Technische Universität München

Alginate-based Edible Coating to Maintain Quality Attributes of Fresh-cut Fruits

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Vollständiger Abdruck der von der Fakultät TUM School of Life Sciences der Technischen Universität München zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften (Dr. rer. nat.)

genehmigten Dissertation.

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Die Dissertation wurde am 03.02.2021 bei der Technischen Universität München eingereicht und durch die Fakultät TUM School of Life Sciences angenommen am 22.06.2021.

Acknowledgments

This work has been prepared at the Fraunhofer Institute for Process Engineering and Packaging IVV, Freising in the research department Retention of Food Quality (QL), in collaboration with The Chair of Food Packaging Technology of TUM, Weihenstephan, Freising. I would like to extend my thanks to the many wonderful people who so generously contributed to the work presented in this thesis directly or indirectly.

First and foremost, I would like to express my sincere gratitude to my primary supervisor Prof. Dr. Horst-Christian Langowski, for inspiring my interest in the development of edible packaging, his useful critiques of this research work, and providing me an opportunity to chase my dream and complete my thesis.

My sincere thanks go to Prof. Dr. Kajetan Müller for accepting to be my secondary supervisor in the middle of my studies. His patient guidance, the encouragement, and advice he has provided are one of the biggest factors in the realization of the thesis. I have been extremely fortunate to have a secondary supervisor who responded to my questions so wisely and cared so much about my work.

I was also very much privileged to work with Prof. Dr. Markus Schmid, who convinced me during our discussions that I should publish my research as articles and who made it possible for me to conclude a cumulative dissertation. He is also a very effective guide with being very kind to share his vast knowledge. I am grateful for all his contributions of time and ideas.

I am also grateful to my mentor, Prof. Dr. Ferruh Erdogdu, for enlightening me whenever I approached him.

The particle size studies discussed in this dissertation would not have been possible without Michael Schott. Similarly, I was extremely fortunate to be able to collaborate with Martina Lindner and Isabell Rothkopf during water barrier studies. I appreciate their significant contributions to the experiments, their impressive knowledge, and characterization skills.

I am grateful to Prof. Dr. Carolin Hauser to help me to start my journey in Fraunhofer. I am also appreciative of Joachim Wunderlich to let me finish my studies in the QL department.

I have had the pleasure to work alongside Dr. Peter Muranyi and grad students Maria Kunde, Bernd Kramer, Nadine Böhner, Julian Tielmann, Thorsten Tybussek, Astrid Pant, Andrea Hickisch, and Christopher Schädle. I want to thank the staff of Retention of Food Quality (QL) Department. They willingly lent me their time, resources, and expertise. I thank Semra Guler Kul, Christopher Schmith, Christine Neumaier, Brigitte Stumpf, Monika Steinbüchl, Christine Berger, Sonja Riedmaier, and dear Sigrid Regnet (RIP).

Members of the Materials Development Department in IVV were kind enough to extend their help at various phases of this research, whenever I approached them. I do hereby acknowledge all of them: Dr. Cornelia Stramm, Zuzana Scheuerer, Marius Jesdinszki, Jana Bytzeck.

I gratefully acknowledge the funding sources that made my Ph.D. work possible. Talenta program of the Fraunhofer Institute had funded my first years of Ph.D. studies.

Completion of doctoral studies does not only require academic assistance but also requires support in various everyday issues. I express my thanks to the staff in Information Technology (IT) and workstation departments in the Fraunhofer IVV. During my studies, they have always supported me in the shortest possible time to handle the issues when they arise. Many thanks also go to Maggie Stürzlmayer, who supported me and gave me such attention and time whenever I needed someone to talk to.

I am deeply grateful to Dr. Barbara Stelzer-O'Neill and Don O'Neill for correcting any grammar, spelling, punctuation or simple typing errors in the manuscript.

Last but by no means least, I would like to thank my family for all their almost unbelievable support, love, and encouragement. I am very much indebted to my mom, Hatice Karadeniz, who supported me in every possible way and gave me the strength to chase my dreams. And most of all, for my loving, encouraging, and patient husband Stefan Parreidt and my little son Egon Parreidt whose faithful support during tough times in the Ph.D. pursuit is so appreciated. They are the most important people in my world.

Undertaking Ph.D. studies has been a truly life-changing experience for me. Thank you so much to all who walked with me on this path.

Acronyms and Abbreviations

The following abbreviations are used in this thesis:

ADI	Acceptable daily intake
ANOVA	Analysis of variance
a-PET	Amorphous polyethylene terephthalate
a_w	Water activity
Beta Bio 40	Hop extract, 40% β-acids in propylene glycol
BOPP	Biaxially-oriented polypropylene
CA	Contact angle
CAGR	Compound annual growth rate
CDC	Centers for Disease Control and Prevention
CFR	Code for Federal Regulations
CI	Creaming index
CIE	International Commission on Illumination
CMC	Carboxymethylcellulose
c-PET	Crystalline polyethylene terephthalate
DSA	Drop Shape Analyzer
EC	The European Commission
EC	Edible coating
EDTA	Ethylenediaminetetraacetic acid
EF	Edible film
EFSA	The European Food Safety Authority
Eos	Essential oils
EPS	Exopolysaccharide, extracellular polymeric substance
EU	European Union
FAO	Food and Agriculture Organization of the United Nations

FARRP	Food Allergy Research and Resource Program
FDA	US Food and Drug Administration
FEDIOL	EU Vegetable Oil & Protein Meal Industry
FFA	Free fatty acid
Flavor-Tex®	A commercial alginate-based coating formulation
GMP	Good manufacturing practice
GRAS	Generally regarded as safe
H_2O_2	Hydrogen peroxide
HLB	Hydrophilic–lipophilic balance
HMP	Sodium hexametaphosphate
HPC	Hydroxypropylcellulose
HPMC	Hydroxypropyl methylcellulose
IFPA	The International Fresh-cut Produce Association
IU	International Unit is a measure of biological activity and is different for each substance
LAB	Lactic acid bacteria
LbL	Layer-by-layer or multilayer coating
LSD	Least Significant Difference tests
MA	Modified atmosphere
MC	Methylcellulose
MW	Molecular weight
NAD	Nicotinamide adenine dinucleotide
WORK	Owens, Wendt, Rabel, and Kaelble method
PCA	Principal component analysis
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PHL	Postharvest loss
PMA	Produce Marketing Association
PS	Potassium sorbate
PTFE	Polytetrafluoroethylene

RH	Relative humidity
RSM	Response surface methodology
RTE	Ready-to-eat
SFE	Surface free energy
span 60	Sorbitan monostearate
span 80	Sorbitan monooleate
TBA	Thiobarbituric acid
TBARS	Thiobarbituric acid reactive substances
TCA cycle	tricarboxylic acid cycle, also known as a citric acid cycle, CAC and Krebs cycle
TMA-N	Trimethylamine nitrogen
TukeyHSD	Tukey Honest Significance Test
TPC	Total psychrophilic count
TVB-N	Total volatile basic nitrogen
TVC	Total viable count also referred to as aerobic plate count and the standard plate count
tween 40	Polyoxyethylenesorbitan monopalmitate
tween 80	Polyoxyethylenesorbitan monooleate
VI	Vacuum Impregnation
w.b.	wet basis
WHO	World Health Organization
WVP	Water vapor permeability
WVR	Water vapor resistance
WVTR	Water vapor transmission rate

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Chapter I.

Introduction

The current world population is 7.6 billion people; it is projected to reach 9.8 billion by 2050 and 11.2 billion by 2100 [1,2]. Meeting the world's growing demand for food can be very challenging and difficult to satisfy. This challenge can be solved either by increasing the crop production or by diminishing the postharvest losses (PHL).

Although people generally assume that cars, smokestack industries, etc. are the biggest threat to the natural environment, more than 30% of the total human-induced greenhouse gases (i.e., carbon dioxide, methane, and nitrous oxide) emissions are produced by agricultural activities [3]. Cutting of forests to grow crops and livestock (deforestation) in new farmlands causes incalculable environmental damage due to releasing billions of tons of greenhouse gases into the atmosphere and driving thousands of species of animals and plants into extinction [4-6]. Agricultural production has a pivotal role in water pollution by consuming 70% of water worldwide and discharging a huge amount of agrochemicals, organic matter, drug residues, sediments, and saline drainage into rivers and lakes [7]. Extensive growth of agriculture is also a threat to mammal, bird, and plant species and the primary reason for biodiversity loss [8]. Ultimately, the negative environmental impacts of increasing agricultural production urge the researchers to find new methods to reduce the PHL of agricultural commodities.

The world's population is increasingly moving from rural areas to urban centers. Currently, 55% of the world's population lives in urban areas; however, projections show that it will increase to 68% by 2050 [9]. Hence, consumption centers of products are located remotely from production areas. The necessity of long-distance transportation and an extension of shelf life periods increase the importance of packaging.

Packaging is one of the postharvest activities that determine the quality of the final product (consumed by the end-user) substantially. Food packaging is a coordinated system of food science, processing, and preservation [10]. It is designed for the efficient delivery of high quality, safe food products with the fulfillment of principal functions, i.e., protecting food from external damage and contamination to allow for transport and provide information about the content of the package to consumers [10].

The design of the packaging is expected to meet various functional requirements such as mechanical strength, preservation of its content from moisture, oxygen, light, foreign odors, flavors, cost-effectiveness, machineability, and fulfilling all the legal requirements in terms of food safety, etc. [11].

The number of health-conscious consumers has been increasing recently. Consumers are becoming more aware of their weight, their nutritional health, and the positive health effects of consuming fresh produce. On the other hand, modern lifestyles such as women joining the workforce, increasing purchasing power, lack of time for long food preparation routines change the eating habits of consumers dramatically. The demand for fresh-like processed food products is rising, and the sector expands rapidly [12]. Nevertheless, consumers still demand high-quality attributes such as appearance, texture, and flavor similar to those of the raw produce [12].

Another emerging trend is the growing level of environmental awareness of consumers. Non-renewable, non-biodegradable packaging materials have serious environmental drawbacks. They have been considered a major source of solid waste and environmental pollution by consumers and environmental activists [13,14]. Studies show that consumers are eager to pay the extra cost for environmentally friendly, bio-degradable, sustainable packaging materials. It has also driven companies and researchers to pay attention to the environmental aspects of the packaging materials. To solve the solid waste problem, they have been working on ways to develop new packaging strategies with environmentally friendly, abundant biodegradable packaging materials made from renewable natural polymers [13,15]. Edible coatings and films have been considered as one of the potential packaging applications to meet this demand.

Edible coatings and films can prevent quality losses of fresh-cut products in several ways [10,16]: (i) acting as a barrier and reduce the transmission rate of moisture and gases between the food product and surrounding air; (ii) reducing the quality changes of the chemical composition of the food (e.g., oxidation of lipids, vitamins, pigments, flavor compounds); (iii) improving structural integrity and textural properties; (iv) carrying food additives.

1.1 Research Aims and Objectives of the Study

The general technical aim of this research was to supply an edible coating method that allowed a better quality of fresh fruits, either cut or whole.

The general aim led to a diverse range of technical and scientific objectives. The first group of technical sub-aims were to develop methods and materials of edible coatings with barrier to liquid water and water vapor, and also to explore options if there were possible antimicrobial effects of selected agents to decrease the fast deterioration of the product.

In connection with the general goal and the preliminary studies; the following objectives were specified; i.e., the formulated coatings (material, solvent, additives) and the coating methods should allow for:

- Coherent, homogeneous layer formation, which could be achieved with high wettability of coating on the substrate surface.

- Good wetting properties on the substrate; in other words, highly adhesive coating formation, with required accurate measurement of surface energy characteristics of the food sample.
- Designing of coating formulation based on surface tension values, regarding surface free energy of the target surface.
- Sufficient barrier properties against liquid water and water vapor transport necessitating suitable material properties in the form of permeability against them, and having some understanding of the water transport properties of the coated layer-substrate combination.
- Neutral/good sensorial properties, i.e., the coating should not negatively affect the sensorial properties of the coated product and reduce consumer acceptance.

1.2 Overview

The remainder of this thesis is structured as follows: Chapter Two Section One outlines the background information about horticultural produce. Chapter Two Section Two gives brief information about antimicrobial additives used in the preliminary studies. Chapter Two Section Three focuses on a summary of surface free energy measurements of solid materials. Chapter Two Section Four provides brief information about wettability. Chapter Two Section Five lists the major hydrocolloid and lipid materials that have been extensively used for the formation of edible coatings. Chapter Two Section Six presents the literature review of "alginate-based edible films and coatings for food packaging applications" in a published article (Publication I). Chapter Three is a shelf-life evaluation of coated and uncoated cantaloupe with the incorporation of antimicrobial agents. The results show that edible coating formulation and the process should be re-designed taking the characteristics of the surface of the fruit into account. The following chapters focus on finding answers to the questions that arose during preliminary tests. Chapter Four examines "dipping and vacuum impregnation coating techniques" (Publication II). Chapter Five focuses on a "novel technique for the evaluation of the surface free energy of food" (Publication III). Chapter Six investigates the "effect of presence and concentration of plasticizers, vegetable oils and surfactants on the coating formulation" (Publication IV), and Chapter Seven critically traces the formation of "uniform alginate-based coating and the water barrier characteristics of it" (Publication V). The sections that were published in peer-reviewed journals were included in the texts in the format they were published.

The thesis is finally framed and concluded in Chapter Eight with the concluding discussion. Chapter Nine and Chapter Ten summarize the content of the thesis in English and German, respectively.

1.3 Scientific Contributions

1.3.1 List of publications directly related to the present Ph.D. thesis

Articles are listed in the same order as they are presented in the chapters.

I. Senturk Parreidt, T.; Müller, K.; Schmid, M. Alginate-based edible films and coatings for food packaging applications. *Foods* **2018**, 7, 170.
II. Senturk Parreidt, T.; Schmid, M.; Müller, K. Effect of dipping and vacuum impregnation coating techniques with alginate based coating on physical quality parameters of cantaloupe melon. *Journal of Food Science* **2018**, 83, 929-936.
III. Senturk Parreidt, T.; Schmid, M.; Hauser, C. Validation of a novel technique and evaluation of the surface free energy of food. *Foods* **2017**, 6, 31.
IV. Senturk Parreidt, T.; Schott, M.; Schmid, M.; Müller, K. Effect of presence and concentration of plasticizers, vegetable oils, and surfactants on the properties of sodium-alginate-based edible coatings. International Journal of Molecular Sciences **2018**, 19, 742.
V. Senturk Parreidt, T.; Lindner, M.; Rothkopf, I.; Schmid, M.; Müller, K. The development of a uniform alginate-based coating for cantaloupe and strawberries and the characterization of water barrier properties. Foods **2019**, 8, 203.

1.3.2 Other related publications within the time period of doctoral studies

VI. Hauser, C.; Parreidt, T.S. Antimicrobial hop extracts and their application on fresh produce. *Multidisciplinary Approaches for Studying and Combating Microbial Pathogens* **2015**, 49.
VII. Hauser, C.; Parreidt, T.S.; Kowalska, U.; Suminska, P. Shelf-life extension of fresh produce by edible coating. *Italian Journal of Food Science* **2015**, 41-45.

Chapter II.

Background and State of the Art

The literature review in this chapter is presented in various viewpoints:

Sections (i) to (v) do not contain published papers while with section (vi) a published peer-reviewed review article is presented.

(i) A literature review of the fresh produce used in coating studies

(ii) A literature review of the antimicrobial additives used in coating studies

(iii) A literature review of surface free energy and its measurement methods

(iv) A literature review of wettability

(v) A literature review of possible components of edible coatings

(vi) A literature review of alginate and alginate-based edible coatings

2.1 Fruits and Vegetables

Vegetables are defined as plants or parts of plants used as food, while fruits are the major ovaries of plants with their seeds [17]. Fruit and vegetable processing markets comprise the markets of both processed fruits and vegetables (i.e., fresh, fresh-cut, canned, frozen, dried/dehydrated, convenience), and processing equipment. The global fruit and vegetable processing market was valued at USD 230.96 Billion in 2016 and is estimated to reach USD 346.05 Billion by 2022, at a CAGR (compound annual growth rate) of 7.1% from 2017 [18].

2.1.1 Chemical composition and nutritional value of fruits and vegetables

Fruits and vegetables supply dietary fibers, vitamins, minerals, phytochemicals (i.e., perform functions such as phytoestrogens, antioxidants, anti-inflammatory agents, etc.) to the diet [19,20]. There is a strong link between fruit and vegetable intake and decrease in risk of cancer, heart disease, stroke, cataracts, diverticulosis, chronic obstructive pulmonary disease, and hypertension; therefore, the consumption of fruit and vegetable must be increased to optimize nutrition uptake and promote health [21]. The main classes of nutrients in plant origin food can be listed as follows:

Water: Fruits and vegetables contain high amounts of water (≈61-95%) [19,20]. There is a wide variation in the water content of the fresh produce even within the same species due to the dependency of the water content of individual cells, availability of water to the tissue at the time of harvest, and changes in the environment (i.e., fluctuations in temperature and relative humidity) [20].

Carbohydrates: In general, they are the second abundant constituents (2-40 g/100 g of produce). Although carbohydrates are present across a wide molecular weight range, the main sugars can be specified as sucrose, glucose, and fructose. Glucose and fructose are present in all produce at a similar level, while sucrose is found only in approximately two-thirds of produce [20]. Apart from these, starch can be counted as the other important energy source. Furthermore, cellulose, noncellulosic polysaccharides such as hemicellulose, and pectic substances are the main carbohydrate polymers that constitute dietary fibers [20].

Protein: Generally, fruits and vegetables contain low levels of proteins; 1 g to 2 g protein/100 g produce. Nevertheless, Brassica vegetables (3-5 g protein/100 g produce) and legumes (5 g protein/100 g produce) have the highest protein contents.

Lipids: Except for the avocado and olive, fruits and vegetables contain generally low amounts of lipid, which is mainly present in the protective cuticle layers on the surface and the cell membrane [20]. Low lipid content of fresh produce is considered a positive factor by the health authorities, in communities, which increase their consumption [20].

Organic acids: Fruits and vegetables supply organic acids more than it is required for the operation of the tricarboxylic acid cycle (TCA cycle, also known as a citric acid cycle, CAC and Krebs cycle) and other metabolic pathways [20]. Furthermore, organic acids contribute significantly to the flavor; sugar-acid balance in fruit affects the taste of the specific horticultural produce (sweetness, sourness or acidity and low or no astringency) [20,22]. Apart from the dominant acids (i.e., citric and malic acids), fresh produce contain tartaric acid, oxalic acid, isocitric acid, etc. that can be dominant in certain species [20].

Vitamins: Fruits and vegetables supply three of the most important human health phytonutrients, i.e. vitamin C (>90% of vitamin C (ascorbic acid) supplied by fruits and vegetables), vitamin A (β-carotene) and B9 (folic acid) [23-25].

Minerals: Minerals take part in secondary metabolic pathways that generate phytochemicals [26]. Most vegetables and fruits contain important minerals such as potassium, magnesium, calcium, phosphorus, iron, zinc [26].

Volatiles: Volatile compounds are predominantly esters, alcohols, acids, carbonyl compounds (aldehydes, and ketones) [20,22].

Antioxidants: Phytochemicals in fruits and vegetables serve as antioxidants, scavenging free radicals, and act as saviors of the cell [27]. Furthermore, the U.S. Food and Drug Administration (FDA) defined the antioxidants as substances used to preserve food by retarding deterioration, rancidity, or discoloration caused by oxidation [28]. Polyphenols, flavonoids, conjugated isomers of linoleic acid, D-limonene, epigallocatechin, gallate, soybean proteins, isoflavones, vitamins A, B, C, E, tocopherols,

selenium, calcium, chlorophyllin, aliphatic sulfides, catechin, tetrahydrocurcumin, sesaminol, glutathione, uric acid, indoles, thiocyanates, and protease inhibitors are well-characterized antioxidants in fruits and vegetables [27,29].

2.1.2 Postharvest

The World Health Organization (WHO) and Food and Agriculture Organization of the United Nations (FAO) recommend 400 g daily intake of fruits and vegetables for the prevention of several micronutrient deficiencies, heart disease, cancer, diabetes, etc. [30,31]. However, it is stated by the same organizations that only a small minority of the world's population consumes the recommended amount of fresh produce [31]. According to the lowest possible assessment, 12 million low birth-weight infants are born each year, approximately 162 million pre-school children and a billion people of all ages are suffering from hunger and malnutrition [32]. The given data reveals the enormity of the problem and underlines the essentialness of working to increase the food supply worldwide. The supply of fruits and vegetables can be improved either by increasing crop production or by diminishing the postharvest losses (PHL). Together with roots and tubers, fruits and vegetables have the highest food waste rates of any food products; 45% of all the fruit and vegetables produced are wasted globally [33].

Postharvest can be described as all the activities that take place after the production of agricultural commodities (e.g., storage, procurement, transportation, processing, packaging, marketing) until their consumption [34].

Postharvest deterioration does not constitute a problem for the simple marketing supply chains, where the fresh produce is transferred from the producer to the end-user in a short period [20]. However, increasing urbanization and the mass movement of people to cities enhance the remoteness of the production areas from the population centers, create complex marketing systems, and international trading, which prolongs the time from the farm to the market considerably [20]. Consequently, PHL occurs and causes severely reduced shelf life, products with poor quality, and low nutritional value. Although the rate of deterioration depends on the type of produce and their overall rate of metabolism, in general, fresh produce deteriorate very rapidly [20].

Factors affecting the postharvest quality of horticultural produce should be defined well to extend the postharvest, or in other words, the shelf life of horticultural produce. Factors contributing to PHL can be classified into two main categories [35]:

(i) External factors: factors outside of the food supply chain
Environmental and socio-economic factors [35]

(ii) Internal factors: factors in the food supply chain
Harvesting, lack of availability of pre-cooling facilities, transport systems, improper storage facilities and conditions, grading, secondary processing, biological-microbiological-chemical causes, and improper packaging (lack of proper packaging technologies and materials) [35]

Postharvest technologies can be described as the designed methods by which deterioration of the products can be confined to the utmost during the period between harvest and end-use [20]. The achievement of the stated purpose is strongly related to the understanding of the structure, composition, biochemistry, and physiology of the produce both for decreasing the deteriorative effects of the natural metabolism and to avoid inducing abnormal events [20].

Appropriate postharvest technologies must be developed to cope with the different structure and metabolism of different types of produce.

2.1.3 Fresh-cut fruits

To accommodate the rapid trend of living, consumers have changed their behavior, especially in their eating habits [36]. Accelerated lives, fast-paced city lifestyles increase the interest in easy, time-saving, and convenient foods (in other words, prepared consumer foods) [37,38]. Fruit and vegetable producers respond to this trend with freshly cut fruit and vegetables, seedless fruits, snack vegetables, easy peelers, individually sized products (e.g. mini watermelons, papayas), ready-to-eat products with increased shelf-life [37].

The International Fresh-cut Produce Association (IFPA) defines the fresh-cut products as fruit or vegetables that have been trimmed and/or peeled and/or cut into 100% usable product that is bagged or pre-packaged to offer consumers high nutrition, convenience, and flavor while still retaining its freshness [39,40].

According to the Produce Marketing Association (PMA), U.S. fresh-cut fruit and vegetable is one of the fastest-growing segments with an estimated $27 billion market [41]. The fresh-cut fruit and vegetable market has also been on the rise in the European Union (EU) [42,43]. Euromonitor International presented a report in 2015 and announced that 19% per capita volume growth for fresh-cut fruit in Western Europe was recorded [44].

