE were the best with respect to sugars content. The MC+CH+AA coated strawberry fruits and the GE+CH coated apricot fruits recorded the highest sugars content reaching 53.23% and 64.39%, respectively at the end of the storage period.

12. Anthocyanins are the main pigment in strawberries and responsible for the red color while, the main pigment in apricot are carotenoids. The storage period led to a significant decrease in pigments content of fruits, but the coated fruits recorded the highest values especially which contained CH. Formulae containing MC resulted in strawberry fruits with the highest anthocyanin content. The apricot fruits treated by GE are the best in preservation of carotenoids. The MC+CH+AA coated strawberry fruits and the GE+CH coated apricot fruits recorded the highest pigments content reaching 210.60 and 28.20 mg/100g DM, respectively at the end of the storage period.
13. Addition of CH to the coating formulae produced fruits with higher ascorbic acid content compared with other formulae. The treatments containing MC for strawberry fruits and containing GE for apricot fruits were the best in preserving ascorbic acid. It was also noted that the addition of AA produced fruits with superior ascorbic acid values when compared with the rest of formulae. The MC+CH+AA coated strawberry fruits and the GE+CH+AA coated apricot fruits recorded the highest ascorbic acid content reaching 435.73 and 267.72 mg/100g DM, respectively at the end of the storage period.

14. The decline in firmness values, sugars and pigments content influence the sensory qualities of the fruits (color, taste, texture, flavor, and overall acceptability). The coated fruits had higher sensory scores than uncoated fruits during storage period. CH addition to coating formulae maintained the sensory properties of fruits especially with MC+AA for strawberries and GE for apricot fruits 6.1 and 7.8 for color, 5.3 and 7.0 for taste, 5.5 and 7.2 for texture, 5.3 and 7.0 for flavor and 5.5 and 7.2 for overall acceptability, respectively at the end of the storage period.

**The study timeline:**

<table>
<thead>
<tr>
<th>Year</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>PhD registration.</td>
</tr>
<tr>
<td>2008-2012</td>
<td>Attending courses, collecting references, implementation of the practical part, recording results.</td>
</tr>
<tr>
<td>2015</td>
<td>Discussion of the thesis.</td>
</tr>
</tbody>
</table>