Specific Produce:

2.1.3.1 Cantaloupe

The principal melons (*Cucumis melo*) of commerce are grouped into (i) *C. melo* Cantalupensis (cantaloupe, muskmelon, rockmelon, and sweet melon); (ii) *C. melo* Inodorus (honeydew, crenshaw casaba and juan canary types) [45].

Cantaloupe plant is mainly andromonoecious (have hermaphrodite and male flowers on the same plant, with occasional female flowers) [45,46]. The fruit has a round or oval shape, tan or straw-colored and separate from the peduncle (main stalk, slip) at maturity [45]. As illustrated in Figure 1, the surface is covered with net tissue (i.e., a meshwork of raised tissue) [47].

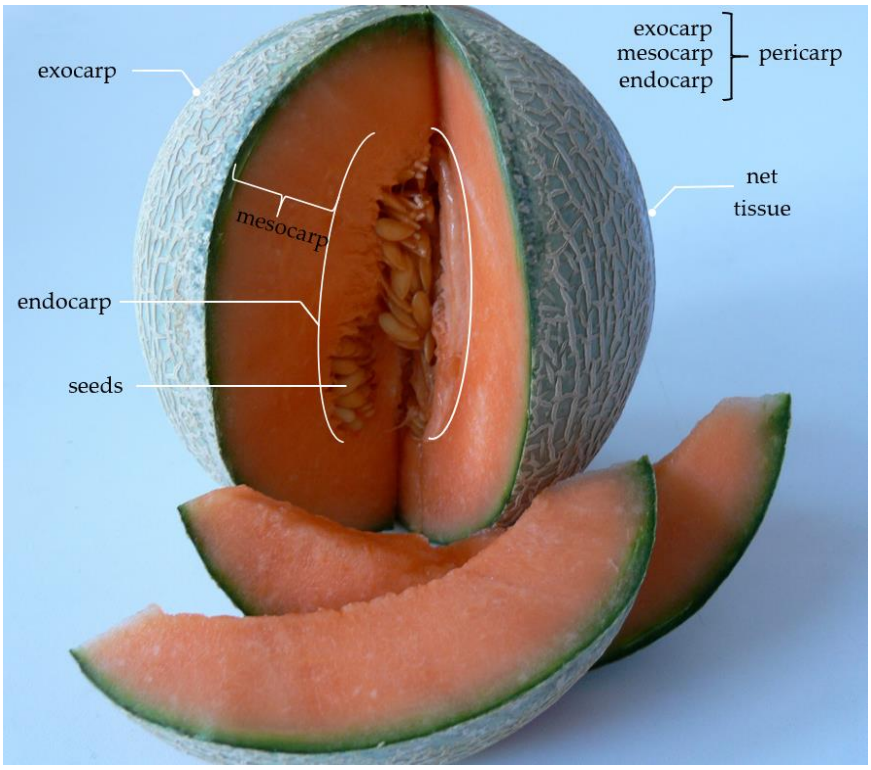

Figure 1. Image of the fresh cantaloupe and the parts of the fruit (own photograph).

Nutritional constituents of cantaloupe fruit are given in Table 1. It is composed of ~90% water and contains important micronutrients such as potassium, sodium, vitamin C.

Table 1. Nutritional composition of cantaloupe melon (Source: United States Department of Agriculture (USDA) - Agricultural Research Service [48]).

Nutrient	Value per 100g	Nutrient	Value per 100g
water	90.15 g	fiber, total dietary	0.9 g
energy	34 kcal	potassium, K	267 mg
protein	0.84 g	sodium, Na	16 mg
total lipid (fat)	0.19 g	phosphorus, P	15 mg
ash	0.65 g	vitamin C, total ascorbic acid	36.7 mg
carbohydrate, by difference	8.16 g	folate, total	21 µg
sugars, total	7.86 g	carotene, beta	2020 µg

The main reason for the popularity of cantaloupe is its availability in many countries all year round [49]. Lately, fresh-produce marketing has been focused not only on whole cantaloupes but convenience products in packages, pre-cut products, and salad bars [49]. Fresh-cut processing of cantaloupe fruit is rather complicated; these are sorting, cleaning with a brush, spraying water, heat treatment with hot water/steam, peeling, deseeding, chunking, rinsing with sanitized water and packaging [50]. In addition, determination of the effects of various parameters in fresh-cut processing, packaging, storage conditions is

needed for a better understanding of quality changes during storage of the products. Like many other fruits and vegetables, cantaloupes are also susceptible to various spoilage processes during their postharvest storage.

Non-freezing low-temperature storage (~1 °C) develops a chilling injury in chilling-sensitive foods such as melons that results in postharvest losses (i.e., pitting, surface decay) and restricts the storability of the product [51-53]. Rolle and Chism [54] specified that temperatures cooler than 12.5 °C increased the respiratory rates by showing the injury phenomenon.

Low acidity (pH 5.2-6.7) and high water activity (0.97-0.99) are the major characteristics of cut cantaloupe, which make the fruit a supportive medium for the growth of pathogens and thus lead to potentially hazardous food [55]. Most recently, on July 24, 2018, CDC (Centers for Disease Control and Prevention) reported a multistate (in nine U.S. States) outbreak of *Salmonella adelaide* illnesses that caused 36 hospitalizations and was linked to pre-cut melons, including cantaloupe [56]. Similarly, Zhao [55] listed the pathogens detected in cantaloupe as Salmonella, Shigella, *Escherichia coli* O157:H7.

Wounding, disruption of tissue, and loss of cell integrity lead to softening of tissues, and eventually, the texture and flavor of the fresh-cut cantaloupe will be affected negatively [57-59]. Furthermore, amino acids influence fruit aroma directly. The dominant amino acids at the time of the cutting process of fresh-cut cantaloupe are aspartic acid, glutamic acid, arginine, and alanine [60]. The amounts of these amino acids change depending on the storage temperature [60].

The shelf life of fresh-cut cantaloupe prepared by fruit processors could be as short as 5 days (at 7 °C) [50]. However, the shelf-life of store-cut fruits prepared by retail stores and displayed on shelves is even shorter, i.e., around 2 days [50]. Sapers, *et al.* [61] studied the effects of washing agents on the shelf life of fresh-cut cantaloupes. Researchers concluded that when rinds were washed with water, washing and sanitizing agents, and hydrogen peroxide (H_2O_2), the log reductions on washed-rind plugs were <1, 1-2, and 3, respectively [61]. Hence, H_2O_2 treatment at 50 °C extended the shelf life of cut fruits to 18 days at 4 °C [61]. O'Connor-Shaw, *et al.* [62] reported that microbiologically sterile diced cantaloupe stored under a range of controlled atmospheres at 4.5 °C had a shelf life of up to 28 days.

Fresh-cut cantaloupe is susceptible to various spoilage processes. Physical spoilage, chemical spoilage, and microbial spoilage are the three main spoilage categories, which can also promote the spoilage of others [63].

The action of food spoilage microorganisms (i.e., bacteria, mold, yeast, viruses, and parasites) on the cut surfaces is a major concern for perishable foods such as fresh-cut fruits and vegetables [63,64]. Water activity values of cantaloupe melons were determined as 0.95-0.993 [65-68]. The average pH was found as 6.5 [60]. The high water activity and low acidity of cantaloupe make it highly perishable and favor microbial growth. The studies about the predominant flora of cantaloupe indicated that bacteria are the prevalent microorganisms, on the other hand, fungal growth is minimal during storage [60]. Microscopic examination showed that the microbial flora was composed mainly of Gram(-

) stained rods (e.g., psychrotrophic pseudomonads) for cantaloupe stored at 4 °C, while the flora was Gram(+) mesophilic bacteria (e.g., lactic acid bacteria) in fruits stored at 20 °C [60,69].

The fresh-cut cantaloupe loses its firmness and develops off-odor very rapidly [70]. The relatively high respiration rate of the product makes it susceptible to the microbiological deterioration [70]. Besides, a lot of instabilities and changes in the food occur due to moisture transfer (water loss, gain, or transport) [63]. In addition to microbial and chemical degradation, it may cause the food to be evaluated as unacceptable by the consumers [63].

The reasons of selecting cantaloupe as model food and conducting edible coating studies on this particular food were its high popularity in the fruit market and its important postharvest losses during its short shelf-life, softening of tissues in short periods and the water leakage - water accumulation problem at the bottom of the packages stated by the fruit manufacturers.

2.1.3.2 Strawberry

Most berries, currants, and strawberry belong to soft fruit generic categories [71]. As their name indicates, lack of firm texture is their natural characteristics [71]. They are also known as temperate fruits due to being grown in all temperate regions of the world [71]. The common strawberry is known as the garden strawberry, a hybrid species of the genus *Fragaria* (*Fragaria* × *ananassa*) (Figure 2) [72].

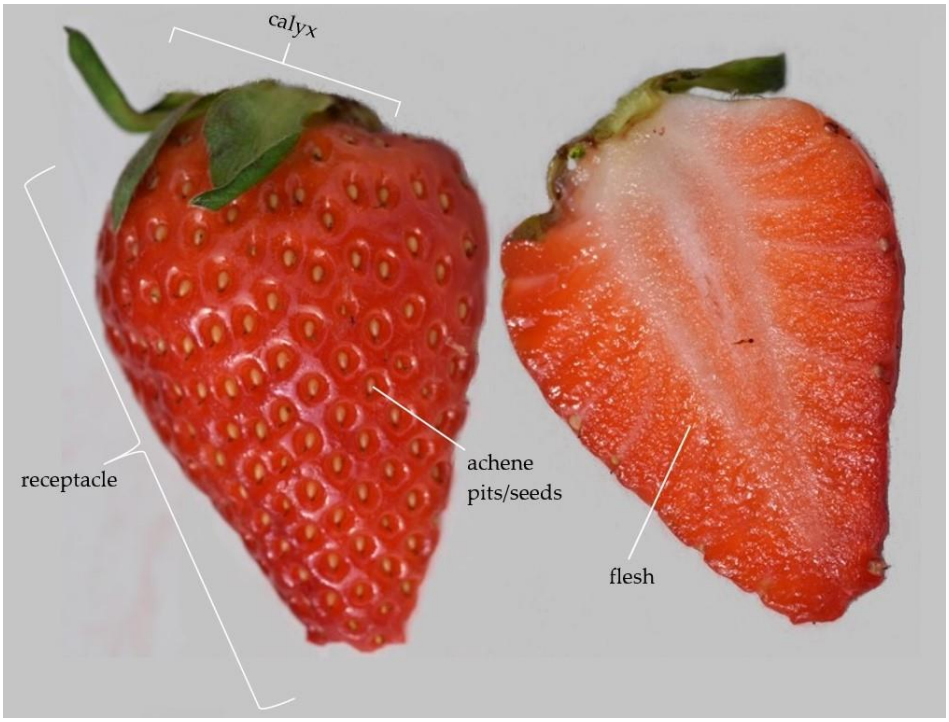

Figure 2. Image of the fresh strawberry and the parts of the fruit (own photograph).

With a total annual production of 1.3 million tons, strawberry is known as the most popular summer soft fruit in Europe [72]. Spain is the largest producer and exporter of strawberries in Europe [72]. In 2016, average consumption per capita in Europe was 1.64 kg/year; however, this amount increases to 2.66 kg/capita when import, export, and production statistics are taken into account [72]. Furthermore, Italy, Germany, and the United Kingdom have the highest consumption per capita with 3 kg/year [72]. Similarly, the per capita consumption of fresh strawberries in the United States gradually increased between 2000-2017 (Figure 3) [73].

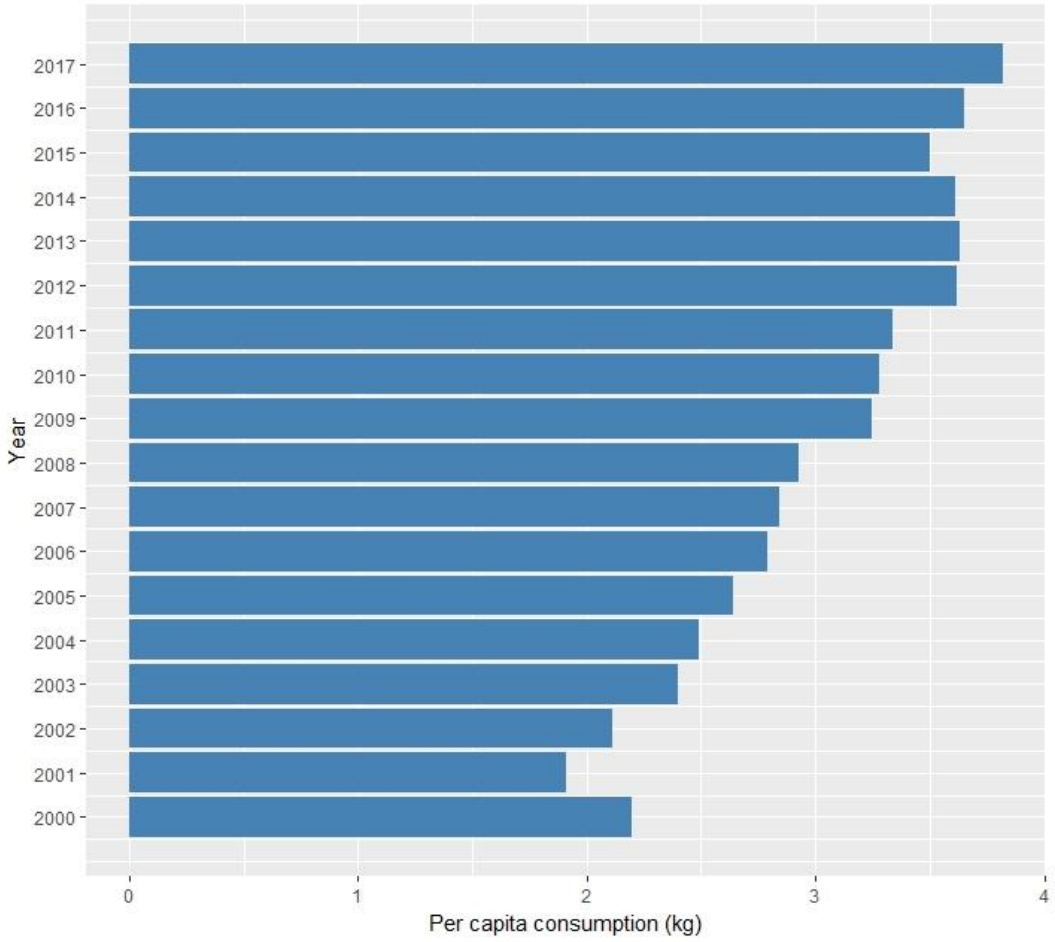

Figure 3. Annual Per capita consumption of fresh strawberries in the USA between 2000 – 2017 (Source: Statista The Statistics Portal [73]).

Strawberry is a non-climacteric fruit. Particularly at temperatures >5 °C and low humidity conditions during ripening, strawberries are subjected to softening of firmness, increasing of anthocyanin content, decreasing chlorophyll amount, while the glossiness diminishes [71,74]. Major organic acids in strawberry fruit were determined as citric, malic, ascorbic, oxalacetic, glyceric, and glycolic acids, and they affect flavor, cellular pH, and tissue color of the fruit [71]. Moreover, soft fruit aroma is affected by the complicated

mixtures of various components such as esters, alcohols, aldehydrates, ketones, furanones, and sulfur compounds [71].

The importance of flavor and appearance of the fruit continues to grow for European consumers [72]. The previous study of Terry [71] indicated that a healthy green calyx is also desirable for consumers and evaluated as a freshness indicator.

The Center for the Promotion of Imports (CBI) [72] specified the characteristics of fresh strawberries in the market as follows:

- intact and undamaged; not affected by rotting or deterioration;
- clean and free of any visible foreign matter;
- fresh in appearance, but not washed;
- free from pests and free from damage caused by pests;
- including fresh, green calyx and stalk (except in the case of wood strawberries);
- free from abnormal external moisture;
- free from any foreign smell and/or taste.

Nutritional constituents of raw strawberry are given in Table 2.

Table 2. Nutritional composition of raw strawberry (Source: United States Department of Agriculture (USDA) - Agricultural Research Service [75]).

Nutrient	Value per 100g	Nutrient	Value per 100g
water	90.95 g	fiber, total dietary	2 g
energy	32 kcal	potassium, K	153 mg
protein	0.67 g	calcium, Ca	16 mg
total lipid (fat)	0.30 g	phosphorus, P	24 mg
ash	0.40 g	vitamin C, total ascorbic acid	58.8 mg
carbohydrate, by difference	7.68 g	vitamin A	12 IU[1]
sugars, total	4.89 g	folate, total	24 μg

[1] **IU:** International Unit is a measure of biological activity and is different for each substance.

In general, strawberries are one of the most perishable fruits in the market [76]. Relatively high metabolic activity and being substantially susceptible to fungal spoilage (i.e., *Botrytis cinerea* is the causal agent of gray mold) are the major causes of food decay in harvested strawberries [76,77]. High initial yeast-mold population (i.e. log cfu/g = 4.87) was enumerated as 6.62 by day 7 [78]. In addition to fungal spoilage, strawberries are also susceptible to a high level of bacterial contamination. A recent study by Tomadoni, Moreira, Pereda and Ponce [78] indicated that log cfu/g of mesophilic bacteria of unprocessed strawberries increased from 4.81 to 7.10 during 7 days of storage. Similarly, the log cfu/g value of psychrophilic bacteria count was changed from 4.38 to 7.37 during the same period.

Additionally, strawberries suffer from mechanical injuries such as bruising and water loss [77].

In addition to cantaloupe, strawberry was selected as a second sample group to conduct edible coating studies on. The main reason for choosing strawberry is its unique surface characteristics. Contrary to the fresh-cut cantaloupe surface, which has high hydrophilicity due to being covered with a water layer; the surface of strawberry is strongly hydrophobic caused by the outermost wax layer. Moreover, the fresh-cut cantaloupe surface is relatively straight, while the strawberry surface is rough, covered with achenes and round shaped.

2.2 Antimicrobial Additives

Naturally occurring antimicrobial compounds can be incorporated into edible coating formulations to control the microbial growth, extend the shelf life of the food, and reduce the level of concern of the customers over the additives' addition. Hop (*Humulus lupulus* L.) extract has been used in beer brewing to add a characteristic bitter flavor to the product [79]. In addition to its specific flavor, hop resins have distinctive antioxidative and antimicrobial properties [80,81]. Teuber and Schmalreck [81] and Schmalreck, *et al.* [82] emphasized that Gram(+) bacteria such as Bacilli, Corynebacteria, Diplococci, Lactobacilli, and Streptomycetes were more sensitive to hop resins compared to Gram(-) bacteria. On the other hand, other microorganisms are either resistant to hop resins, or only high concentrations have an impact on them. Due to their prenyl side chains and the lipophilic character of the molecules, lupulones (β acids) and humulones (α acids) of hop resin were the biologically most active substances, which act on microbial membranes [82-84]. However, Mizobuchi and Sato [84] argued that these substances had also antifungal activities.

Potassium sorbate (E202) is the potassium salt of sorbic acid. It is a polyunsaturated fatty acid used as a conventional preservative in food (i.e., dairy products, fat emulsions, fruit/vegetable products, baked goods, meat products, fish preserves, beverages, sauces), pharma (i.e., cough syrup, antibiotics, antipyretic agents) and animal feed [85-87]. It has antimicrobial effects against yeast, mold, and many bacteria [88]. U.S. Food and Drug Administration (FDA) stated that potassium sorbate is GRAS (generally recognized as safe) when used under GMP (good manufacturing practice) [89]. EFSA noted that the conducted toxicity studies did not show any adverse effects, and ADI (acceptable daily intake) of 11 mg sorbic acid/kg bw per day for potassium sorbate was determined [90,91].

2.3 Surface Free Energy (SFE) of Solids

High wettability of the solid surface is crucial for the production of edible coated products [92]. Surface free energy (SFE) is an important property of the materials and determines interactions such as adhesion, absorption, wetting, and other phenomena [93]. Although the measurement of SFE of a liquid is a straightforward process, direct

experimental measurement of SFE of a solid is not possible but can be done indirectly utilizing the contact angle values of various probe liquids on the respective solid [92,93]. Before listing the measurement methods, it is important to mention about the development of the derivations of the interfacial interactions used in the calculation methods.

2.3.1 Interfacial Interactions

Cohesive forces define the collective intermolecular forces, such as hydrogen bonding and van der Waals forces, and are shared with all neighboring molecules of the same substance [94,95]. Liquid molecules on the surface have no neighboring molecules above, and consequently, they cohere more strongly to other liquid molecules directly associated with them [95]. These attractive forces are responsible for the phenomenon called surface tension [94]. The term is defined as the property of the surface of a liquid that allows it to resist an external force due to the cohesive nature of the water molecules [95]. The liquid surface tends to shrink into the minimum surface area possible.

Young's Equation (Eq.1) considers a drop of liquid in equilibrium on a horizontal solid surface and determines the forces (Figure 4) [96,97].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \quad (1)$$

where γ_{SV} is the surface tension on the solid-gas interphase, γ_{SL} is the surface tension on the solid-liquid interphase, γ_{LV} is the surface tension on the liquid-gas interphase, and θ is the equilibrium contact angle between solid and liquid [92]. Young's Equation is still used as the basis for calculating methods of the SFE [92]. However, it is important to note that the application is limited to ideal surfaces (i.e., perfectly flat, rigid, insoluble, non-reactive, chemically homogeneous and have no contact angle hysteresis) [98].

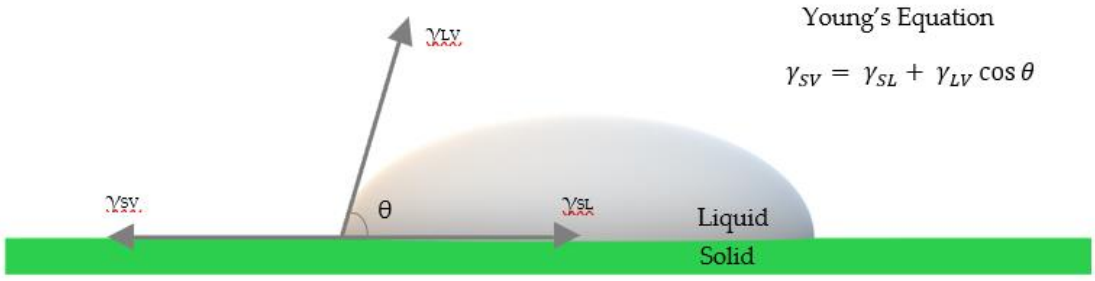

Figure 4. The balance of surface free energy of solid, surface tension of a liquid, and interfacial free energy between solid and liquid.

The measurement of γ_L and θ is straightforward, on the other hand, Berthelot formulated a hypothesis (Eq. 2) for the calculations of the unknown quantity (γ_{SL}), which is partly justified by the theory of the London intermolecular interactions [92,99].

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S \gamma_L)^{0.5} \quad (2)$$

Girifalco and Good [100] modified the equation of Berthelot's hypothesis (Eq.2) and introduced a new parameter (Φ) for the calculation of the interfacial interactions (Eq.3). Φ would be assumed as 1 in the case of an interfacial system when the same type of interactions occurs in both parts [92].

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\Phi(\gamma_S\gamma_L)^{0.5} \quad (3)$$

Three other forms of the equation of state were obtained by Neumann et al. (Eq.4-6) [101]. Eq.4 was derived utilizing the fundamental thermodynamic relations concerning the intermolecular interactions [102].

$$\gamma_{SL} = \{(\gamma_S)^{0,5} - (\gamma_L)^{0.5}\}/\{1 - 0.015(\gamma_S\gamma_L)^{0.5}\} \quad (4)$$

Eq. 5 was obtained with the modification of Berthelot's hypothesis. Additionally, Eq. 6 was derived by the further modification of the same hypothesis. The coefficients β_1=0.0001247 and β_2=0.0001057 were determined experimentally [102].

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S\gamma_L)^{0.5} exp\{-\beta_1(\gamma_L - \gamma_S)^2\} \quad (5)$$

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S\gamma_L)^{0.5}\{1 - \beta_2(\gamma_L - \gamma_S)^2\} \quad (6)$$

Some researches accepted an assumption that γ_{SL} is determined by various interfacial interactions, and its quantity is related to the characteristics of studied liquid and solid surfaces. As shown in Eq.7, Fowkes [103] assumed that the SFE of a solid and a liquid is a sum of independent components; i.e., dispersion ($\gamma_S{}^d$), polar ($\gamma_S{}^p$), hydrogen bonding ($\gamma_S{}^h$), induction ($\gamma_S{}^i$), acid-base components ($\gamma_S{}^{ab}$) and all remaining interactions ($\gamma_S{}^o$) [92].

$$\gamma_S = \gamma_S{}^d + \gamma_S{}^p + \gamma_S{}^h + \gamma_S{}^i + \gamma_S{}^{ab} + \gamma_S{}^o \quad (7)$$

Fowkes studied mainly the two-phase systems containing a solid or liquid substance in which only the dispersion interactions are present [92]. For these systems, Fowkes derived the following equation (Eq.8) for the aforementioned systems [99]. It is important to note that Eq.8 is a modified version of Eq.2. However, the interactions were limited only to the interfacial London interactions [92,104].

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left(\gamma_S{}^d\gamma_L{}^d\right)^{0.5} \quad (8)$$

Owens and Wendt [105] modified the Fowkes approach (stated in Eq.7) while assuming the sum of all components excluding $\gamma_{SL}{}^d$, can be associated with the polar interactions ($\gamma_{SL}{}^p$). The researchers used the geometric means, and the derived equation can be seen in Eq.9 [105].

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left(\gamma_S{}^d\gamma_L{}^d\right)^{0.5} - 2(\gamma_S{}^p\gamma_L{}^p)^{0.5} \quad (9)$$

It is important to note that polar interactions defined by Fowkes in Eq.7 differ from the polar interactions defined by Owens-Wendt in Eq.9 [92].

Wu [106,107] accepted the same approach by Owens-Wendt but used the harmonic means of the interfacial interactions (Eq. 10). According to Zenkiewicz [92], Wu's approach has not been widely used in SFE or wettability studies.

$$\gamma_{SL} = \gamma_S + \gamma_L - 4\{\gamma_S{}^d\gamma_L{}^d/(\gamma_S{}^d + \gamma_L{}^d) + \gamma_S{}^p\gamma_L{}^p/(\gamma_S{}^p + \gamma_L{}^p)\} \quad (10)$$

Also, Van Oss, *et al.* [108] agreed with the partition of the SFE of solids and liquids and divided γ_{SV} into two components, these are long-range interactions called Lifshitz-van der Waals (γ^{LW}) and short-range interactions called acid-base (γ^{AB}), which was considered to be equal to $2(\gamma^+\gamma^-)^{0.5}$. The resulting equation (Eq.11) was formulated as [92]:

$$\gamma_{SL} = \{(\gamma_S{}^{LW})^{0.5} - (\gamma_L{}^{LW})^{0.5}\}^2 + 2\{(\gamma_S{}^+)^{0.5} - (\gamma_L{}^+)^{0.5}\} \cdot \{(\gamma_S{}^-)^{0.5} - (\gamma_L{}^-)^{0.5}\} \quad (11)$$

2.3.2 Calculation of SFE

Fowkes method is especially convenient when it is used for the calculation of nonpolar polymers and polymeric materials, and it is important to underline that the method is based on the independence and additivity of the polar and dispersive interactions (Eq.12) [92,109]. Therefore, water and diiodomethane usage as probe liquids are recommended [92,110].

$$\gamma_S = \gamma_S{}^d + \gamma_S{}^p \qquad and \qquad \gamma_L = \gamma_L{}^d + \gamma_L{}^p \quad (12)$$

For the calculation of SFE of nonpolar solid (i.e., $\gamma_S = \gamma_S{}^d$), Eq. 13 was derived by combining Eq. 1 and Eq. 8 [92,109].

$$\gamma_S = \gamma_S{}^d = \gamma_L{}^2\,(1 + \cos\theta)^2/(4\gamma_L{}^d) \quad (13)$$

After the placement of a non-polar liquid on the solid, the contact angle (θ, the contact angle of liquid, which only forms dispersive interactions) is measured. $\gamma_S{}^d$ can be calculated from the simplified formula (Eq.14) [92]:

$$\gamma_S{}^d = 0.25\,\gamma_L(1 + \cos\theta)^2 \quad (14)$$

As a next step, the contact angle (θ_p, contact angle of a polar liquid) is measured using a liquid, which provides $\gamma_L = \gamma_L{}^d + \gamma_L{}^p$, the $\gamma_S{}^p$ can be calculated from Eq.15 [92].

$$\gamma_S{}^p = \left\{0.5\gamma_L\left(1 + \cos\theta_p - \left(\gamma_S{}^d\gamma_L{}^d\right)^{0.5}\right)\right\}^2/\gamma_L{}^p \quad (15)$$

The Owens-Wendt Method [105] is one of the most common approaches for calculating SFE of polymers [92]. Although Fowkes and Owens-Wendt methods are based on the same mathematical model, they have slight differences in terms of SFE calculations [92]. Owens-Wendt provided a simple method; researchers combined Young's Equation (Eq.1) and their derivation (Eq.9) and obtained the following relationship (Eq.16):

$$\left(\gamma_S{}^d\gamma_L{}^d\right)^{0.5} + (\gamma_S{}^p\gamma_L{}^p)^{0.5} = 0.5\gamma_L\,(1 + \cos\theta) \quad (16)$$

Due to two unknown variables (i.e. $\gamma_S{}^d$ and $\gamma_S{}^p$) the equation shall be solved with measuring at least two contact angles ($\theta_1\ and\ \theta_2$) of two different probe liquids (a liquid which mainly forms dispersive interactions and one with dominant polar component). Thus, two linear equations will be obtained (Eq.17-18), where $x = \left(\gamma_S{}^d\right)^{0.5}$ and $y = (\gamma_S{}^p)^{0.5}$ and a, b, c, d are the coefficients depend on the type of liquid [92].

$$x + ay = b(1 + \cos\theta_1) \quad (17)$$

$$x + cy = d(1 + \cos\theta_2) \quad (18)$$

Other methods

In addition to the methods mentioned above, Van Oss-Chaudhury-Good method (measuring contact angles of three different probe liquids-one nonpolar and two bipolar), the Zisman method (determines critical SFE (γ_C) instead of SFE of a solid (γ_S)), the Neumann Method (requiring only one measurement liquid, however, significant differences can be found between SFE values calculated using Neumann and Owens-Wendt methods) and the Contact Angle Hysteresis method (recently developed, adsorption at the interface was taken into consideration) have been derived by the researchers [92,111-114].

Among all the methods, the Owens-Wendt approach is a standard and most used method for the calculation of SFE.

2.4 Wettability

Wettability (W_S, spreading coefficient) is defined as the ability of a liquid spread on a solid surface [115,116]. Commonly, the wetting between solid and liquid can be expressed by the balance of three interfacial tensions [117] drawn in Figure 4.

Wettability can be calculated using the work of adhesion (W_a) and the work of cohesion (W_c). Wa is defined by Dupre as the reversible thermodynamic work that is needed to separate the interface from the equilibrium state of two phases to a separation distance of infinity (Eq. 19) [118].

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (19)$$

Eq. 19 and Young's Equation (Eq. 1) were combined to get the Young-Dupre Equation for adhesion (Eq. 20), which relates contact angle to the work of adhesion [119]. The wettability calculation was stated in the previous studies of Ribeiro, Vicente, Teixeira and Miranda [116] and Casariego, *et al.* [120]:

$$W_a = \gamma_{LV} \times (1 + \cos\theta) \quad (20)$$

$$W_c = 2 \times \gamma_{LV} \quad (21)$$

$$W_s = W_a - W_c \quad (22)$$

The adhesion forces cause the liquid to spread on the surface, and the cohesion forces cause the liquid to contract (Figure 5) [116].

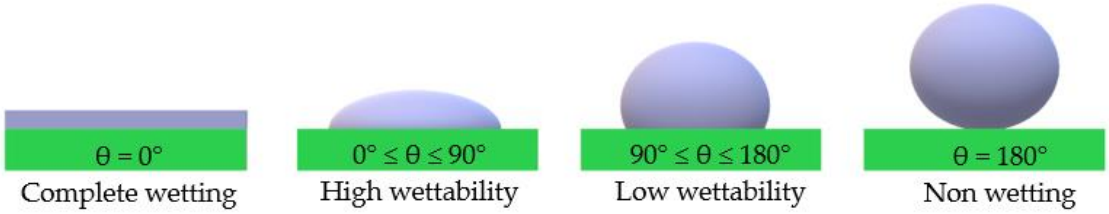

Figure 5. The contact angle and the shape of the liquid droplet are determined by the interactions between two interphases.

As seen in Figure 5, the highest substrate wetting capability is achieved when the coating liquid with low surface tension spreads out totally over the substrate surface without forming a droplet (θ, contact angle = 0). In this case, as seen in Eq. 20-22, cos 0 = 1 and Wa=Wc; therefore, Ws will equal zero. The maximum value that the wettability coefficient (Ws) can have is zero [116]. In general, the wettability is acknowledged as good if θ<90°; and recognized to be bad if θ>90° [117].

The effectiveness of edible coatings for food protection depends primarily on controlling the wettability of the coating solutions; i.e., coating spreads uniformly over the surface of the food and wets it [115,116,121].

2.5 Possible Components of Edible Coatings

Three major components of foods (i.e., proteins, carbohydrates, and lipids) can meet the requirements for the preparation of effective edible coatings [122]. Due to the differences in their chemical structures, the overall coating properties formed by each component are also unalike [122]. Components of edible coatings can be mainly divided into three categories: hydrocolloids, lipids, and composites (i.e., contains both lipid and hydrocolloid components) [16]. To be accepted as an edible coating, materials should be recognized as GRAS (generally regarded as safe) and/or used within limitations specified by regulatory authorities [123]. Hydrocolloid and lipid materials used extensively for the formation of edible coatings are presented in Table 3.

Table 3. Hydrocolloid and lipid materials that have been studied extensively for the formation of edible coatings for food applications [122-132].

Edible Coating Materials	Sources
Hydrocolloid - Polysaccharide	
Agar	Seaweed
Alginate	Seaweed, microorganism
Carrageenan	Seaweed
Cellulose and its derivatives	Plant, microorganism

Methylcellulose (MC)	
Carboxymethylcellulose (CMC)	
Hydroxypropylcellulose (HPC)	
Hydroxypropyl methylcellulose (HPMC)	
Chitosan	Animal, microorganism
Gums	
Arabic gum	Tree (exudates)
Xanthan gum	Microorganism (fermentation)
Galactomannans	Seed
Guar gum	
Locust bean gum	
Pullulan	Microorganism
Pectins	Plant
Kefiran	Microorganism
Starch and derivatives	Plant
Dextrin	Microorganism
Hydrocolloid - Protein	
Milk proteins	Animal
Casein	
Whey protein	
Collagen	Animal
Gelatin	Animal
Myofibrillar proteins	Animal
Fish myofibrillar protein	
Egg white protein	Animal
Peanut protein	Plant
Soy protein	Plant
Pea protein	Plant
Wheat gluten	Plant
Corn zein	Plant
Lipid	
Waxes	
Beeswax	Animal
Carnauba wax	Plant
Candelilla wax	Plant
Rice bran wax	Plant
Vegetable oils	Plant
Fatty acids	Plant
Acetoglycerides (acetylated monoglycerides)	Plant

Resins	
Shellac resin	Animal
Terpene resin	Plant

2.5.1 Hydrocolloids

The term 'hydrocolloids' is used to refer to a heterogeneous group of long-chain polymers (proteins and polysaccharides) that dissolve or disperse in water to form viscous dispersions and/or gels [125,133,134]. The presence of a great number of hydroxyl (-OH) groups significantly improve their affinity for binding water molecules and make them hydrophilic compounds [133]. Moreover, the name 'hydrophilic colloids' or 'hydrocolloids' is attributed to their dispersion forming ability that exhibits the properties of a colloid [133].

Hydrocolloid components can be used in applications where good gas and lipid barrier features or improved mechanical properties are the main objectives but not the control of water vapor transport [16]. Kester and Fennema [135] explained it with the large presence of polar groups and their hydrophilic properties, which support interacts with water vapor but not O_2. The easily condensable water vapor has a high solubility in the barrier hydrocolloid film [135].

The usage of hydrocolloids as food additives is subject to EC Regulation 1333/2008 [136].

In the present study, sodium alginate was selected as gel-forming material due to its high abundance in nature, high industrial production capacity, and its inexpensiveness [137].

2.5.2 Lipids

Lipid coatings are described as good moisture barriers and increase the gloss of coated products; however, they are poor gas barriers [16,122,138]. Although they are referred to as good water vapor barriers, adhesion of lipophilic material on the wet surfaces such as cut fruits and vegetables is weak at the coating-food interface [122]. Therefore, a composite coating (dual-coating) such as one layer crosslinked alginate solution and one layer lipid coating can be one possible solution for the adhesion difficulties [122]. However, even though it would be very small quantities, consumers' reactions to lipid consumption with fruits must be considered very carefully.

2.5.3 Composites

The composite coating is defined as systems where two or more biopolymers are combined to achieve beneficial properties [139]. Composite coatings can be prepared as bilayers (one layer of hydrocolloid and one layer of lipid component) or as conglomerates

(different components are interspersed throughout the formed film) [16]. Composite coatings benefit of the advantages of hydrocolloids and lipids together while each reduces and provides a balance for the other's disadvantages [16,140].

Hydroxypropyl methylcellulose-beeswax or shellac [141], whey protein concentrate-beeswax [142], whey protein isolate-flaxseed oil-beeswax [143], arabic gum-chitosan [144] can be given as examples of composite coatings studied in the literature.

2.6 Alginate-based Edible Coatings

This subsection contains a peer-reviewed article, "Alginate-based edible films and coatings for food packaging applications". It is published in the Open Access Journal "Foods" (Publication I). The author of this thesis is also the first author of the article. Authors' contributions were specified in the article as: "Tugce Senturk Parreidt conceived the focus of the review, conducted the literature search, and drafted the manuscript. Markus Schmid and Kajetan Müller formatted, reviewed, and edited the manuscript upon critical revision of the texts".

Summary of the Publication-I

Edible packaging (i.e., edible coatings and edible films) are thin layers of materials used for enrobing the food products as a superficial coating or between layers of ingredients without affecting the organoleptic properties negatively. They can be consumed as a part of the product; therefore, the materials should conform to the food regulations and laws. They can be used to retard moisture, gas, solute, and oil transport, provide or improve structural integrity, retain volatile flavor compounds, convey food additives and improve aesthetic appearance.

Alginate is mainly derived from brown algae species and composed of unbranched, linear binary copolymers of β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues linked by 1–4 glycosidic bonds. It is used in various industries such as food, beverage, textile, printing, and pharmaceutical as a thickening agent, stabilizer, emulsifier, chelating agent, encapsulation, swelling, a suspending agent or used to form gels, films, and membrane.

The present paper reviews the most recent essential information about alginate-based edible coatings for food packaging applications. Emphasis will be placed on the list of active ingredients incorporated in alginate-based formulations, edible coating/film application methods, research and development studies of coated food products and mass transfer and barrier characteristics of the alginate-based coatings/films.

foods

MDPI

Review

Alginate-Based Edible Films and Coatings for Food Packaging Applications

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Received: 14 August 2018; Accepted: 14 October 2018; Published: 17 October 2018

Abstract: Alginate is a naturally occurring polysaccharide used in the bio industry. It is mainly derived from brown algae species. Alginate-based edible coatings and films attract interest for improving/maintaining quality and extending the shelf-life of fruit, vegetable, meat, poultry, seafood, and cheese by reducing dehydration (as sacrificial moisture agent), controlling respiration, enhancing product appearance, improving mechanical properties, etc. This paper reviews the most recent essential information about alginate-based edible coatings. The categorization of alginate-based coatings/film in food packaging concept is formed gradually with the explanation of the most important titles. Emphasis will be placed on active ingredients incorporated into alginate-based formulations, edible coating/film application methods, research and development studies of coated food products and mass transfer and barrier characteristics of the alginate-based coatings/films. Future trends are also reviewed to identify research gaps and recommend new research areas. The summarized information presented in this article will enable researchers to thoroughly understand the fundamentals of the coating process and to develop alginate-based edible films and coatings more readily.

Keywords: edible coating; edible film; food packaging; alginate; crosslinking; additives; application method; food; transport mechanism

1. Introduction

The principal roles of food packaging are to protect food products from physical, chemical, and biological influences by delaying food deterioration, retaining and prolonging the beneficial effects of processing, and maintaining the quality and safety of the foods with extending shelf life [1]. Broad external influences such as the development of international food markets, legal and technological requirements, raw material availability, consumer demands, etc. caused the food packaging area to change perpetually [2]. A total of 1.3 billion tonnes of municipal solid waste per year was generated in 2012, but it is expected to increase to 2.2 billion tonnes per year by 2025 [3]. Non-renewable, non-biodegradable packaging materials have serious environmental drawbacks. They have been considered a major source to the solid waste and environmental pollution by consumers and environment activists [4,5]. In order to solve this problem, companies and researchers have been working on ways to develop new packaging strategies with environmentally friendly, abundant

biodegradable packaging materials made from renewable natural polymers [4,6]. Furthermore, the rapidly growing interest in the use of edible packaging can also be associated with a growing interest from consumers for minimally processed fresh-like foods with an extended shelf life and trend in improving the quality of food with edible barriers [7].

Edible films and coatings are thin layers of material (their thickness is generally less than 0.3 mm) used for enrobing the food product to replace or fortify the natural layers and can be consumed as a part of the product or with further removal [8,9]. Therefore, the materials used in the formulation should conform to the general food laws and regulations [10]. Additionally, the coatings and films should not affect the organoleptic properties of the food product negatively [6].

Edible packaging can be a superficial coating on the food or continuous layers between compartments/ingredients of the heterogeneous products (e.g., pizza, bakery fillings, and toppings) [8]. The coating can also be applied on individual pieces of the whole product, which have not been individually packaged due to practical arguments, such as fresh-cut melons, kiwis, strawberries, nuts, beans, pears [11].

Edible films and coatings can be used to overcome many obstacles involved in the marketing of foods [12]. These functions can be specified as retarding moisture, gas, solute and oil migration, improving structural integrity, retaining volatile flavor compounds, conveying food additives [12]. In addition, they improved the aesthetic appearance by minimizing the development of physical damage, hiding scars, and improving surface shine [13,14]. For instance, hot-melt paraffin waxes have been used to coat citrus fruits to retard moisture, edible collagen casings have been used for sausages to provide structural integrity and apples have been coated with wax to improve surface shine and prevent physical damage.

The required features expected from edible films and coatings can be assigned by the specific characteristics of the product and changes during production, transportation, and storage periods. Despite providing a barrier, the non-edible packaging is still essential for edible coated food products due to hygienic reasons [8]. Nevertheless, combining edible films and coatings with traditional packaging would likely reduce the non-biodegradable packaging waste of processed foods and environmental effluence [12,15,16].

Although edible coating and edible film terms have been used interchangeably or as synonyms in some sources; their application on the food products constitutes their main difference [9]. Edible films are stand-alone wrapping materials which can be cut and placed on the food product separately due to having enough integrity; on the other hand, edible coatings form a thin layer on the product directly subsequent to the application [8,9,17,18]. Therefore, although produced from the same gelling agent, the characteristics of edible films and coatings can be very different [9].

Alginate-based food coatings and films attracted widespread interest. A wide range of scientific research has been published in the literature. This overview summarizes the literature information with dividing into categories in a layout:

1. General information about alginate and gel formation
2. Lists of additives incorporated into the alginate-based edible films and coatings in the literature
3. Types of film production and coating application
4. Sums up the research findings on alginate coated fruits-vegetables, meats, poultry, seafood, cheese
5. Transport of the products' molecular components
6. Future trends

Our present study can be used as a guide for researchers both in the academy and industry who plan to work on alginate-based coatings, will select the components of their formulations, and plan their future studies and experiments.

2. Film-Forming Materials

Film-forming biopolymers are generally classified according to the type of film-forming material, which form cohesive and continuous matrices [8]. These are hydrocolloids (polysaccharides and proteins), lipids and composites (Figure 1) [12,19]. Hydrocolloids are composed of hydrophilic polymers of microbial, vegetable, animal, or synthetic origin [15]. Mostly, they are large molecules with many hydroxyl groups [15,20]. Hydrocolloid film applications do not target to control water vapor migration due to their hydrophilic nature [12]. However, the continuous polysaccharide film can be referred to as a sacrificial moisture agent. That is, moisture evaporates from the film instead of the food surface [21–24]. Subsequent to the desiccation of the coating film, the food product would lose its moisture [24].

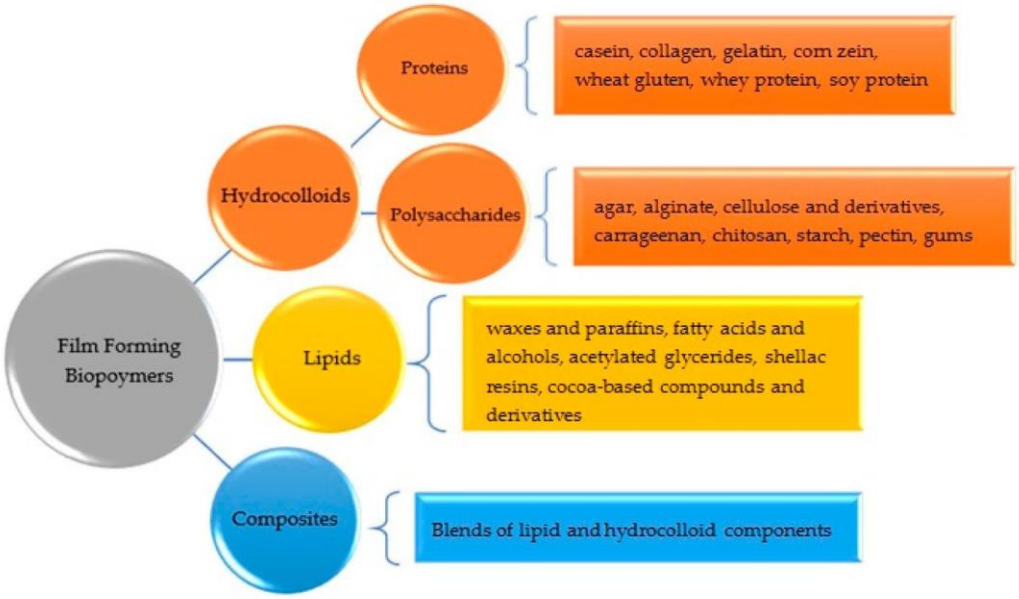

Figure 1. The film-forming biomaterials that have been studied extensively for the formation of edible coatings and films (Donhowe and Fennema [12], Embuscado and Huber [25]).

In general, polysaccharides are used as gas barriers; lipids reduce water transmission, while proteins provide mechanical stability [9]. The main disadvantages of lipid-based films and coatings are their opaqueness, fragility, and instability (rancidity), on the other hand, hydrocolloid films and coatings have a more neutral taste [6]. Composites are formulated using both lipid and hydrocolloid components, which are incorporated into the formulation in order to benefit from their advantages together [12]. Composites can be formed as a bilayer or as a conglomerate [12].

3. Alginate

Alginates are naturally occurring, indigestible polysaccharides commonly produced by and refined from various genera of brown algae (mainly *Laminaria hyperborean*, *Macrocystis pyrifera*, *Ascophyllum nodosum*; lesser extent *Laminaria digitate*, *Laminaria japonica*, *Eclonia maxima*, *Lesonia negrescens*, *Sargassum* sp.) [26–30]. Some bacteria such as *Azotobacter vinelandii* or mucoid strains of *Pseudomonas aeruginosa* also synthesize alginate like polymers as exopolysaccharide (i.e., extracellular polymeric substances, EPSs) [29,31]. Alginate production from Marine algae [32] and *A. vinelandii* [33] are explained elsewhere.

The molecular structure of alginates is composed of unbranched, linear binary copolymers of β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues linked by 1–4 glycosidic bonds (Figure 2a) [27,28,34,35]. An algal alginate structure could be separated into three fractions (three uronic

acid blocks): These are homopolymeric regions of M and G blocks, and alternating MG blocks containing both polyuronic acids [27,35,36]. Bacterial alginates have O-acetyl groups, while they are not present in the structure of algal alginates [37]. Additionally, bacterial alginates have higher molecular weights compared to the algal polymers [33].

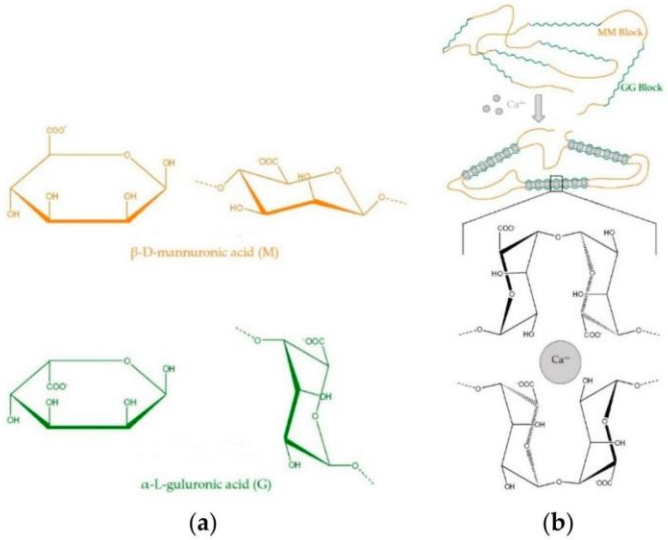

Figure 2. The structural formulae of monomeric units in alginate and the schematic representation of the egg-box model (**a**) Left hand side: Haworth conformation; right hand side: Chair conformation (**b**) Gelation of poly L-guluronate blocks (G Blocks,) with Ca^{2+} ( ) (Peteiro [32], Lee and Rogers [38]).

The source of the alginate affects the ratio of M and G residues, which have an impact on the physical and chemical properties of the alginate, as well as the viscosity of the coating solution and thickness on the product [28,36,39]. Martinsen, et al. [40] characterized the relationship of physical properties of alginate gel beads with a polymer composition, sequential structure, and molecular size of the several different alginate sources.

Alginic acid was first discovered and isolated by Dr. E.C.C. Stanford in 1881 [35]. Alginates (i.e., sodium alginate (E401), potassium alginate (E402), ammonium alginate (E403), and calcium alginate (E404)) are monovalent salts of alginic acid (E400) [27,41,42]. Alginic acid and calcium alginate are insoluble in water while sodium alginate, potassium alginate, and ammonium alginate are water-soluble polymers [42,43]. They have a limited solubility at low pH values [44]. The solubility of different types of alginates in numerous solvents and solutions were listed by Kimica Corporation [45].

The U.S. Food and Drug Administration (FDA) classifies food grade sodium alginate as GRAS (generally regarded as safe) substance in Title 21 of the Code for Federal Regulations (CFR) and lists its usage as an emulsifier, stabilizer, thickener, and gelling agent [46]. The European Commission (EC) listed alginic acid and its salts (E400–E404) as an authorized food additive [41].

Alginate is widely used in various industries such as food, beverage, textile, printing, and pharmaceutical as a thickening agent, stabilizer, emulsifier, chelating agent, encapsulation, swelling, a suspending agent, or used to form gels, films, and membrane [28,47]. Sodium alginate is the most common salt of alginate [48].

4. Crosslinking

It is widely well-known that alginate is polyuronide, a natural ion exchanger [49]. The charged state of alginate is beneficial for film formation. In the absence of bivalent ions, alginate can be only used to increase viscosity [38]. However, the addition of certain bivalent cation into the alginate

solution leads to a gel formation through ion exchange [42,47]. The affinity of alginate for the alkaline earth metals increases in the order $Ca^{2+} < Sr^{2+} < Ba^{2+}$ [38,49]. Monovalent cations and Mg^{2+} ions do not form a gel [50]. Even though divalent cations such as $Pb^{2+,}$ Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+} can also induce gelation, their toxicity limits their utilization [51].

Alginate gel formation is rather a complex process. The proportion and length of the guluronic acid block (G-blocks) in the polymeric chain, the capacity to bind the number of divalent ions, the type of gelling ions and gelling conditions affect strongly the hydrogel properties of alginate [39,52–54]. The introduction of divalent cations (usually Ca^{2+} ions) to the system induces conformational changes in alginate such as alignment of the G-blocks and the formation of the egg-box model [54] due to bounding of calcium ions between two chains and forming divalent salt bridges (Figure 2b) [39,40]. A higher amount of G-Blocks will create rigid and dense gels, while a higher amount of M-Blocks will build flexible, porous gels [54–57]. Therefore, the diffusional resistance of gels containing predominantly high polyguluronic alginate content against high-molecular-weight-compounds is high [56,57]. Besides, the study by Olivas and Barbosa-Cánovas [58] revealed that films containing higher proportions of G-Block (in other words, lower M/G ratio) showed better moisture barrier characteristics.

There are two types of procedures for the incorporation of gelling ions into the alginate solution to form hydrogel (i.e., external and internal gelling modes) [59,60]. (1) For external gelation (the traditional method), alginate solution is directly exposed to the solution of gelling ions, Ca^{2+} instantaneously reacts with carboxylic groups of guluronic acid residues and hydrogel is formed irreversibly due to the diffusion of ions [52,59,61]. (2) On the other hand, the internal gelling method consists in incorporating an insoluble source of gelling ions with alginate solutions and afterward, the gelling ions are released by processes that lower the pH: the addition of organic acids or slowly hydrolyzing lactones [52,59]. When these two methods are compared, internal gelation forms more homogeneous but less dense gel matrices with larger pore sizes compared to the external gelation due to the displacement of Ca^{2+} by H^{+} with the acid addition [60,61].

According to Mancini and McHugh [53], gel formation by cooling of the hot solution, which contains all the components, can be evaluated as the third method to initiate the controlled alginate gelation. Due to the thermal energy that the alginate solution possesses, a calcium-induced hydrogel formation can only take place after cooling [53].

The source of calcium ions (i.e., calcium chloride, calcium lactate, calcium gluconate, calcium nitrate, and calcium propionate) has an influence on gel formation. Allen et al. (as cited in Reference [62,63]) reported that crosslinking with calcium chloride generated stronger alginate gels compared to calcium gluconate, calcium nitrate, and calcium propionate. The calcium source also affects the kinetics of gelation; in other words, the rate of gelation and Ca^{2+} concentration is positively correlated [38]. Calcium chloride has the highest solubility (75 g/100 mL) followed by calcium lactate (8 g/100 mL) and calcium gluconate (3 g/100 mL) at 20 °C [38]. The steady-state gel strength was reached fastest by calcium chloride followed by calcium lactate and calcium gluconate [52]. On the contrary, according to the study by Chrastil [64], the gelation kinetic constants did not depend on the calcium source. However, the strength of the formed gel and the resistance against calcium diffusion are not dependent on the calcium source type [38,52].

Despite its high solubility, calcium chloride is not an attractive calcium source due to imparting a bitter taste on the food [38]. On the other hand, calcium gluconate and calcium lactate can be used in coating applications where the taste attributes are important [38].

In situ gelation of alginate, and strongly homogeneous structure forming are also an interest of biotechnology (e.g., tissue engineering, immobilization of cell and enzyme systems, carriers for drug delivery system). A technique to prepare homogeneous alginate gels with a slow release of calcium ions has been reported [65,66]. In a similar approach, Kuo and Ma [67] used calcium carbonate D-glucono-δ-lactone ($CaCO_3$ -GDL) or calcium sulfate dihydrate ($CaSO_4.2H_2O$ -$CaCO_3$ -GDL) as a gelation agent due to their very low solubilities, which allows for a uniform distribution of the $CaCO_3$

in the alginate solution and, therefore, a more controlled and more uniform gel formation. In their subsequent research, the dimensional stability (swelling tendency of the gel due to an increased tendency of the carboxyl and hydroxyl groups to interact with water molecules and osmotic pressure) was controlled by controlling the calcium ion concentration of the external aqueous environment, crosslinking density, and polymer concentration of the gel and chemical composition of alginate [68].

It was pointed out by Pavlath, et al. [69] that two type of reactions take place when an alginate film/coating is immersed in crosslinking calcium solution: diffusion of the multivalent ion which induces formation of calcium linkage with the carboxyl groups for the insolubilization of the alginate film, and the dissolution of alginate by the solution [58]. The increased concentration of the multivalent ion diminishes the dominance of the dissolution process [69]. Rhim [70] also noticed the same phenomena and added that the method of $CaCl_2$ treatment affected the thickness of the film, i.e., direct addition of the crosslinking agent lead to thicker films compared to immersing the alginate films into a crosslinking solution.

The properties of the formed film are also dependent on the mixing temperatures; although mixing at ~20 °C caused an immediate gel formation that could not be cast, mixing at ~50 °C formed a viscous solution which could be poured into the frames [69].

The degree of crosslinking affects the swelling ability of the 3D structure of the alginate in the solvent, and we end up with a decrease in the permeability to various solutes and being used in drug controlled release systems [71]. In the study by Zactiti and Kieckbusch [71], the degree of swelling decreased (in other words, the crosslinking was increased) with the increasing concentration of Ca^{+2} ions in the crosslinking solution and, therefore, the solubility and elongation of the alginate films decreased, while the tensile strength increased. Similarly, Rhim [70] observed that an increase in the $CaCl_2$ concentration caused an increase in the tensile strength and a decrease in the percentage elongation at break.

The literature on the effects of calcium chloride dipping alone (without coating) has shown that $CaCl_2$ can be used as an effective firming agent due to the ability of calcium to bind cell wall polymers, maintain its structure, and diminish the water solubility of pectic substances with forming calcium pectate [72–74]. Improvement in firmness increases with increasing concentration of $CaCl_2$, however, this is independent from the dipping time [75].

5. Additives

The mechanical, functional, organoleptic, and nutritional characteristics of edible films and coatings can be modified with the incorporation of various natural or chemical additives [12].

5.1. Plasticizers

The mechanical properties of biodegradable packages can be improved by the plasticization of the polymer-network with plasticizers, which are generally non-volatile and miscible with the polymer. The primary objectives of the plasticizers are increasing the free volume or molecular mobility of polymers, decreasing the intermolecular forces, bestowing flexibility, reducing brittleness, improving tear impact resistance, and regulating the flow of the coating material [26,76–79]. Furthermore, the plasticizers should have the same solubility properties with the polymer in the solvent system (to prevent plasticizer or polymer separation during film/coating application), possess a high boiling point, and should be able to change the physical and mechanical properties of the substance when incorporated into the formulation [6,76].

Water is the most common and most effective plasticizer; still, the plasticizing effect of water in hydrophilic biopolymers is difficult due to the dependency of the environmental conditions such as relative humidity and temperature [6,8]. Apart from water, glycerol, sorbitol, acetylated monoglyceride, polyethylene glycol, sucrose, etc. have been used as plasticizers in food coating studies [12]. The addition of hydrophilic plasticizers to the formulation generally promotes water vapor permeability (WVP) and influences the mechanical properties of the coating material [12,80].

Therefore, the type and the quantity of the plasticizer are very important in the designing of the edible coating formulation. Parris, et al. [81] stated that based on the total solid content of the film, the plasticizer amount should be determined between 10% and 25% as lower concentrations cause brittleness whereas higher concentrations lead to stickiness.

Glycerine and sodium lactate lead to stronger and more elastic alginate-based films compared to sorbitol, which was stiffer [81]. However, sorbitol added films exhibited better water vapor barrier properties at the same concentration due to being less effective in reducing intermolecular hydrogen bonding between polymer molecules [81]. Jost, Kobsik, Schmid, and Noller [80] compared the effects of glycerol and sorbitol addition to alginate films in terms of their mechanical properties and determined that both plasticizers decreased equilibrium moisture content and porosity. On the other hand, the incorporation of glycerol caused higher WVP and oxygen permeability, while sorbitol did not alter barrier properties [80]. Similarly, Olivas and Barbosa-Cánovas [58] analyzed the effects of different plasticizers (glycerol, sorbitol, polyethylene glycol (PEG), and fructose) on WVP and the mechanical properties of calcium alginate films in two different RH values. WVP increased in the order of fructose, sorbitol, glycerol, and PEG incorporated films. Plasticizers induced a sharp increase in moisture content in the moisture sorption isotherm graphs and modified the mechanical properties with an increasing tensile strength.

In several studies, glycerol has been used as a plasticizer, particularly for alginate films and coatings. However, the amount used is variable. Rojas-Graü, et al. [82] reported that the water vapor resistance (WVR) of alginate coatings increases with an increasing glycerol concentration up to 1.75% (v/v) in the formulation; however, WVR decreases at higher concentrations of glycerol. Likewise, Azarakhsh, et al. [83] observed the same type of effect during the optimization of the alginate coating formulation and determined the amount as 1.16% (w/v). On the other hand, Tapia, Rojas-Graü, Carmona, Rodríguez, Soliva-Fortuny, and Martin-Belloso [39] determined that glycerol concentrations above 1.5% (w/v) decreased the WVR.

High wettability and uniform spreading ability of the edible coating on the targeted food product are desired characteristics of edible coatings while designing the formulations [84–86]. Therefore, the effects of the components on the surface tension of the coating solutions are an important factor. Yet, glycerol and sorbitol do not have a significant effect on the surface tension of the solutions due to not being tensio-active substances [87,88].

High amounts of plasticizer (>10%) have also been incorporated in alginate-based edible coating formulations in the literature [89–93].

Some studies combined more than one plasticizer in order to overcome the brittleness of the alginate films and coatings. Fan, et al. [94] chose glycerol, palmitic acid, β-cyclodextrin, and glycerol monostearate in film formulation. Su Cha, et al. [95] used a 1:1 concentration of polyethylene glycol and glycerol combination.

5.2. Surfactants

Adhesion on hydrophobic, rough surfaces and obtaining a uniform edible coating can be very difficult due to the low surface free energy of the surface [9]. Addition of surface active agents (surfactants) are the key ingredients to increase the wettability of the product and improve the adhesion of the coating material [88]. Moreover, with a reducing superficial water activity, surfactants and emulsifiers had a decreased rate of moisture loss when they were incorporated into the coating formulation [96].

The major characteristics of the surfactants are being present at the surface of the interfaces (liquid-air, liquid-liquid, liquid-solid) at higher concentrations compared to the bulk of the liquid [97]. Surfactants can be classified based on two characteristics: charge type of the surface active part and the chemical structure of the hydrophilic groups [97]. Accordingly, these groups are; anionic (negatively charged), non-ionic (no charged group), cationic (positively charged), and amphoteric (can be positively or negatively charged, or both, depending on the circumstances) surfactants [97].

The uniform spreading ability of the coating on the targeted product is a very important effectiveness indicator of an edible coating. Therefore, researchers checked the surface free energy of the food products, the surface tension of the edible coatings, and spreading coefficient (W_s) while designing their coating formulations. Senturk Parreidt, Schott, Schmid, and Müller [88] characterized the alginate-based coating formulations with various concentrations and types of surfactants (0–5% tween 40, tween 80, span 80, span 60, and soy lecithin).

5.3. Antimicrobials

The addition of antimicrobial and antioxidant agents to the edible coatings and films is beneficial compared to their direct application to food products due to providing the opportunity of gradually releasing the agents and maintaining a critical concentration for a prolonged period [26,71,98,99]. In contrast with the migration of antimicrobials from the coating, the direct addition of antimicrobials to food will cause immediate microbial inhibition while the recovery of the injured cells and the later growth of the undestroyed cells may cause quality losses and/or foodborne diseases [100].

A great variety of antimicrobial agents have been incorporated into alginate-based edible films and coatings (Table 1). The summarized results show that alginate forms an effective base for antimicrobials to decrease the microbial load of coated food products.

Antimicrobial properties, mode of action, and the potential uses of essential oils (EOs) have been revealed in various studies in the literature [101–104]. These natural preservatives have also been added into edible films and coatings to introduce antimicrobial properties [105]. The limiting factor of their usage is their strong flavor, which originates from the phenolic compounds (i.e., abietane diterpenes, carnosol, ursolic acid) they contain [105].

Table 1. The incorporation of antimicrobials in alginate-based edible films and coatings.

Food	Coating/Crosslinking	Antimicrobial	Result	Source
fresh-cut apple	alginate-apple puree/$CaCl_2$ (EC [1])	oregano, lemongrass, vanillin	high concentrations of Eos [1] inhibited the growth of *Listeria innocua*, psychrophilic aerobic bacteria, yeasts, and molds.	Rojas-Graü, et al. [106]
fresh-cut apple	alginate/$CaCl_2$ (EC)	thyme oil	15 EOs were evaluated. EC-thyme oil significantly inhibited the TPC [1], total coliform, LAB [1], yeast and mold growth.	Sarengaowa, et al. [107]
fresh-cut melon [108], apple [109]	alginate/calcium lactate (EC)	malic acid, cinnamon, palmarosa, lemongrass, clove EOs, and their active compounds	malic acid went through antimicrobial action alone. However, when EOs or their active compounds were incorporated, the effect was increased even further.	Raybaudi-Massilia et al. [108,109]
fresh-cut watermelon	alginate/calcium lactate (EC)	*trans*-cinnamaldehyde	EC-antimicrobial agent was significantly effective against psychrotrophs, coliforms, yeasts, and molds.	Sipahi, et al. [110]
fresh-cut pineapple	alginate, sunflower oil/$CaCl_2$ (EC)	lemongrass EO	yeast, mold, and the total plate count were significantly reduced, and the shelf-life was prolonged.	Azarakhsh, et al. [111]
strawberry	alginate (EC)	carvacrol, methyl cinnamate	carvacrol was effective against both *E. coli* and *B. cinereal*, on the other hand, methyl cinnamate inhibited only *B. cinerea*.	Peretto, et al. [112]
strawberry	alginate/$CaCl_2$ (EF [1])	*Cryptococcus laurentii*	microbial decay due to psychrotrophs, yeasts, and molds was significantly reduced.	Fan, Xu, Wang, Zhang, Sun, Sun, and Zhang [94]
capsicum	alginate/$CaCl_2$ (EC)	pomegranate peel extract	EC-pomegranate peel extract possessed antimicrobial and antifungal activities.	Nair, et al. [113]
beef pieces and steak	alginate-maltodextrin/$CaCl_2$-CMC (EC)	hypochlorous acid (HOCl)	EC-HOCl had no inhibitory effect, although HOCl inhibited the bacterial growth when treated alone.	Williams, et al. [114]
ground beef	alginate/$CaCl_2$ (EC)	nisin, acetic acid, lactic acid, potassium sorbate chelating agents: EDTA [1], HMP [1]	only acetic and lactic acid inhibited *E. coli*. Immobilization in EC enhanced the activity of only some of the antimicrobial agent/combination.	Fang and Tsai [115]
ground beef	alginate/$CaCl_2$ (EF)	nisin	load of *Brohothrix thermosphacta* significantly decreased until day 7.	Cutter and Siragusa [116]
beef tissue	alginate/$CaCl_2$ (EC)	acetic acid, lactic acid	EC-immobilized acids were more effective in reducing *L. monocytogenes* compared to their direct application. Lactic acid had a higher inhibitory effect against Gram (−) at the same pH.	Siragusa and Dickson [117,118]
chicken fillet	alginate alone or alginate-galbanum gum/$CaCl_2$ (EC)	EO of *Ziziphora persica*	alginate coating alone had no microbial inhibition effect. Composite coating and addition of EO to formulation had a significant microbial reduction.	Hamedi, et al. [119]
chicken breast fillet	alginate-maltodextrin/$CaCl_2$-CMC [1] (EC)	lactoperoxidase enzyme	EC-lactoperoxidase decreased the microbial load of *Enterobacteriaceae*, *P. aeruginosa* and aerobic mesophilic bacteria but had no effect on the LAB.	Yousefi, et al. [120]
chicken thigh meat	alginate-whey protein/$CaCl_2$ (EC)	lactoperoxidase enzyme	Antimicrobial effect increased with increasing concentration of the lactoperoxidase.	Molayi, et al. [121]
northern snakehead fish	alginate/$CaCl_2$ (EC)	nisin, EDTA	EC did not increase the effectiveness of antimicrobials against TVC [1] and TPC.	Lu, et al. [122]
smoked salmon	starch-alginate/calcium gluconate (EF)	two strains of LAB, nisin	EF with LAB strains and nisin inhibited *L. monocytogenes* growth.	Concha-Meyer, et al. [123]
smoked salmon	alginate (EF)	sodium lactate, sodium diacetate, commercial formulation consists of both (Opti.Form)	EC-antimicrobials delayed the growth of *L. monocytogenes* during cold storage [124] and greatly prolonged the microbial shelf life during frozen storage [125].	Neetoo, Ye, and Chen [124] and Ye, Neetoo, and Chen [125]

Table 1. *Cont.*

Food	Coating/Crosslinking	Antimicrobial	Result	Source
smoked salmon	alginate/$CaCO_3$ (EC)	oyster lysozyme, hen egg white lysozyme, nisin	both EC-oyster and EC-hen egg white lysozyme inhibited *L. monocytogenes* and *S. anatum*. Addition of nisin enhanced the antimicrobial activity.	Datta, et al. [126]
abalone	alginate/$CaCl_2$ (EC)	bamboo leaf extract, rosemary extract	EC-rosemary extract enhanced bacterial inhibition. PCA [1] was used to correlate between the microbial count and biogenic amines.	Hao, Liu, Sun, Xia, Jia, Li, and Pan [93]
rainbow trout fillet	alginate/$CaCl_2$ (EC)	resveratrol	coating with antimicrobial agent decreased bacterial, yeast, and mold growth.	Bazargani-Gilani [127]
silver carp fillet	alginate-CMC/$CaCl_2$ (EC)	clove EO	EC-clove EO has antimicrobial activity against *L. monocytogenes*, *S. aureus* and *E. coli*, in a decreasing order. Gram (+) bacteria were more sensitive then Gram (−). Concentration increase had a significant effect.	Jalali, et al. [128]
bighead carp fillet	alginate/$CaCl_2$ (EC)	horsemint EO	combined effect of EC-horsemint EO significantly decreased the growth rate of TVC and TPC.	Heydari, et al. [129]
winter flounder (fish)	alginate/$CaCl_2$ (EC)	glucose oxidase (GOx)	enzyme-alginate blankets exhibited very low surface pH values.	Field, et al. [130]
sea bass	alginate (EC)	tea polyphenols	EC decreased TVC, the reduction was even higher with the incorporation of tea polyphenols into the coating.	Nie, et al. [131]
sea bass [132], red sea bream [133]	alginate/$CaCl_2$ (EC)	ϵ-polylysine [132], 6-gingerol [133]	EC-ϵ-polylysine and EC-6-gingerol reduced microbial counts, even more effectively than antimicrobial agent or coating, alone.	Cai et al. [132,133]
sea bass [134], Fior di Latte cheese [135]	alginate/$CaCl_2$ (EC)	reuterin produced by *Lactobacillus reuteri*	EC system containing biopreservative *L. reuterin* was designed [135]. EC-reuterin was effective in the improvement of microbiological quality [134,135].	Angiolillo et al. [134,135]
kashar cheese	alginate-whey protein isolate (EC)	ginger EO	EC-ginger EO had a bacteriostatic and bactericidal effect on *E. coli* and *S. aureus*, respectively.	Kavas, et al. [136]
mozzarella	alginate/$CaCl_2$ (EC)	potassium sorbate, sodium benzoate, calcium lactate, calcium ascorbate	active compounds showed a similar effect in terms of the growth of *Pseudomonas* spp. and *Enterobacteriaceae*. EC–3% potassium sorbate decreased the growth rate.	Lucera, et al. [137]
low-fat cut cheese	alginate-mandarin fiber (EC)	oregano EO	An oregano EO concentration $\geq$ 2% was effective against *S. aureus*, psychrophilic bacteria, molds, and yeasts.	Artiga-Artigas, et al. [138]
- [2]	alginate/$CaCO_3$ (EF)	microencapsulated lemongrass oil	release kinetics were studied. *L. monocytogenes* and *E. coli* were successfully inhibited.	Bustos, et al. [139]
- [2]	alginate/$CaCl_2$ (EF)	potassium sorbate	the permeability and release of potassium sorbate were modeled.	Zactiti and Kieckbusch [71,140]
- [2]	alginate clay bionanocomposite (EF)	marjoram, clove, cinnamon essential oils	nanocomposite EF-Marjoram was the most effective in controlling foodborne pathogens due to possessing a high content of phenolic compounds.	Alboofetileh, et al. [141]
- [2]	alginate/$CaCl_2$ (EF)	garlic oil	the inhibitory effect was dependent on the Gram character and increased in the following order: *S. typhimurium* < *E. coli* < *S. aureus* < *B. cereus*.	Pranoto, et al. [142]
- [2]	alginate (EF)	lysozyme, nisin, grapefruit seed extract, EDTA	EF with grapefruit seed extract alone or in combination with EDTA showed good antimicrobial protection.	Su Cha, Choi, Chinnan, and Park [95]
- [2]	alginate-CMC/$CaCl_2$ (EF)	pyrogallic acid	EF-pyrogallic acid had significant inhibitory effect against *E. coli* and *S. aureus*.	Han and Wang [143]

[1] EC: edible coating; EF: edible film; EO: essential oil, EDTA: ethylenediaminetetraacetic acid; HMP: sodium hexametaphosphate; LAB: lactic acid bacteria; TVC: total viable count; TPC: total psychrophilic count; PCA: principal component analysis; CMC: carboxyl methylcellulose. [2] No food product was covered.

5.4. Antioxidants

Antioxidants have been defined by FDA as "substances used to preserve food by retarding deterioration, rancidity, or discoloration due to oxidation" [144]. Autoxidation comprises of a free radical chain mechanism in which unsaturated fatty acids react with free radicals [145]. Apart from autoxidation, lipid quality deterioration can arise from photooxidative conditions, oxidation via lipoxygenase-assisted process or oxidation under high temperatures [145].

Coatings can also serve as carriers of antioxidative substances to protect against discoloration, degradation and oxidative rancidity [96]. Table 2 lists antioxidant agents used in alginate-based edible films and coatings. The application of an edible coating with incorporated antioxidants decreases the oxidation successfully due to the gas barrier properties of alginate coating and the synergistic effect between two factors.

Phenolic antioxidants, which have often been incorporated into alginate-based coatings and films, do not work as oxygen absorbers but prevent the formation of fatty acid-free radicals and, therefore, their absorbance of oxygen in autooxidation [128].

Table 2. The incorporation of antioxidant agents in alginate-based edible films and coatings.

Food	Coating/Crosslinking	Antioxidant	Result	Source
fresh-cut papaya	alginate, sunflower oil/$CaCl_2$ (EC [1])	ascorbic acid	total ascorbic acid content was almost doubled throughout the storage due to oxygen barrier properties.	Tapia, Rojas-Graü, Carmona, Rodríguez, Soliva-Fortuny, and Martin-Belloso [39]
guava	alginate/$CaCl_2$ (EC)	pomegranate peel extract	EC increased the antioxidant activity; the effect was even promoted with the addition of pomegranate peel extract.	Nair, et al. [146]
fresh-cut pears	alginate, sunflower oil/$CaCl_2$ (EC)	N-acetylcysteine, glutathione	EC-antioxidant agents had significant antioxidant activities, although EC alone did not.	Oms-Oliu, et al. [147]
sliced carrots	alginate/$CaCl_2$ (EC)	citric acid	coating process, when applied together with a modified atmosphere, enhanced the shelf life extension effect.	Amanatidou, et al. [148]
ground beef patties	alginate, starch, stearic acid (EF [1])	tocopherols	regardless of their incorporation method, tocopherols were effective. Additionally, tocopherols improved the moisture barrier properties.	Wu, et al. [149]
buffalo meat patties	alginate/$CaCl_2$ (EC)	sodium ascorbate, citric acid	EC with antioxidants retarded lipid oxidation.	Chidanandaiah, et al. [150]
chicken fillet	alginate-galbanum gum/$CaCl_2$ (EC)	EO of *Ziziphora persica*	both galbaum gum and Ziziphora EO [1] have high antioxidant activities due to the high phenolic and flavonoid content.	Hamedi, Kargozari, Shotorbani, Mogadam, and Fahimdanesh [119]
pork chops	alginate, modified starch/$CaCl_2$ (EC)	rosemary oleoresin	lipid oxidation was inhibited.	Handley, et al. [151]
bream	alginate/$CaCl_2$ (EC)	vitamin C, tea polyphenols	EC decreased TBA [1] significantly due to being resistant to oxygen diffusion. Vitamin C was more effective in decreasing lipid oxidation.	Song, et al. [152]
red sea bream	alginate (EC)	6-gingerol	EC and antioxidant alone led to an equal inhibition effect; on the other hand, their combination had minimum lipid oxidation values in terms of TBA.	Cai, Wang, Cao, Lv, and Li [133]
bighead carp fillet	alginate/$CaCl_2$ (EC)	horsemint EO	EC caused lower oxidation values after the 8^{th} day of storage; the addition of horsemint EO increased this effect even further.	Heydari, Bavandi, and Javadian [129]
silver carp fillet	alginate/$CaCl_2$ (EC)	clove EO	EC-clove EO significantly decreased the lipid oxidation probably due to the combined effect of EO and oxygen barrier properties of the alginate coating.	Jalali, Ariiai, and Fattahi [128]
rainbow trout fillet	alginate/$CaCl_2$ (EC)	resveratrol	EC-resveratrol coating reduced lipid oxidation significantly.	Bazargani-Gilani [127]
rainbow trout fillet	alginate-clay nanoparticles/ $CaCl_2$ (EC)	lycopene	although the EC-lycopene combination helped decrease the FFA [1], other fat oxidation parameters such as peroxide and TBA values could not be significantly decreased.	Ehsani, et al. [153]
sea bass	alginate (EC)	tea polyphenols	EC, tea polyphenols inhibited lipid oxidation when they were applied alone, however, the inhibition was higher in their combination due to the synergistic effect.	Nie, Wang, Wang, Lei, Hong, Huang, and Zhang [131]
- [2]	alginate/$CaCl_2$ (EF)	white, red, and extruded white ginseng extracts	EC-ginseng extract showed good antioxidant activity, which can be even increased with controlling the extrusion process.	Norajit, et al. [154]

[1] EC: edible coating; EF: edible film; EO: essential oil; TBA: thiobarbituric acid; FFA: free fatty acid. [2] No food product was covered.

5.5. Antibrowning Agents

Color is a critical quality parameter. Browning reactions during the shelf life of fresh-cut fruits and vegetables result from both enzymatic and non-enzymatic oxidation of phenolic compounds [155–157]. Fresh-cut fruits and vegetables undergo minimal processing operations such as cutting, peeling, trimming, coring etc., that disrupt cellular compartmentalization, thus, browning proceeds much rapidly [156]. It is well known that browning in fruits and some vegetables mainly originate by the enzymatic oxidation (polyphenol oxidases) of phenolic compounds [156,157]. Polyphenol oxidase requires oxygen to start browning reactions; therefore, implementing an oxygen barrier can be beneficial in preventing browning [156,157]. Additionally, antibrowning agents are utilized against oxidative rancidity, degradation, and enzymatic browning in fruits and vegetables [82].

Edible coatings can be effective carriers for antibrowning agents withholding the agents on the surface of the cut tissues [79]. Antibrowning agents are commonly incorporated in crosslinking solutions and applied after the adhesion of the edible coating solution on the surface of the fresh produce [79]. Rojas-Graü et al. and Raybaudi-Massilia et al. incorporated N-acetylcysteine [79,82,109] and glutathione [82,109] into a calcium chloride bath to control the browning of fresh-cut apples and accomplished to keep apple wedges free from browning during storage. Likewise, Oms-Oliu, Soliva-Fortuny, and Martín-Belloso [147] used the same agents to avoid the browning of fresh-cut pears. Azarakhsh, Osman, Ghazali, Tan, and Mohd Adzahan [111], Montero-Calderón, et al. [158] and Sarengaowa, Hu, Jiang, Xiu, and Feng [107] added ascorbic and citric acid into a calcium chloride solution for coating fresh-cut pineapples and apples.

5.6. Flavors, Pigments, Nutritional Improvements

The organoleptic properties of the coated products can be improved with the addition of some ingredients such as flavorings, coloring agents, sweeteners, spices, and seasonings to the coating matrix [6,11,26]. Hambleton et al. encapsulated n-hexanal [159,160] and D-limonene [160] in alginate-based emulsified films with the help of lipid addition. Several nutritional additives such as vitamins, minerals, and probiotics have been incorporated in the edible films and coatings without damaging the integrity of the product [26]. Lipids (especially sunflower oil) have been extensively incorporated into alginate-based coating formulas and have increased their water resistance characteristics [82,83,147,158,161]. However, in addition to water resistance improvement, consumption of vegetable oils has also some health benefits. For instance, the European Food Safety Authority (EFSA) and EU Vegetable Oil & Protein Meal Industry (FEDIOL) declare that sunflower oil is rich in unsaturated, polyunsaturated fatty acids, and vitamin E content [162–164]. Although sunflower oil has been generally preferred as a lipid source in the literature, other vegetable oils have also been incorporated into the formulations. Ramana Rao, et al. [165] prepared a composite coating consisted of alginate and olive oil enriched with ascorbic and citric acid. Bazargani-Gilani [127] added resveratrol as a dietary supplement into a calcium-alginate gel. Tapia, Rojas-Graü, Rodríguez, Ramírez, Carmona, and Martin-Belloso [161] incorporated viable *Bifidobacterium lactis* Bb12 for a probiotic coating of apple and papaya cylinders, while Rößle, et al. [166] added prebiotics, oligofructose, and inulin to the coating of fresh-cut apples. Nair, Saxena, and Kaur [146] enriched the alginate-based coating with a pomegranate peel extract to enhance the phytochemical level of quava. Artiga-Artigas, Acevedo-Fani, and Martín-Belloso [138] added a mandarin fiber with prebiotic properties to the alginate coating and increased the nutritional value of the low-fat cut cheese.

6. Application Methods

Film formation methods and conditions of coating processes have important impacts on the physical properties of the formed film [26]. Uniform and defect-free (i.e., no air bubble and mechanical damage) film forming is very crucial to optimize its functionalities [26].

6.1. Film Formation

The mechanisms of edible film formation are listed below [10]:

1. Simple coacervation: The precipitation or phase change of the hydrocolloid, which is dispersed in water, is achieved following to (i) the solvent evaporation process (i.e., drying); (ii) incorporation of hydrosoluble non-electrolyte (in which the hydrocolloid is not soluble, e.g., ethanol); (iii) the pH adjustment with the addition of electrolyte, which impel salting out or cross-linking.
2. Complex coacervation: The precipitation of the polymer complex is achieved by mixing two hydrocolloid solutions, which have opposite electron charges.
3. Gelation or thermal coagulation: Precipitation or gelation is accomplished by heating of the macromolecule which causes its degradation (e.g., proteins such as ovalbumin) or the cooling of hydrocolloid dispersion (e.g., agar, gelatin).

The production principles of shelf-standing film techniques are similar to those for thermoplastic films: solvent casting and extrusion, although the conditions are different [26].

6.1.1. Solvent Casting

It is the most frequently used film-forming technique, which consists of spreading of water or water-ethanol solutions/dispersions on a suitable surface and later air drying during several hours in a ventilated oven such as infrared drying chambers [26,167]. Following the evaporation of the solvent, the film is peeled from the surface without any damage. The structure of the film is depended on the composition of the casting solution, wet casting thickness, temperature and relative humidity of the drying conditions [26]. Rapid drying of the casting solution should be avoided due to reducing the solvent concentration very fast, and therefore limiting the mobility of the polymer chain and development of intermolecular interactions in the film [26].

6.1.2. Extrusion

The extrusion technique is based on the thermoplastic properties of the polymers [167]. Subsequent to the plasticizer addition, the solution is heated above its glass transition temperature under low water content conditions [26,167]. The extrusion method is preferred in commercial applications due to the lack of solvent addition and evaporation steps [167].

The co-extrusion technique can be utilized to form multilayer films. However, due to the differences in the chemical-physical characteristics of each film-forming material, mechanical, optical, and barrier defects can come into existence [26].

6.2. Coating Application

Application method and the ability of the coatings to adhere to the food surface are the two important characteristics regarding edible coatings [167].

6.2.1. Dipping

Food products are usually coated by a dipping or spraying technique, in which a thin film was formed on the surface that acts as a semipermeable membrane to control moisture loss and gas transfer [168,169].

This method consists of four steps: sample immersion into the alginate dispersions followed by withdrawing the sample and draining the excessive film-forming solution covering the product. Then, a second immersion of the alginate coated sample into the crosslinking bath to achieve the gel formation and draining of the excessive solution [170]. The dipping process is generally very short, therefore the evaporation from solvents in the coating and crosslinking solutions are neglected [171]. The duration of the dipping and draining times differ from each study, but it is generally between 30

s to 5 min. The main advantage of the method is its total coating even around complex and rough surfaces [172].

Due to the hydrophilic surface of the cut surfaces of the food products, a good adhesion cannot be easily accomplished by the simple dipping of the food product into the coating material. Multilayer coating or the layer-by-layer (LbL) technique has been used to minimize the sticking difficulty of the coating on the hydrophilic surface of the cut surfaces [26,110,173,174]. The process is based on the dipping of food product into different coating solutions that contain oppositely charged polyelectrolytes to achieve physical and chemical bonding to each other [110,174]. Currently, the LbL technique is applied mainly on fruits and vegetables [175].

The dipping method forms thick coatings. Additionally, Duan, Wu, Strik, and Zhao [92] pointed out that dipping might have diminished the efficacy of the coating application due to the dilution and dissolving effect.

6.2.2. Spraying

The spraying method is another conventional technique used to form a semi-permeable membrane on the surface of food products [89]. The spraying system distributes the coating solution through the formation of droplets over the targeted food surface area with the help of nozzles [172]. The spraying technique needs less amount of coating material to achieve good coverage due to high spraying pressure (approx. 60–80 psi) [176]. The other advantages of this method are the uniform coating, control of thickness, possibility of multilayer applications, avoidance of coating solution contamination, temperature control of the solution and enabling of working with large surface areas [172].

The spraying solution should not have a high viscosity. Spray-flow characteristics are dependent on (i) liquid properties (i.e., density, viscosity, surface tension), (ii) operating conditions (flow rate, air pressure, etc.), and (iii) system conditions (nozzle design, spray angle, etc.) [172,177].

Earle and McKee [22] sprayed the dispersion containing water-soluble algin and, later, a gelling agent on the freshly slaughtered hanging animal carcasses. Researchers determined the viscosity of the solution as the critical point of the vertical spraying application to have a uniform adherence to the alginate film. Papajová, Bujdoš, Chorvát, Stach, and Lacík [59] designed a setup to prepare externally gelled planar alginate hydrogels with the airbrushing aerosols of a gelling solution. Amanatidou, Slump, Gorris, and Smid [148] applied a different spraying procedure. Carrot slices were initially dipped in $CaCl_2$ solutions and, following the drying, an alginate-based solution was sprayed on the surface of the slices.

6.2.3. Vacuum Impregnation

The Vacuum Impregnation (VI) method has been used for the enrichment of the product with vitamins and minerals in food research. Recently, studies showed that VI coating can form a thicker and more effective film with the incorporation of solutes into the air containing porous food matrices such as fruits and vegetables [178,179].

The VI method consists of the same dipping-draining steps, which were explained in the dipping subsection. However, instead of dipping tanks, the samples are submerged into two airtight vacuum chambers connected to vacuum pumps. Subsequent to the vacuum application, products are subjected to atmospheric restoration while they remain immersed in the coating solution under atmospheric pressure. Vacuum period, vacuum pressure and atmospheric restoration time are important parameters in the VI process [180].

7. Alginate-Based Coatings and Film Applications

There are many potential uses of sodium alginate-based edible films and coatings.

7.1. Fresh-Cut Fruits and Vegetables

Natural barriers (i.e., cuticle, skin, rind, etc.) that surround the whole and intact fruits and vegetables, protect the products against microbial contaminations and quality losses [181,182]. Lately, fresh-cut fruits and vegetables attract consumers' attention due to increased awareness of healthy eating habits and having less time for food preparation [96,183]. The preferences of the consumers change in the direction of convenient consumption without any loss of quality characteristics [184]. Minimally processed fresh cut fruits and vegetables are subjected to preparation steps such as washing, peeling, cutting, slicing, coring, which remove these barriers, induce lesions of tissues, damage the integrity of the fruit, and cause wounding stress [79,106,185]. Thus, the product becomes vulnerable to contamination, enzymatic browning, undesirable volatile formation, and alterations in texture [183]. Deteriorative effects, as well as the growth of spoilage and pathogenic bacteria, can be prevented by enhancing the natural barriers or replacing it with artificial barriers surrounding the product such as an edible film and coating applications [182,186,187].

The delay of respiration and physiological processes are requisites for the shelf life extension of fruits and vegetables [10]. In this manner, coatings and films with the ability to modify the gas transport have the potential for applications in fresh produce coating [10,13,188]. In particular, polysaccharide-based coatings have been used to reduce the respiration of fruits and vegetables due to their selective permeabilities to the O_2 and CO_2 gases [27]. The swelling ratio and water solubility of alginate films are very important properties in case of fresh-cut fruits with high moisture surfaces. Tapia, Rojas-Graü, Rodríguez, Ramírez, Carmona, and Martin-Belloso [161] stated that alginate films have a resistance to being dissolved in water and, therefore, have the potential for coating high moisture fresh-cut fruits.

The studies conducted with alginate coated fresh/fresh-cut produce are shown in Table 3.

Table 3. The application of alginate coatings on fresh-cut fruits and vegetables.

Food	Effects	Source
fresh-cut apples	Optimum composition of alginate-based EC [1] was determined for achieving high water and firmness retention during storage.	Ghavidel, et al. [189]
fresh-cut apples	Shelf life of coated apples were prolonged three times compared to uncoated samples. EC maintained firmness, although it increased fermentative metabolites' (i.e., acetaldehyde and ethanol) production due to MA [1].	Rojas-Graü, Tapia, and Martín-Belloso [79]
fresh-cut apples	Base solution was developed with alginate and 26% apple puree. Ethylene, CO_2 production, and O_2 consumption were reduced. However, solely vanillin incorporated formulations could achieve acceptable test scores in contrast with other EOs [1].	Rojas-Graü, Raybaudi-Massilia, Soliva-Fortuny, Avena-Bustillos, McHugh, and Martín-Belloso [106]
fresh-cut apples	The soluble solid content was increased; stable browning index, acidity, and firmness levels were achieved due to coating with prebiotics incorporated EC.	Rößle, Brunton, Gormley, Wouters, and Butler [166]
apples	Alginate and gelatin-based coatings not only preserved the freshness of the fruit, but also improved the appearance and attractiveness of the fruit.	Moldão-Martins, et al. [190]
apple pieces	Apple pieces were coated with double layers of polysaccharide/lipid (alginate/acetylated monoglyceride) EC to decrease respiratory activity.	Wong, Tillin, Hudson, and Pavlath [184]
fresh-cut apples	Thyme oil had the highest antimicrobial activity among the tested 15 EOs. Physical, chemical and microbial qualities of coated (thyme incorporated) samples were assessed.	Sarengaowa, Hu, Jiang, Xiu, and Feng [107]
fresh-cut apples [109], fresh-cut melon [108]	The effect of malic acid, EOs and their active compounds on quality characteristics were assessed. Due to the inhibition of microflora, respiration and anaerobic fermentation were decreased. However, physicochemical characteristics of the products were affected differently with respect to the type of EOs and concentrations.	Raybaudi-Massilia et al. [108,109]
fresh-cut melon	Sodium alginate-sunflower oil maintained the firmness, however, the coating could not present good barrier properties against O_2, CO_2, ethylene, and could not reduce the loss of vitamin C and microbial load.	Oms-Oliu, et al. [191]
fresh-cut melon	LbL technique with oppositely charged alginate-chitosan presented a superior performance on firmness, gas exchange, and microbial growth.	Poverenov, Danino, Horev, Granit, Vinokur, and Rodov [174]
fresh-cut watermelon	LbL coating did not affect the pH and °Brix but preserved the textural firmness and decreased weight loss.	Sipahi, Castell-Perez, Moreira, Gomes, and Castillo [110]
ber fruit	The quality was retained with the application of the composite edible coating, consisting of sodium alginate and olive oil, enriched with ascorbic and citric acids.	Ramana Rao, Baraiya, Vyas, and Patel [165]
strawberry	The quality of the products was enhanced by implementing a yeast antagonist to the formulation.	Fan, Xu, Wang, Zhang, Sun, Sun, and Zhang [94]
strawberry	Effects of alginate, chitosan, pullulan-based EC on antioxidant enzyme system and quality characteristics were compared. All the polysaccharide-based coatings decreased quality losses and extended shelf life.	Li, et al. [192]
strawberry	Incorporation of carvacrol and methyl cinnamate changed the physical properties of the alginate coatings such as turbidity, transparency, and viscosity, depending on their concentration.	Peretto, Du, Avena-Bustillos, Berrios, Sambo, and McHugh [112]
strawberry	The effectiveness of alginate and soy-based coatings on the pH and vitamin C content of the samples were compared.	Ahmed, et al. [193]
blueberry	Numerous ECs (including alginate) were compared in terms of their ability to control quality losses.	Duan, Wu, Strik, and Zhao [92]
blueberry	Performances of chitosan and alginate coatings were compared. Although alginate coatings promoted firmness, lightness and total phenolic content; yeast and mold growth in the samples were induced.	Chiabrando and Giacalone [194]

Table 3. *Cont.*

Food	Effects	Source
cherry	The storability period of the coated products increased from 8 to 16 days with a delay in the post-harvest ripening and maintaining higher amounts of total phenolics and antioxidant activity.	Díaz-Mula, Serrano, and Valero [90]
fresh-cut pear	EC with antibrowning agents (N-acetylcysteine and glutathione) reduced microbial growth, increased vitamin C, and the total phenolic content without affecting the firmness of product.	Oms-Oliu, Soliva-Fortuny, and Martín-Belloso [147]
pear	Alginate coated samples had a higher tensile strength, elongation, and elasticity; on the other hand, they had a lower water loss, pH increase, metabolic activities with maintained firmness and green color.	Moraes, et al. [195]
plums	Particularly 3% alginate coating significantly inhibited ethylene production, softening, acidity and water losses, and slowed down carotenoid and anthocyanin increase (and therefore delayed color change) throughout the storage period of plums.	Valero, Díaz-Mula, Zapata, Guillén, Martínez-Romero, Castillo, and Serrano [91]
fresh-cut papaya	The study consisted of two steps: RSM [1] was used to determine the number of ingredients in the formulation in terms of WVR [1]; the chosen formulations helped to achieve increased firmness. On the contrary of several previous studies, the alginate coating did not affect the respiratory rate and ethylene production.	Tapia, Rojas-Graü, Carmona, Rodríguez, Soliva-Fortuny, and Martin-Belloso [39]
Guava	EC-pomegranate peel extract improved the visual and nutritional parameters with delaying senescence.	Nair, Saxena, and Kaur [146]
mango	EC-ascorbic acid retarded firmness loss improved the phenolics and carotenoids content and sensory scores; however, the antimicrobial efficiency was not significant.	Salinas-Roca, et al. [196]
fresh-cut pineapples	The concentration of ingredients in EC was formulated with the help of RSM [83]. Incorporation of lemongrass EO and ascorbic-citric acid into EC prolonged the shelf life whilst maintaining quality attributes.	Azarakhsh et al. [83], [111]
fresh-cut pineapples	Shelf life of the product was significantly improved.	Montero-Calderón, Rojas-Graü, and Martín-Belloso [158]
Peach	Shelf life was increased with maintaining quality.	Maftoonazad, et al. [197]
tomato	Reduced ethylene production, respiration rate, weight loss, a diminution rate of hue angle values (indicated that ripening was delayed) as well as a higher fruit firmness, TSS (total soluble solids concentration), titratable acidity (TA), organic acids (citric, malic and, ascorbic acids), sugars (glucose and fructose), and sensory scores of coated products were achieved.	Zapata, Guillén, Martínez-Romero, Castillo, Valero, and Serrano [89]
potato strips	Possibility of using the alginate coating and ultrasound process as an alternative to blanching of potato strips were investigated. EC was not effective for diminishing the color changes and microbial load.	Amaral, et al. [198]
garlic bulbs	Natural compound isolated from the garlic skin was added into EC. The effects of coating on the mechanical and barrier properties were demonstrated.	Nussinovitch and Hershko [199]
carrot	A 5- to 7-day shelf-life extension of the coated samples was achieved.	Amanatidou, Slump, Gorris, and Smid [148]
lettuce	1-Methylcyclopropene incorporated EC reduced the discoloration, respiration rate, ethylene synthesis (therefore senescence) of samples.	Tay and Perera [200]

[1] EC: edible coating; MA: modified atmosphere; EO: essential oil; WVR: water vapor resistance; RSM; Response surface methodology.

7.2. Meats, Poultry, and Seafood

There are various challenges associated with meats, poultry, and seafood products throughout their shelf life. They can be defined as moisture loss and its effects on texture, color, and flavor; unappealing dripping of the product juice (purge losses); lipid oxidation and brown discoloration; microbial spoilage; volatile flavor loss and/or gathering foreign odor [62,201,202].

In the patents, Earle et al. designed an alginate-based coating formulation commercially known as Flavor-Tex® [203,204]. Meat, seafood, and poultry products were immersed into an aqueous dispersion of water-soluble algin and carbohydrate comprising mono and/or disaccharide sugar and gelatinized with a $CaCl_2$-CMC solution (the addition of CMC to the calcium crosslinking bath reduced the gelling time and required concentration of the $CaCl_2$) [203,204]. Lazarus, West, Oblinger, and Palmer [23]; West, Lazarus, Oblinger, and Palmer [24]; and Williams, Oblinger, and West [114] evaluated the effects of Flavor-Tex® on lamb carcasses and beef pieces/steaks. Although calcium alginate coating acted as a sacrificing agent rather than a moisture barrier, maintaining a lower water activity (a_w) on the surface together with the toxic effect of $CaCl_2$ lead to lower microbial counts [23,114]. Nevertheless, the coating helped to stabilize the meat color, reduced shrinkage and obtained the same sensory scores compared to the uncoated meat samples [23,114]. Flavor-Text was also used to coat pork patties for solving the flavor and texture problems of precooked meat products [205]. Coating decreased the oxidative rancidity, cooking losses, and increased meat tenderness. To the contrary of the findings presented previously [23], calcium alginate coated row and precooked products received the highest sensory scores, which indicated that the higher structural integrity given by the coating was favored by consumers [205].

The usage of gelatinized alginate in the block freezing process of fishery products was patented in Norway, 1956 [206]. By this means, the detrimental effects of direct water contact on the products were eliminated [206].

Studies on alginate coated meat, poultry, and seafood products are presented in Table 4.

Table 4. The application of alginate coating on meat, poultry, and seafood products.

Food	Effects	Source
ground beef patties	Incorporation of stearic acid into the modified starch-alginate formulation improved the barrier properties against moisture loss and decreased lipid oxidation. Addition of tocopherols increased these effects.	Wu, Weller, Hamouz, Cuppett, and Schnepf [149]
buffalo meat patties	EC [1] significantly improved quality attributes such as overall shear force, TBA [1], tyrosine value, and microbial counts, etc.	Chidanandaiah, Keshri, and Sanyal [150]
lamb meat	Alginate-maltodextrin coating crosslinked with $CaCl_2$-CMC [1] led to a decrease in the total volatile nitrogen for refrigerated meat, there was no statistical difference for frozen meat. Although a decrease in the total count of refrigerated meat was only due to calcium ions in the crosslinking solution, EC achieved psychrophilic bacterial inhibition during the frozen storage.	Koushki et al. [207,208]
pork chops	Composite coating with modified starch-alginate with rosemary oleoresin inhibited lipid oxidation and formation of hexanal, pentane, and total volatiles.	Handley, Ma-Edmonds, Hamouz, Cuppett, Mandigo, and Schnepf [151]
pork cuts	Alginate (>1%), helped to decrease the thawing loss; concentration of Ca^{2+} influenced the tenderness of the meat. Optimum coating conditions were defined as 3% alginate, 7% $CaCl_2$ with 5–7 min crosslinking time to diminish thawing loss, TBARS [1], and an increase in the total protein solubility.	Yu, et al. [209]
cut-up poultry parts	Water evaporated from coating instead of meat. One thick coating application was more convenient than repeating number of coats due to preventing residual calcium salts from being transferred into the alginate dipping solution and the easiness of pealing.	Mountney and Winter [21]
chicken breast and chicken thigh meat	Lactoperoxidase addition into the alginate-based coating system led to higher bacterial and sensorial quality values of chicken meat. The effect was even increased with the increasing concentration of lactoperoxidase.	Yousefi, Farshidi and Ehsani [120], Molayi, Ehsani, and Yousefi [121]
films/casing for breakfast pork sausages	Study assessed the ability of food polymers including gelatin-sodium alginate blends for the formation of stable packaging film. The optimum processing conditions were presented during the extrusion process [210]. The effects of different oil additions on quality parameters of the films/casings [211] and their usage in the manufacturing of sausages were determined [212].	Liu et al. [210–212]
bream	EC reduced the rate of quality losses of bream in terms of water loss, pH, TVB-N [1], and K-value. A 5% vitamin C content incorporated coating maintained the best quality and sensory results.	Song, Liu, Shen, You, and Luo [152]
red sea bream	EC-6-gingerol coated products obtained a 20-day shelf life extension.	Cai, Wang, Cao, Lv, and Li [133]
japanese sea bass	The synergistic effect of EC and ϵ-polylysine helped products to maintain a fresh color and tissue hardness, reduce lipid oxidation, protein degradation, and nucleotide breakdown.	Cai, Cao, Bai and Li [132]
japanese sea bass	EC-tea polyphenols provided the greatest effect on quality (TVB-N, lipid oxidation, protein decomposition) and sensory results compared to their effects alone.	Nie, Wang, Wang, Lei, Hong, Huang, and Zhang [131]
sea bass	New biopreservation coating with the addition of food supplement *Lactobacillus reuteri* and its substrate glycerol to EC was developed. The production and antimicrobial effects of reuterin material were evaluated after 2 different fermentation periods.	Angiolillo, Conte, and Del Nobile [134]
sea bass	Two protective processes: salting application of liquid smoke suspension containing resveratrol and alginate coating were used to enhance the quality. Although the treatment combination was effective in reducing oxidation, it could not inhibit bacterial growth.	Martínez, et al. [213]
rainbow trout	0.2% resveratrol improved the effect of EC with the highest inhibition of chemical changes and microbial growth.	Bazargani-Gilani [127]
rainbow trout	Effects of EC with or without lycopene were investigated in terms of various quality parameters.	Ehsani, Paktarmani, and Yousefi [153]

Table 4. *Cont.*

Food	Effects	Source
silver carp fillet	Fillets were coated with alginate-CMC. With the help of the controlled release of clove oil, the coating lead to an 8-day shelf life extension without affecting the sensorial properties.	Jalali, Ariiai, and Fattahi [128]
bighead carp fillet	Lower microbial deterioration and auto-oxidation of fish fillets throughout storage were achieved.	Heydari, Bavandi, and Javadian [129]
kilka fish	Shelf life extension was achieved with an alginate-whey protein coating.	Seyfzadeh, et al. [214]
northern snakehead fillets	Contrary to the previous findings of EC-nisin [115,116], researchers did not find any significant evidence that calcium alginate containing nisin increased the effectiveness of the antimicrobial agent. Nevertheless, inhibition of lipid oxidation, TMA-N [1], TVB-N, promoting water barrier properties and sensory scores were achieved.	Lu, Liu, Ye, Wei, and Liu [122]
minced fish patties	EC was applied in a different manner: All the ingredients such as minced fish patties, soy protein concentrate, onions, celery, as well as sodium alginate, were blended. The patties were pre-coated initially with soybean oil and afterward dipped in the $CaCl_2$ solution for film formation, which prevented the patties from sticking to surfaces during processing.	Rockower, et al. [215]
abalone	An EC-3.5% rosemary extract was successful for the preservation of the product due to reducing TVB-N, controlling biogenic amines, and maintaining better sensory scores.	Hao, Liu, Sun, Xia, Jia, Li, and Pan [93]

[1] EC: edible coating; CMC: carboxymethyl cellulose; TBA: thiobarbituric acid; TBARS: thiobarbituric acid reactive substances; TVB-N: total volatile basic nitrogen; TMA-N: trimethylamine nitrogen.

7.3. Cheese

The main quality losses of cheese products take place in a storage period and can be summarized as microbial contamination, moisture loss, and the development of off-flavor and other undesirable organoleptic properties [216]. It is very important to underline that the addition of an extra calcium with the aim of crosslinking is not an essential step in cheese coating due to possessing calcium itself [138].

Edible coatings and films have been applied and studied in several types of cheese as packaging system to prevent the quality losses. Zhong, et al. [217] investigated the performance of three different coating materials (i.e., sodium alginate, chitosan, soy protein isolate) with four various application methods on mozzarella cheese. The results showed that alginate-coated samples possessed better overall qualities due to its better wettability on the product surface [217]. Lucera, Mastromatteo, Conte, Zambrini, Faccia, and Del Nobile [137] demonstrated that the antimicrobial activity of potassium sorbate, sodium benzoate, calcium lactate, and calcium ascorbate, which were incorporated into an alginate coating and used to coat mozzarella cheese, were similar. The main difference arose from the sensory point of view. Kavas, Kavas, and Saygili [136] fortified the composite coating of alginate-whey protein isolate coatings with ginger EO and obtained kashar cheese with a lower acidity and higher fat level.

7.4. Only Coating/Film, Without Food Application

Alginate is an acidic anionic polysaccharide and able to form covalent bonds and charge-charge electrostatic complexes with protein [218,219]. Especially following heat denaturation of the protein, stronger interactions are formed [218,219]. Studies on alginate-protein interactions and other investigations on alginate-based edible coatings and films (without their application on food products) are presented in Table 5.

Table 5. The studies on alginate-based coatings/films without food application.

Study	Source
The effects of soy isolate-sodium alginate and soy isolate-PGA [1] interactions on the functional properties of the film formation were investigated and it was found that protein-polysaccharide interactions enhanced the film-forming properties.	Shih [219]
≈10% PGA addition to the soy protein increased the whiteness and tensile strength and decreased the yellowness, percentage elongation at break, WVP [1], and water solubility of the multicomponent EF [1].	Rhim, et al. [220]
Films formed from alginate-whey protein complexes had higher tensile strength, elastic modulus, and elongation than whey protein alone.	Coughlan, et al. [221]
Different protein-polysaccharide films were compared in terms of oxygen and WVP, tensile strength, transparency, etc.	Yoo and Krochta [48]
By using a Box-Behnken experimental design and RSM [1] (for 3 factors; sodium alginate, low acyl gellan, glycerol concentration), a biofilm formulation was designed in terms of mechanical properties.	González-Cuello, et al. [222]
EF formulation was prepared by mixing sodium alginate with a variable quantity of cashew tree gum. However, tensile strength and water barrier properties were weakened due to the competition between two gel-forming polysaccharides for the interaction with calcium ions in the crosslinking step.	Azeredo, et al. [223]
Gelation of calcium alginate with rice starch and/or rice flour was examined. Coarser and more rigid gel structures with an increased diffusion coefficient, a heterogeneous structural resistance constant, and a decreased gelation rate constant were obtained.	Chrastil [64]
Incorporation of garlic oil as a natural antibacterial agent caused darker, yellowish color formation, reduced tensile strength and elongation at break while garlic oil interfered with the calcium ion interactions due to being incorporated before crosslinking.	Pranoto, Salokhe, and Rakshit [142]
Ginseng extract (white, red and extruded white extract) was inserted into the film formulation and a slight decrease in moisture content, and increase in water solubility, transparency, and alteration in the mechanical properties of EF was observed.	Norajit, Kim and Ryu [154]
A new multilayer film, which contained chitosan in the top layer, ornidazole-incorporated polyvinyl alcohol middle and sodium alginate sublayer, with an enhanced swelling rate, water absorption capacity, control of water vapor transmission, and light transmittance, was developed.	Pei, et al. [224]
Incorporation of pyrogallic acid into the sodium alginate-CMC [1] matrix increased the gas, vapor, and UV barrier properties of EF.	Han and Wang [143]
Interactions between encapsulated n-hexanal (aroma compound) and alginate matrix affected the barrier, permeability, and surface properties of emulsified alginate EF.	Hambleton, Debeaufort, Bonnotte, and Voilley [159]
Enzyme activity of pig liver esterase with enhanced encapsulation efficiency (i.e., chitosan coating of alginate beads) was studied.	Pauly, et al. [225]
With a novel approach, the alginate film was designed based on the RGB image analysis and color changes. Alginate surface concentration and surface color were modeled to predict the physical properties of the film with a non-destructive method.	Acevedo, et al. [226]

[1] EF: edible film; PGA: propyleneglycol alginate, produced with the reaction of alginic acid and propylene oxide; WVP: water vapor permeability; CMC: carboxymethyl cellulose; RSM: response surface methodology.

8. Transport Mechanisms

Ideal edible coatings and films should create a barrier to impede the loss of water vapor, flavor volatiles, and the exchange of CO_2 and O_2, in other words, to control the rate of transport of the food products' molecular components [96]. In this way, the adverse reactions with deteriorative effects (such as respiration and ethylene production) can be diminished or slowed down [96,227,228]. Mass transfer and barrier characteristics are one of the most important properties of edible films and coatings due to their enormous impact on product quality [229]. Mass transport properties of polymer films can be represented by three coefficients: the diffusion coefficient, solubility coefficient, and permeability coefficient, which have been described in detail by Miller and Krochta [230], Donhowe and Fennema [12], McHugh and Krochta [231].

8.1. Moisture Barrier Applications

Moisture barrier characteristics (i.e., moisture content, water vapor permeability (WVP), water vapor resistance (WVR), and water vapor transmission rate (WVTR)) have been commonly studied in the literature of alginate-based edible films and coatings since moisture barrier properties are very critical in designing the coating process. In raw, untreated fruits and vegetables, epidermal cell layer and cuticles reduce weight loss and edible coatings and films created an additional extra barrier layer on the stomata and decrease transpiration (and, therefore, weight loss) [90].

The primary mechanism of moisture loss from food product is the vapor-phase diffusion, which was impelled by the water vapor pressure difference between the product and the surrounding air [90,197]. The thickness of the formed film, moisture permeability, temperature, and relative humidity of the surrounding medium are important factors in defining the mass transfer rate [232].

As a simple method, juice leakages from fresh-cut pineapples [158], garlic bulbs [199], ber fruits [165], blueberries [194], fresh-cut watermelon [110], apples [107], plums [91], kilka fish [214], kashar cheese [136], low-fat cut cheese [138], ground beef patties [149] were significantly reduced with the alginate coating application in moisture loss (or weight loss) experiments conducted very often in studies of alginate coated food products.

WVP is another topic that has been widely studied. For the edible films and coatings formed from hydrophilic components, increasing the water activity (a_w) causes an increase in film moisture content and WVP, due to the swelling of the network with water [8].

Incorporation of additives can alter the moisture transfer properties of the formed film. Various studies showed that lipid addition into the coating formulation helped to decrease the moisture transport [8,39,147,159,191]. The amount of decrease depends on the type, amount, and chain size of the lipid added in the formulation [183]. Pranoto, Salokhe, and Rakshit [142] observed that the addition of 0.4% garlic oil into alginate film formulation decreased WVP significantly. WVR of sunflower oil incorporated alginate coating on fresh-cut apples [82] fresh-cut melon [191], fresh cut pears [147] were determined. Tapia, Rojas-Graü, Rodríguez, Ramírez, Carmona, and Martin-Belloso [161] compared the WVP of both alginate films and coatings on fresh-cut apples and papayas and presented the effect of the sunflower oil addition to the formulations. On the other hand, the addition of plasticizer to the formulation may increase the WVP values of the film due to reducing the intermolecular bonds between polymer chains [39,80,159]. {Olivas, 2008 #108} and Jost, Kobsik, Schmid, and Noller [80] determined the effect of different plasticizers (glycerol, sorbitol [58,80], PEG-8000 (polyethylene glycol), fructose [58]) on WVP.

There has been an increasing interest in using EOs as antimicrobial agents in alginate coating/film formulations. Rojas-Graü, et al. [233] reported that the addition of plant essential oils did not modify the WVP of alginate-apple puree film. Similar results were presented by Norajit, Kim, and Ryu [154] for ginseng extract incorporated alginate films that no significant effect on WVP was observed. On the contrary, Artiga-Artigas, Acevedo-Fani and Martín-Belloso [138] determined that oregano EO incorporated alginate-mandarin fiber coated low-fat cut cheese exhibited higher WVR values than the uncoated samples and the effect increased with increasing concentrations of EO. Kavas, Kavas,

and Saygili [136] fortified alginate-whey protein isolate coating with a 1.5% ginger EO and coated kashar cheese.

The water vapor barrier properties of alginate films were intended to be improved with the addition of other gel-forming biopolymers. Parris, Coffin, Joubran, and Pessen [81] developed alginate-milk based materials (i.e., whole or non-fat milk, whey, sodium caseinate). Films containing whole milk had decreased WVP up to 35% [81]. Likewise, Coughlan, Shaw, Kerry, and Kerry [221] have demonstrated that films formed from alginate-whey protein complexes had lower WVP. Rhim, Wu, Weller, and Schnepf [220] found that up to 10% PGA addition decreased the WVP of soy protein isolate films. Han and Wang [143] evaluated the WVP of sodium alginate-CMC films containing pyrogallic acid.

The type of film formation method also affects water barrier properties. Poverenov, Danino, Horev, Granit, Vinokur, and Rodov [174] demonstrated that LbL-coated melons (with the alginate-chitosan combination) had superior water vapor barrier properties compared to uncoated, only-alginate or only-chitosan coated samples.

Mathematical models were also created to predict the water transport properties of alginate-based edible coatings and films [234].

8.2. Gaseous Barrier Applications

Coatings act as barriers to gas exchange, reduce O_2 uptake and CO_2 production (in other words, respiration) by the fruit and create a modified atmosphere [90,197]. Still, the coating designer should keep in mind that the modified atmosphere should not create anaerobic conditions to induce the anaerobic growth in the product [96].

Gas barrier properties (especially O_2) are the second frequently studied transport mechanism. Capillary diffusion (predominant in porous, imperfect materials) and activated diffusion (includes solubilization of the gas in the film, diffusion through the film and release at the other side of the film) are the two mechanisms that occur in gas transport [12]. Transport rates of O_2 and CO_2 are strongly influenced by RH at which product is stored [10,96,235]. An increase in RH causes more interaction between water and film/coating molecules, which leads to a plasticized structure that favored mass transfer [235]. Therefore, the permeability characteristics of a coating on a fresh-cut surface are very difficult to predict due to the high RH of the surface [96]. For edible films made from hydrophilic gelling matrices, a higher a_w promotes both gas diffusivity and gas solubility due to the water solubility of these gases and, therefore, the gas permeability properties increase [8].

The other influential factor is temperature; high storage temperatures cause the respiration rate increase [96]. For instance, in case the storage temperature increases during the later stages of the product storage, the created MA by the coating/packaging can cause anaerobic respiration [96].

Polarity and the structure of the film also affect the gas transfer properties. More polar films have a more ordered (less porous) structure, therefore, the film becomes less permeable to oxygen, with a high affinity to moisture [76].

The affinity of the fat compounds for oxygen leads to an increase in permeability [159]. Nevertheless, Azarakhsh et al. determined that alginate-sunflower oil coated fresh-cut pineapple pieces had a lower respiration rate due to an increasing internal CO_2 and decreasing O_2 concentration [83] and incorporation of lemongrass to the formulation, increased this effect even more [111]. Rojas-Graü, Avena-Bustillos, Olsen, Friedman, Henika, Martín-Belloso, Pan and McHugh [233] noted that the oxygen barrier properties of alginate-apple puree films were not affected by the addition of plant essential oils.

Jost, Kobsik, Schmid, and Noller [80] found that the oxygen permeability of alginate films increased with increasing concentration of glycerol, while the incorporation of sorbitol did not significantly change the gas barrier properties.

Earle and McKee [236] patented an alginate-based coating with O_2 barrier properties, particularly for dough products with fillings.

Han and Wang [143] analyzed the O_2 permeability of a sodium alginate-CMC film containing pyrogallic acid.

Buonocore, Conte, and Del Nobile [234] presented a mathematical model, which was fitted to the experimental data of oxygen barrier properties of the alginate-based film.

The respiration rate of alginate coated sweet cherry fruit [90], strawberry [192], peach [197], apples [107,166], pineapples [83], guava [146], and lettuce [200] were evaluated in the literature. Due to being a hydrocolloid, the alginate-based films and coatings generally decreased the respiration rate during storage and, in this way, achieve retention of the quality attributes of the food products. Sipahi, Castell-Perez, Moreira, Gomes, and Castillo [110] stated that the LbL coating application method inhibited the respiration process of fresh-cut watermelon.

Another important change is the amount and/or presence of some internal volatiles of anaerobic conditions, which is created by the high gas barrier properties of the edible coating or film [188]. For instance, higher acetaldehyde and ethanol production compared to the uncoated samples indicate the presence of a modified atmosphere in the alginate coated fruits [79].

8.3. Active Compound Release Applications

The edible coating containing active compounds could be very efficient by maintaining a higher concentration of the target compound with a slow migration for an extended period of storage time. Although diffusion of small molecules (such as ethanol and glycerol) is only influenced by the pore size of the matrix, diffusion of larger molecules (such as proteins) from the gel matrix is influenced by the molecular weight of the substance [40,237,238].

The control of the release process with well-determined release rates and migration amounts are very crucial, especially in biotechnology. For this reason, various studies were conducted in the literature. Diffusion of low molecular weight substances such as glucose, L-tryptophan, and α-lactoalbumin and higher molecular weight substances such as albumin, γ-globulun, and fibrinogen [237], and insulin [238] into and from the gel beads were characterized. The release rates of hemoglobin [57,61] and nicotinamide adenine dinucleotide (NAD) [57], as well as the permeability of immunoglobulin G [239] from various alginate films/gels/coatings, were examined. Alginate concentration, α-L-guluronic acid content, the charge of the protein, and the isoelectric point of the protein affected the diffusion rates [51].

Wang and Zhang Newby [240] showed that LbL polyelectrolyte alginate microgels significantly retard the release of small hydrophilic molecules (MW < 250 g/mol).

Zactiti and Kieckbusch modeled permeability [140] and the release of potassium sorbate [71] from alginate films and evaluated the effect of three levels of alginate crosslinking (with different calcium chloride concentrations) on the permeability and release model. As the calcium ion concentration increased, which increased the degree of crosslinking, the mobility of the active substance was prevented and the permeability constant decreased. Moreover, an increase in the sorbate concentration also caused an increase in the permeability values.

Wong, et al. [241] measured the permeability properties of calcium alginate films, which were prepared with the in situ gelation method or the cooling of hot gels when small molecule preservatives sorbate and ascorbate incorporated into the film formulation.

Bustos, Alberti, and Matiacevich [139] evaluated the release parameters of microencapsulated lemongrass oil from the alginate matrix. For this purpose, researchers began with the microencapsulation process, followed by the film preparation and analysis of the release kinetics from the films with the help of assessing antimicrobial activity against *E. coli*.

Transport parameters of n-hexanal [159,160] and D-limonene [160] were determined. Aroma compounds preferably interacted with fat compounds [159]. Therefore, the permeability of aroma compounds is dependent on the interactions between the aroma compounds and film matrices [160].

9. Future Trends

Studies about film forming and coating food products with edible biopolymers have been expanded recently. Edible/biodegradable films and coatings can be used to maintain the quality during the shelf life of the product. Promising results have been achieved on fresh cut fruits, vegetables, and meat products coated with alginate solutions with incorporated additives. However, further improvements could be obtained by incorporating new antimicrobial, antioxidative, antibrowning agents to enhance food safety and food quality. A better understanding of any synergistic effect among alginate coating and active agents can be developed.

Blending of film-forming biopolymers to improve the properties of the structure is also a promising strategy. Developing new synergistic gelling systems can be identified as another research gap.

Diffusion properties of active substances from the alginate gel matrix and its structure can be studied in more detailed with varying the concentrations of alginate and cross-linking agents. Comparative studies can be conducted.

The effects of different calcium salts (e.g., calcium chloride, calcium lactate, calcium gluconate) on the quality parameters can be identified in detail with clarified mechanisms.

Most studies on alginate coating applications have been conducted at the laboratory scale and commercial applications are still very limited. Further research with practical applications should focus on the industrial implementation to commercialize the alginate coated food products with increased shelf life. Coating application methods can be readjusted so as to implement a recycle process that does not waste too much of coating solution, decrease microbial load of the solution during recycling, design spraying method for irregular surfaces, design industrial size vacuum tanks, etc. to prevent the disadvantages of the application methods. Therefore, sodium alginate-based edible films and coatings could be used to an even greater extent than they are currently.

10. Conclusions

In an ideal case, an edible coating or film should decrease the evaporation of the water content, loss of desirable odor and flavor volatiles, prevent microorganism growth, suppress respiration, and gas exchange; while the modified atmosphere created by the barrier should not cause anaerobic respiration (and, therefore, anaerobic growth) and undesirable volatiles. On the basis of the evaluation of the previous literature on alginate-based edible films and coatings, it can be concluded that the alginate-based edible films and coatings can be efficiently used to accomplish these aims with an enhancing shelf life of fresh-cut fruits and vegetables, meat, poultry, seafood, and cheese. The information summarized here can lead researchers to design successful coating applications.

Author Contributions: T.S.P. conceived the focus of the review, conducted the literature search, and drafted the manuscript. M.S. and K.M. formatted, reviewed, and edited the manuscript upon critical revision of the texts.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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Chapter III.

Preliminary Measurements of Alginate-based Edible Coatings in Improving Fresh-cut Fruits Quality Attributes and Related Consequences for the Aims of This Thesis

This chapter does not consist of a peer-reviewed article. Some results were published in an article "shelf-life extension of fresh produce by edible coating" in an open-access journal "Italian Journal of Food Science" [145] and in a book chapter ("Antimicrobial hop extracts and their application on fresh produce") in "Multidisciplinary Approaches for Studying and Combating Microbial Pathogens" [146]. The writer of this thesis is the second co-author in the two papers mentioned above.

The present chapter was designed to investigate the effect of alginate-based edible coatings (prepared according to a previous study in the literature) with the incorporation of antimicrobial agents on the quality of fresh-cut cantaloupe and the ability to extend its shelf life. To this end, two types of antimicrobial agents (i.e., hop extract and potassium sorbate) were incorporated in different stages of the coating process.

Problems encountered during the fresh-cut fruit coating process, observations throughout the shelf life measurements, as well as the measured results showed that there were several limitations and interesting outcomes in the alginate-based edible coating process. These are (i) coating defects on fresh-cut surface, (ii) apparent lack of adhesion to the fruit surface, (iii) effect of coating ingredients on the adhesion ability of the coating, (iv) insufficient technical information about the effect of dipping parameters (i.e., dipping time, draining time, etc.), (v) reduction of water accumulation at the bottom of the fresh-cut fruits' packaging although it is a well-known fact that polysaccharides are hydrophilic materials and they provide low protection against water transmission, (vi) the sinusoidal water loss curve that uncoated cantaloupe pieces formed.

Principally, the preliminary measurements helped to focus on the right scientific questions and to formulate superior coatings.

3.1 Materials and Methods

3.1.1 Materials

Sodium alginate (Manugel GHB, FMC Biopolymer Co., Philadelphia, PA, USA), glycerol (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), sunflower oil (Rewe Bio, Rewe Markt GmbH, Cologne, Germany), tween 40 (polyoxyethylenesorbitan monopalmitate) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), span 80 (sorbitan monooleate) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), hop extract (Beta Bio 40, 40% β-acids in propylene glycol; brown, clear liquid; Hopsteiner GmbH, Mainburg, Germany), potassium sorbate (potassium salt of sorbic acid, Nutrinova®, Celanese Co., Frankfurt, Germany) and calcium L-lactate hydrate (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were used in coating formulations. Glycerol was employed as the plasticizer. Tween 40 and span 80 were viscous liquid-formed surfactants.

Amorphous polyethylene terephthalate (a-PET) packages and crystalline polyethylene terephthalate (c-PET) sealing film were sent from silver plastics® GmbH & Co. KG (Troisdorf, Germany).

3.1.2 Preparation of coating solution

The alginate-based coating solution was prepared according to the Azarakhsh, *et al.* [147]. 1.25 g of sodium alginate was dissolved in distilled water while stirring at 70 °C. 2 g of glycerol as a plasticizer, 0.1 g Tween 40 and 0.6 g Span 80 as surfactants and 0.125 g sunflower oil as lipid source were added into the solution. Sunflower oil was added also to improve water barrier properties, coating plasticity, and surface tension properties. The total weight of the solution was increased to 100 g with distilled water. The mixture was homogenized with ultra turrax (Miccra D-8, ART modern Labortechnik GmbH, Müllheim, Germany) at 10500 min^{-1} for 5 min. The solution was put in an ultrasonic bath (Transsonic 460/H, Carl Roth Gmbh Co. KG, Karlsruhe, Germany) at a frequency of 35 kHz for 10 min.

To induce a crosslinking reaction, 2 g calcium L-lactate hydrate was dispersed in distilled water, and the final amount of solution was increased to 100 g.

3.1.3 Preparation of fruit samples, coating application, and storage conditions

Whole cantaloupe melons *(Cucumis melo* var. *cantaloupensis)* were transported directly from a food production facility (Gartenfrisch Jung GmbH, Jagsthausen, Germany) to the laboratory in Freising. They were stored at 4°C in the cold storage room until they were processed (less than 24 hours).

As recommended by the producer, whole cantaloupes were washed with tap water. They were peeled, cut into two halves, the seeds were removed, and the remaining fruits

were cut into ~ 3 × 2 × 2 cm cuboid pieces (~ 8 g). The pieces were transferred into a large food container with lid and assigned to the treatments randomly. Therefore, the drying or dehydration of the food product was prevented.

The coating of the products with the hydrocolloid agent was composed of four steps: immersion of the cantaloupe pieces into the alginate-based solution (2 min), draining of the excessive hydrocolloid solution (3 min), the second immersion of the hydrocolloid coated food product into the crosslinking bath to form a gel (2 min), and draining of the excessive gel (2 min).

As stated by the producer (Gartenfrisch Jung GmbH, Jagsthausen, Germany) for the experiments in this chapter, coated and uncoated samples were packed in a-PET trays without lid and sealed with clear heat seal c-PET film. Subsequent to packaging, coated and uncoated samples were stored at 8°C for 8 days in a constant climate chamber (APT.Line KBF, WTB Binder Labortechnik GmbH, Tuttlingen, Germany).

Shelf life analyses were undertaken immediately after coating and packaging (day 0), at intervals throughout 8 days storage, until the fruit became unfit for consumption. Before measurements, samples were left at ambient temperature (~21 °C).

3.1.4 Microbiological analysis

30 g samples were blended with 10 ml of sterile 0.1% ringer solution (Sigma Aldrich GmbH, Steinheim, Germany) in a sterile stomacher bag and were homogenized for 2 min. Aliquots (1 ml) of diluted or undiluted extract were plated. Bacterial and fungal counts were expressed as colony-forming units (cfu/g). Total viable counts (TVC) were determined using PCA (plate count agar, Merck KGaA, Darmstadt, Germany) and pour plate technique, and plates were aerobically incubated at 30 °C for 48 hours. YGC medium (yeast extract glucose chloramphenicol, Merck KGaA, Darmstadt, Germany) was used for selective enumeration of yeasts and molds. The plates were prepared with a pour plate method and aerobically incubated at 25 °C for 3 days for the enumeration of yeasts and 5 days for the enumeration of molds.

3.1.5 Weight loss (%)

Coated and uncoated cantaloupe pieces were weighed using an analytical laboratory scale with 0.01 g sensitivity. Weight loss was determined in each package at different sampling dates by the percentage of weight loss with respect to day 0 ($weight_{initial}$). The formula for the percentage of weight loss calculation was expressed by Equation (23). Measurements were performed in triplicate (n=3). Weight loss (%) graphs were plotted with respect to storage time.

$$Weight\ loss\ (\%) = \frac{Weight_{initial} - Weight_{final}}{Weight_{initial}} \times 100 \quad (23)$$

3.1.6 Color analysis

CIE L*a*b* system; i.e., the intensity of lightness (L*), color opponents red-green (a*), yellow-blue (b*) were measured with a computer-controlled digital imaging system (DigiEye 2.8.0.3, VeriVide Ltd., Leicester, U.K.), that consisted of illumination cabinet (VeriVide Ltd.) with D65 diffuse illumination, digital camera (Nikon D90 and Nikkor AF Nikkor 35 mm 1:2D, Nikon Corporation, Tokyo, Japan), and a desktop computer (HP Inc., CA, U.S.A.). The system was standardized and calibrated with the DigiEye Digitizer Chart. ΔE_{Lab} refers to the numerical comparison of the samples' color to Day 1. ΔE_{Lab} of 5 specimens per treatment group (n=5) was calculated according to the following equation (24) [148]:

$$\Delta E_{Lab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (24)$$

3.1.7 Headspace gas concentration in packages

The change in oxygen (O_2) and carbon dioxide (CO_2) concentrations (%) in the headspace of the packages that filled with uncoated and coated samples was monitored using a combined O_2 and CO_2 measuring device (DAN-Sensor CheckMate 9900, PBI-Dansensor Deutschland GmbH, Bendorf, Germany). Experiments were performed in quintuplicate (n=5). The gas concentration was monitored by inserting the equipment's needle through an adhesive silicon septum attached to the packaging surface.

3.1.8 Sensory evaluations

Panelists (n=10) were initially selected from Fraunhofer IVV employees and students on the basis of the liking of the fruit. Five-point hedonic scale (i.e., 1=dislike very much, 2=dislike moderately, 3=neither like nor dislike, 4=like moderately, 5=like very much) was used to assess the overall acceptability of samples. If the unpleasant smell was noticed or microbial colonies on the fruits were observed, then only appearance was scored. Fruit pieces from different packages (same treatment group) were presented to each panelist at each session in transparent bowls under daylight. The bowls were coded using random 3 numbers. All samples were presented at one session and served at ambient temperature (~21 °C) to panelists.

3.1.9 Statistical evaluations

The mean and standard deviation were determined in Microsoft Excel 2010 (Microsoft Corp., Redmond, WA, USA). Graphics and statistical evaluations were performed using R 3.3.2 for Windows with the packages ggplot2 [149], grid [150], gridExtra [151], car [152], lsr [153], MASS [154]. Results were subjected to outlier analysis, log transform, N-factorial analysis of variance, and post hoc tests (i.e., Tukey Honest Significance Test (TukeyHSD)) to determine significant differences ($p \leq 0.05$) between

groups. The types of statistical tests applied to the results were denoted individually in the relevant results and discussion sections.

3.2 Results and Discussion

3.2.1 Pretrial: Sensorial evaluations

Hop is a natural product, and there is not any legal limit for its usage. However, its application as a natural preservative in foods (such as fruits and vegetables) has been limited by its strong flavor. Therefore, the highest possible hop concentration in terms of consumer acceptance was determined with sensorial pre-trials (Table 4).

Table 4. Alginate (1.25% alginate + 2% glycerol +0.125% sunflower oil + 0.1% TW 40 + 0.6% Span 80, w/w) coated cantaloupe pieces containing different hop concentrations and cross-linked with 2% calcium lactate, w/w). Preference results of the panelists.

Concentration of hop extract (μg/g)[1]	Number of panelists
12.5	8
125	10
625	6
1250	0

[1] Panelists were able to select more than one concentration.

Even though more panelists preferred coated products in which 125 μg/g hop incorporated, to achieve the highest possible microbial effect, 625 μg/g hop was chosen as an antimicrobial concentration for the following experiments.

3.2.2 Microbial counts

Total viable count (TVC, also referred to as aerobic plate count and the standard plate count) provides a general indication of the microbiological quality of samples [155]. Although it cannot be used as an indicator of safety, it is a useful tool to predict general quality assessment, including that of extended shelf-life of the product [155,156].

Changes in TVC of fresh-cut cantaloupe pieces for 8 days storage are given in Figure 6. Subsequent to the induction period (approx. 2 days), rapid bacterial growth occurred in all treatment groups. The high initial microbial load of cantaloupe pieces (i.e., log cfu/g = 3.62±0.32) could be attributed to the inefficient surface sanitation performed with drinkable tap water. Likewise, Ukuku, *et al.* [157] found that the initial populations of aerobic mesophilic bacteria of the fresh-cut cantaloupe pieces were log cfu/g = 3.2±0.02 when the rind of the fruit was washed with water. Sapers, Miller, Pilizota and Mattrazzo [61] compared surface sanitization practices and found that no decontamination treatment on whole cantaloupe rind resulted in premature microbiological spoilage of fresh-cut

flesh. Due to the necessity of following the same production procedures that the fresh-cut industry has been applying, additional sanitizing agents were not incorporated to the washing water.

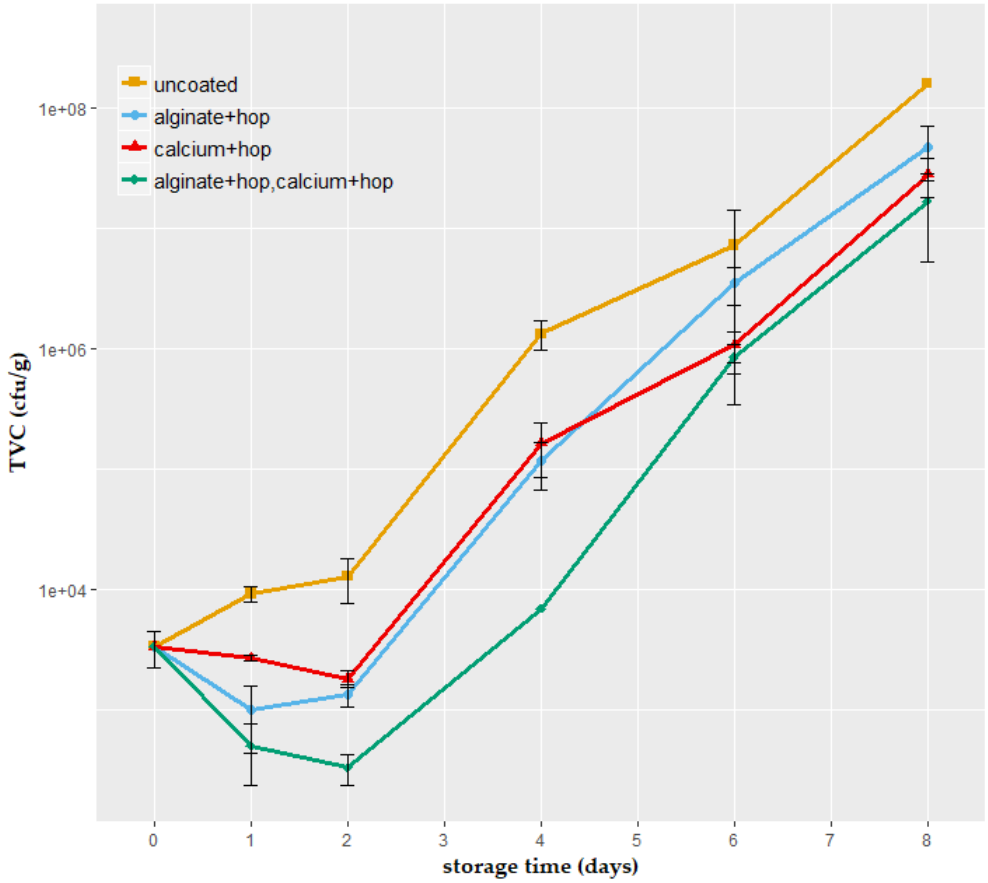

Figure 6. Microbial growth (TVC, cfu/g) in fresh-cut cantaloupe at 8 °C. Alginate-based coating (1.25% alginate + 2% glycerol + 0.125% sunflower oil + 0.6% span 80 + 0.1% tween 40 and 2% calcium lactate (crosslinking agent), w/w). **Uncoated:** control; **alginate+hop:** 625 µg/g Beta bio 40 was added to only alginate solution; **calcium+hop:** 625 µg/g Beta bio 40 was added to only crosslinking solution; **alginate+hop,calcium+hop:** 625 µg/g Beta bio 40 was added to both coating and crosslinking solutions.

Log transformation was used to reduce skewness and to make data to conform to normality. Afterward, two-way ANOVA was conducted to examine the effect of treatment groups and storage days on the microbial load of the samples. Treatment groups, storage time, and their interaction were all statistically significant ($p<0.05$). TukeyHSD multiple comparisons test showed that uncoated samples had significantly higher microbial load compared to other groups ($p<0.05$). Although hop addition into only one coating step decreased the microbial amount significantly, the addition stage of hop (either in alginate solution or calcium solution) did not differ significantly ($p>0.05$). On the other hand, the inhibitory effect increased with the addition of hop extract to both coating and crosslinking steps. Hop addition to both steps had the significantly lowest

microbial load (i.e., log cfu/g reduction was 1) at the end of the storage period. Increased antimicrobial effect of hop addition into both steps can be elucidated with the help of gel formation mechanisms. Pavlath, *et al.* [158] stated that when alginate was immersed in a calcium solution, two types of reactions took place. These reactions were; formation of calcium linkage with carboxyl groups (gel formation and insolubilization of alginate film); and dissolution of alginate by the crosslinking solution. When an antimicrobial agent is incorporated to both coating and crosslinking solutions, the amount of antimicrobial present in the formed gel is higher compared to the formed gel in which antimicrobial is added in only one step. Moreover, during the dissolution of alginate in the calcium solution, the amount of antimicrobial agent decreases, too.

Fresh fruits and vegetables harbor normal microbial flora; therefore, they have an inherent high plate count [159]. Hence, TVC limits are not applicable (N/A) for fresh ready-to-eat (rte), uncooked fruits, and vegetables [159]. In general, TVC<10^6 cfu/g indicates mixed microflora of the food sample [155]. The sensorial quality and acceptability of the food will be affected by predominant microorganisms [155]. For instance, when the predominant microflora comprises mainly Gram(-), spoilage happens at 10^7- 10^8 cfu/g with slime production [155].

A total viable count of 10^7 cfu/g was reached in the uncoated cantaloupe sample after the 6th day. On the other hand, hop addition to both solutions (i.e., coating and crosslinking) led to a slight shelf-life increase. This limit was reached after 7.5 days. O'Connor-Shaw, *et al.* [160] determined the shelf life of cantaloupe pieces at 4°C as 4 days.

As a second step, the same amount of potassium sorbate (PS, 625 μg/g) was incorporated to different steps of the alginate coating process for the comparison of antimicrobial agents (Figure 7a and 7b). TVC results of Beta bio 40 added samples (in Figure 7a) correlated well with previous findings in Figure 6; the antimicrobial effect of hop extract led to approximately a log reduction of 1 throughout the storage time.

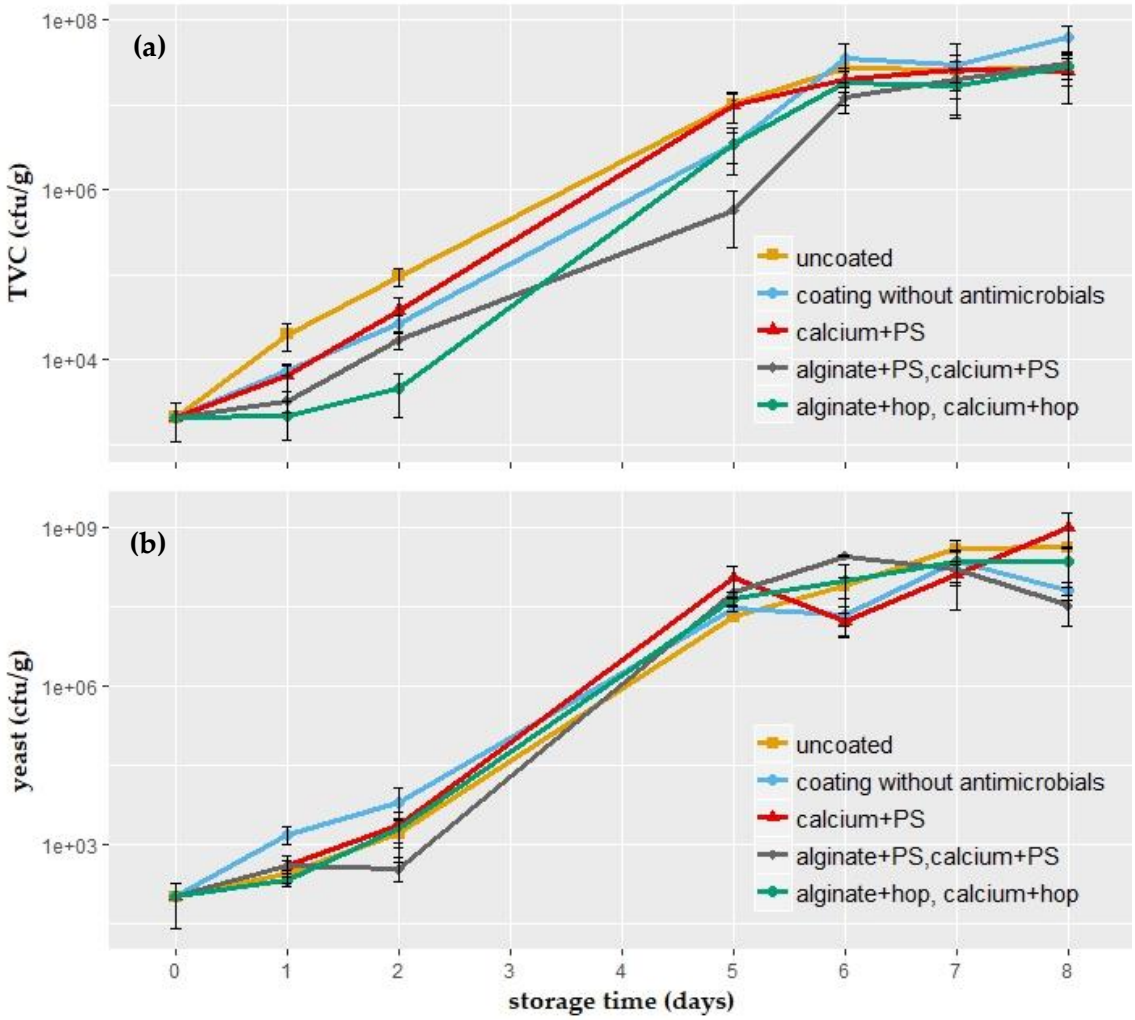

Figure 7. (a) TVC (cfu/g) and **(b)** yeast count (cfu/g) in fresh-cut cantaloupe at 8 °C. Alginate-based coating (1.25% alginate + 2% glycerol + 0.125% sunflower oil + 0.6% span 80 + 0.1% tween 40 and 2% calcium lactate (crosslinking agent), w/w). **Uncoated:** control; **coating without antimicrobials**: hop and/or potassium sorbate were not incorporated; **calcium+PS:** 625 μg/g potassium sorbate (PS) was added to only crosslinking solution; **alginate+PS, calcium+PS:** 625 μg/g potassium sorbate (PS) was added to both coating and crosslinking solutions; **alginate+hop,calcium+hop:** 625 μg/g Beta bio 40 was added to both coating and crosslinking solutions.

Two-way ANOVA model on log-transformed data revealed that treatment groups, storage time, and their interaction had significant effects on TVC ($p<0.001$). It was interesting to note that there was no significant difference between uncoated, coating without antimicrobials and calcium+PS groups ($p>0.001$). Moreover, hop incorporated samples did not differ significantly from alginate+PS, calcium+PS group ($p<0.001$). Furthermore, the microbial load of all groups equalized after the 6th storage day ($p>0.001$), which can be explained as the entrance into the stationary phase of the microbial growth.

Changes in yeast populations for 8 days storage is given in Figure 7b. The data were subjected to similar statistical evaluations, as indicated in previous microbial analyses. Results showed that hop did not reduce yeast count and did not differ statistically from uncoated and coating without antimicrobial groups ($p>0.05$). However, potassium sorbate addition to the coating formulation had a significant effect on the reduction of yeast amount of the sample ($p>0.05$). Also, Ozdemir and Demirci [161] found that potassium sorbate (0.05 kg/100 kg cheese) addition into Kashar cheese did not decrease total aerobic mesophilic bacteria and lactic acid bacteria, proteolytic microorganism, and lipolytic bacteria counts. On the other hand, it reduced coliform bacteria, S. aureus, yeast, and mold counts.

Potassium sorbate is typically used as a fungistatic agent in bakery products at concentrations of 1000 to 3000 μg/g [162]. Similarly, it is used against yeast spoilage of confectionery components when incorporated at concentrations 1000 – 2000 μg/mg [162]. A 350 μg/ml potassium sorbate addition into fermentation brine of cucumbers limited the growth of molds and yeasts in the product [163]. Up to 100 – 200 μg/ml potassium sorbate is added to control yeast growth in some white wines [164]. In the present study, 625 μg/g potassium sorbate was incorporated into the coating and crosslinking solutions. However, the antimicrobial agent presented in the gel layer on the coated food was a much smaller amount. In our previous study [165], 2 min dipping into both alginate and calcium lactate solutions led to an average of 9.3% weight increase on coated cantaloupe samples (≈10 g), which is equal to ≈58 μg PS/g coated cantaloupe. Therefore, ineffective antimicrobial properties of antimicrobial agents can be explained with the dilution of the agents in coating and crosslinking solutions.

Fungal growth was below the detection (sensitivity) limit throughout the storage period. Similarly, Lamikanra, Chen, Banks and Hunter [60] stated that bacterial growth was predominant during storage at 4°C and 20°C. Notwithstanding this, fungal growth was minimal.

Even though hop extract incorporated edible coatings achieved a bacterial reduction in the early storage days (<6 days), the effect can be enhanced with the reduction of the pH of the coating solution. The studies of Simpson and Smith [166], Bhattacharya, *et al.* [167], Shen and Sofos [168] and Kramer, Thielmann, Hickisch, Muranyi, Wunderlich and Hauser [80] have shown that addition of acids (e.g., lactic, citric, ascorbic acid, etc.) into the media can reduce the neutral pH and promote the activity of hop extract.

3.2.3 Weight loss (%)

The most notable changes were observed in water loss results (Figure 8). The results were expressed as the percentage of weight loss to eliminate the difference in the sample sizes. Analysis by two-way ANOVA showed that coating application decreased the water loss amounts of samples significantly ($p<0.05$). On the other hand, the type of antimicrobials did not cause any significant difference between sample groups ($p>0.05$).

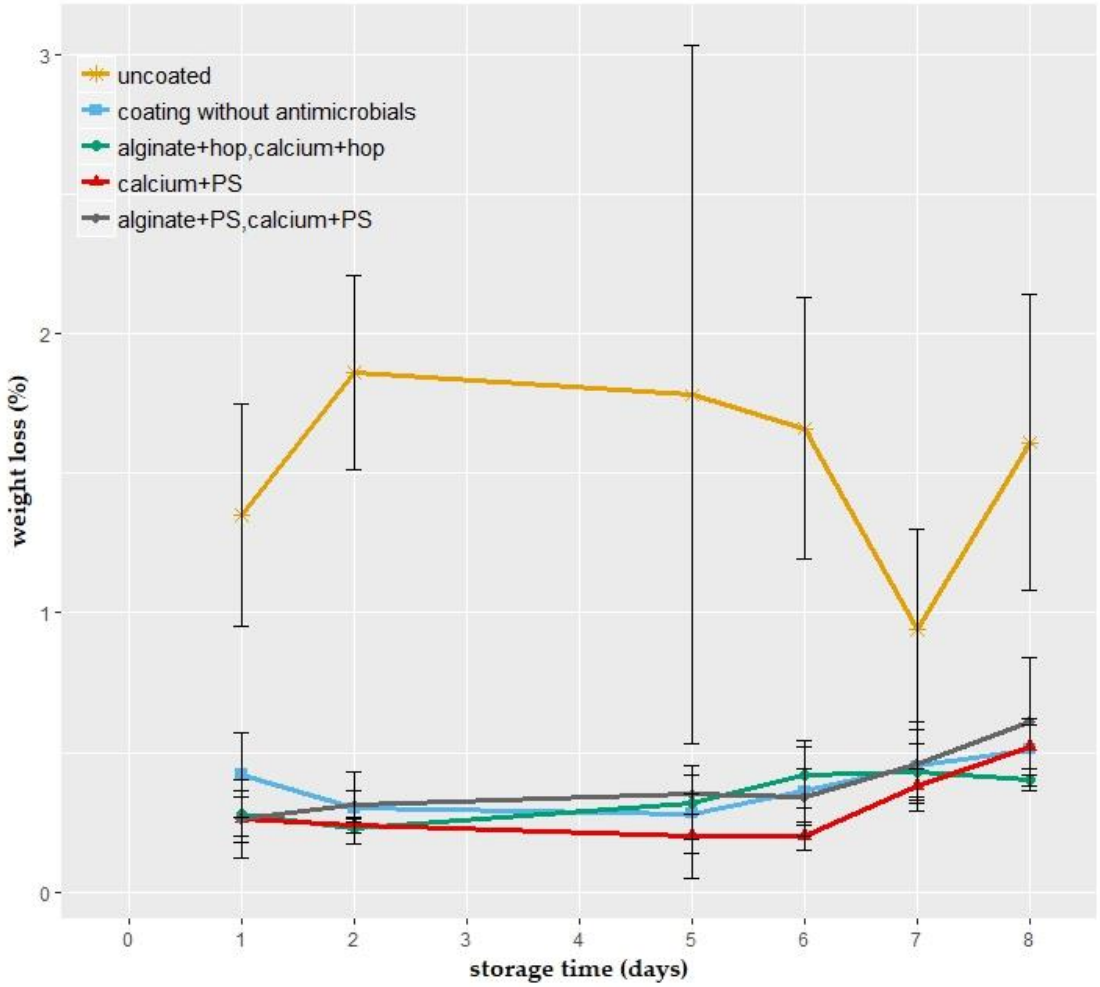

Figure 8. Weight loss (%) of fresh-cut cantaloupe coated with an alginate-based solution (1.25% alginate + 2% glycerol + 0.125% sunflower oil + 0.6% span 80 + 0.1% tween 40 and 2% calcium lactate (crosslinking agent), w/w) during storage at 8°C. **Uncoated:** control; **coating without antimicrobials**: hop and/or potassium sorbate were not incorporated; **alginate+hop,calcium+hop:** 625 µg/g Beta bio 40 was added to both coating and crosslinking solutions; **calcium+PS:** 625 µg/g potassium sorbate (PS) was added to only crosslinking solution; **alginate+PS, calcium+PS:** 625 µg/g potassium sorbate (PS) was added to both coating and crosslinking solutions.

The pattern of water loss increase was similar for all alginate-coated groups; however, the water loss of uncoated samples formed a sinusoidal curve with ≈1.5% mid-line. The results raised interesting questions; therefore, weight loss (%) of cantaloupe samples were investigated in detail in Chapter VII.

3.2.4 Color

Visual appearance and color are important characteristics that affect the marketability of food products. The comparisons of the color results of uncoated and coated fresh-cut

cantaloupe pieces were made in terms of L*, a*, b*, and ΔE_{Lab} parameters and are given as bar charts in Figure 9a-d. Treatment types, storage time, and their interaction (treatment × time) had significant effects on color values ($p<0.05$). Coating application affected luminosity and yellowness significantly ($p<0.05$). Similarly, Jost, *et al.* [169] stated that alginate films had a strong impact on the yellowness. Also, Peretto, *et al.* [170] found that alginate coating increased the b* values of coated strawberries significantly.

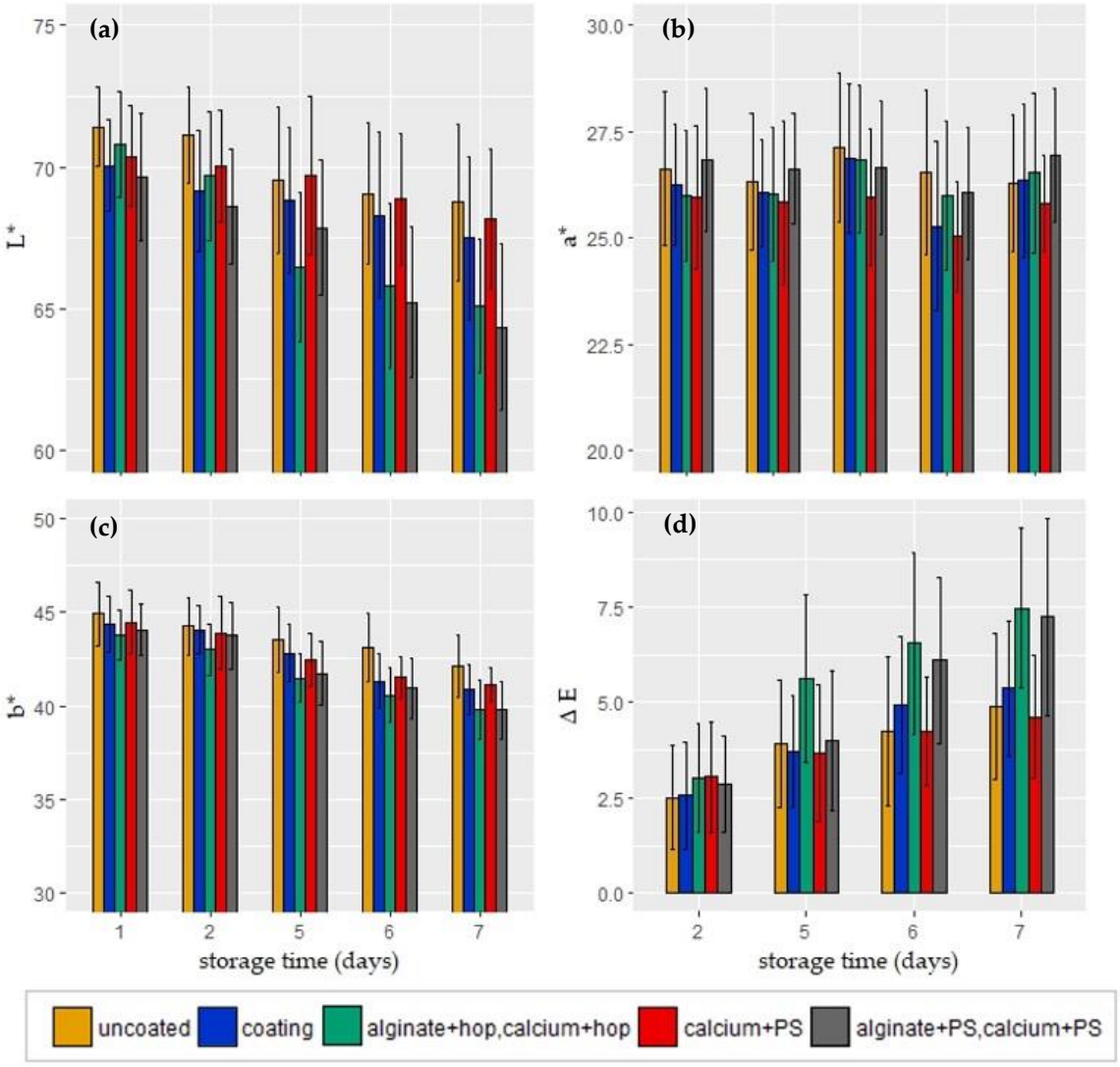

Figure 9. Color parameters (L*, a*, b*, and ΔE_{Lab}) of cantaloupe samples during 7 days of storage at 8 °C. Coating was composed of 1.25% alginate, 2% glycerol, 0.125% sunflower oil, 0.6% span 80, 0.1% tween 40 and 2% calcium lactate as crosslinking agent, w/w. **Uncoated:** control; **coating:** hop and/or potassium sorbate were not incorporated; **alginate+hop,calcium+hop:** 625 μg/g Beta bio 40 added to both coating and crosslinking solutions; **calcium+PS:** 625 μg/g potassium sorbate (PS) was added to only crosslinking solution; **alginate+PS, calcium+PS:** 625 μg/g potassium sorbate (PS) was added to both coating and crosslinking solutions.

As the storage time increased, luminosity and yellowness decreased significantly, while the redness of the samples stayed relatively constant; on the other hand, ΔE increased (i.e., the color of the sample compared to Day 1). ΔE values show the quantitative representation of perception of the color difference by the human eye. 0<ΔE<1 indicates an unnoticeable color difference, 1<ΔE<2 can be noticed only by experienced observers, while even inexperienced observers can notice the color difference when 2<ΔE<3.5 [148]. 3.5<ΔE<5 indicates a clear color difference and finally, 5>ΔE represents two different colors. Therefore, longer storage periods led to noticeable color changes in the samples. Most particularly, antimicrobial substances promoted the color changes of the fresh-cut cantaloupe pieces. Incorporation of hop into the coating formulation affected both L*, b*, and ΔE values. This effect can originate from the dark color of the hop concentrate. On the other hand, Figure 8 demonstrates that even white-colored potassium sorbate addition into both coating steps led to clear color differences. Similar to our findings, Barzegar, *et al.* [171] found that the addition of potassium sorbate decreased L* and increased b* values and thus led to a significant increase in ΔE in starch-clay nanocomposite films. Famá, *et al.* [172] stated that oxidation caused a reduction in the sorbate concentration over time. Therefore, the color changes associated with PS addition can be most likely explained with oxidative browning.

3.2.5 Headspace gas composition

As a rule of thumb, fat-based coatings reduce water transfer, protein-based layers increase mechanical stability while polysaccharide-based films are used to control gas transfer [122]. In addition, the incorporation of plasticizers can increase gas permeability due to causing structural changes.

Figures 10a and 10b show the O_2 and CO_2 concentrations (%) in the headspace of the packages throughout the storage time. Similar to the previous findings of Oms-Oliu, *et al.* [173] and Rojas-Graü, *et al.* [174] all treatment groups followed similar increasing/decreasing trends; O_2 concentrations decreased up to 2.5–8% while CO_2 concentrations increased up to 27–35%.

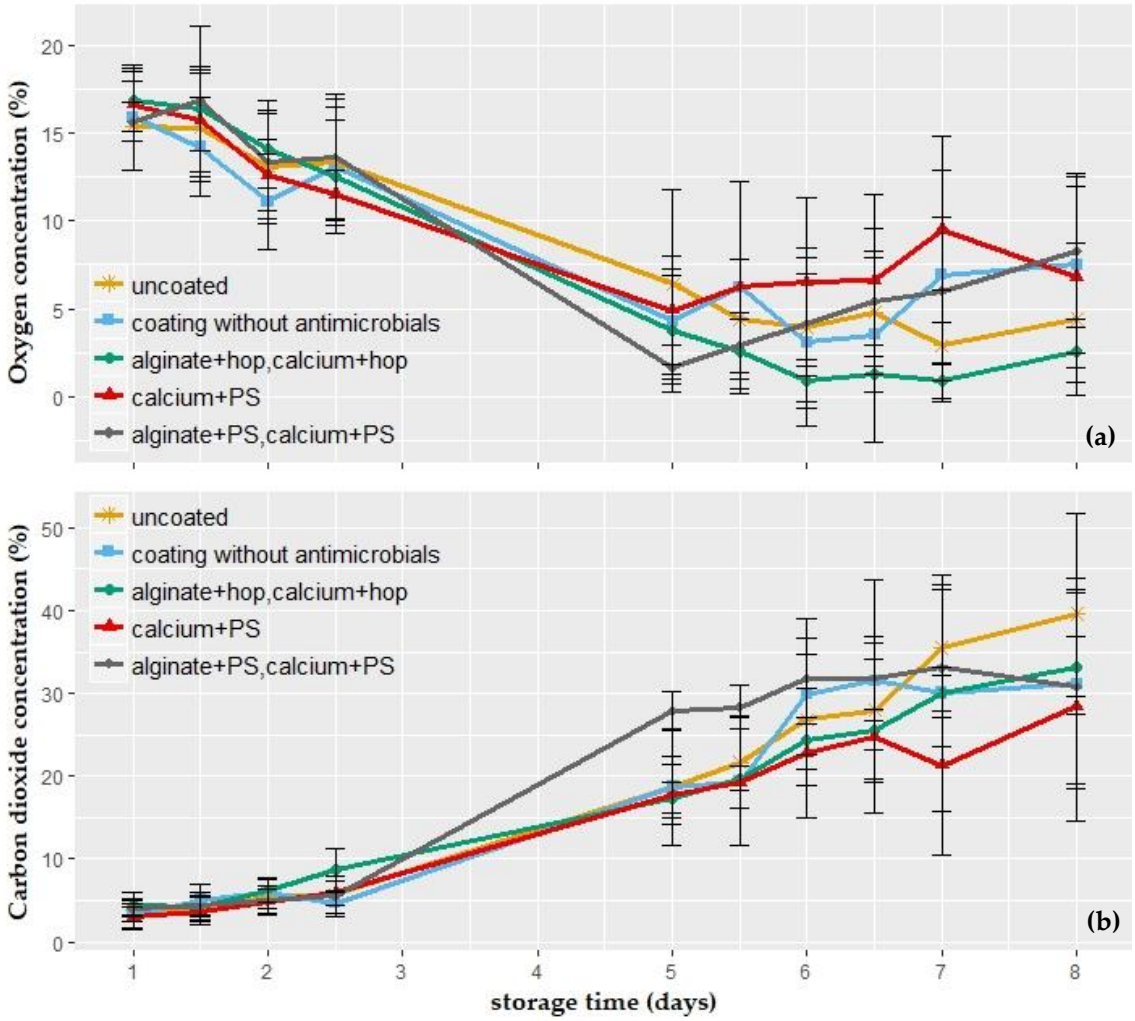

Figure 10. O_2 and CO_2 headspace gas concentration in packages containing coated and uncoated fresh-cut cantaloupe pieces during storage at 8°C. Coating: 1.25% alginate + 2% glycerol + 0.125% sunflower oil + 0.6% span 80 + 0.1% tween 40 (w/w); crosslinking: 2% calcium lactate (w/w) during storage at 8°C. **Uncoated:** control; **coating without antimicrobials:** hop and/or potassium sorbate were not incorporated; **alginate+hop,calcium+hop:** 625 μg/g Beta bio 40 was added to both coating and crosslinking solutions; **calcium+PS:** 625 μg/g potassium sorbate (PS) was added to only crosslinking solution; **alginate+PS, calcium+PS:** 625 μg/g potassium sorbate (PS) was added to both coating and crosslinking solutions.

Outlier analysis was conducted to the multivariate data set prior to N-factorial analysis of variance. Two-way ANOVA results showed that there was no significant difference between treatments. Only the storage period had a significant effect on gas concentrations in the headspace. Contrary to the prediction of the theory that polysaccharide-based coatings modify the gas transfer, the coating application (with or without antimicrobial agents) did not change gas concentration accumulated in the headspace of the packages. However, this unexpected ineffectiveness was also previously observed by other researchers in the literature [174]. It could be explained by the

permeability of the plastic film, which led gases to transfer and prevented their accumulation in the headspace of the packaging.

3.2.6 Sensory

Affective testing using a five-point hedonic scale was employed to establish the consumer acceptability and preference for alginate coated cantaloupe samples through liking and disliking. By using the hedonic scale, the panelists compared their overall acceptance of uncoated, coated, hop, or potassium sorbate incorporated coatings. Figure 11 presents the panelists' intention to consume coated products over uncoated samples. Generally, uncoated cantaloupe was preferred over coated counterparts during the whole storage period. Two-way ANOVA tests showed that both treatment, storage time, and their interaction (treatment×time) affected the overall impressions of panelists significantly. Statistical evaluations denoted that potassium sorbate addition did not influence the sensorial properties. On the contrary, hop extract incorporated coatings had significantly the lowest sensorial scores due to its characteristic bitter taste.

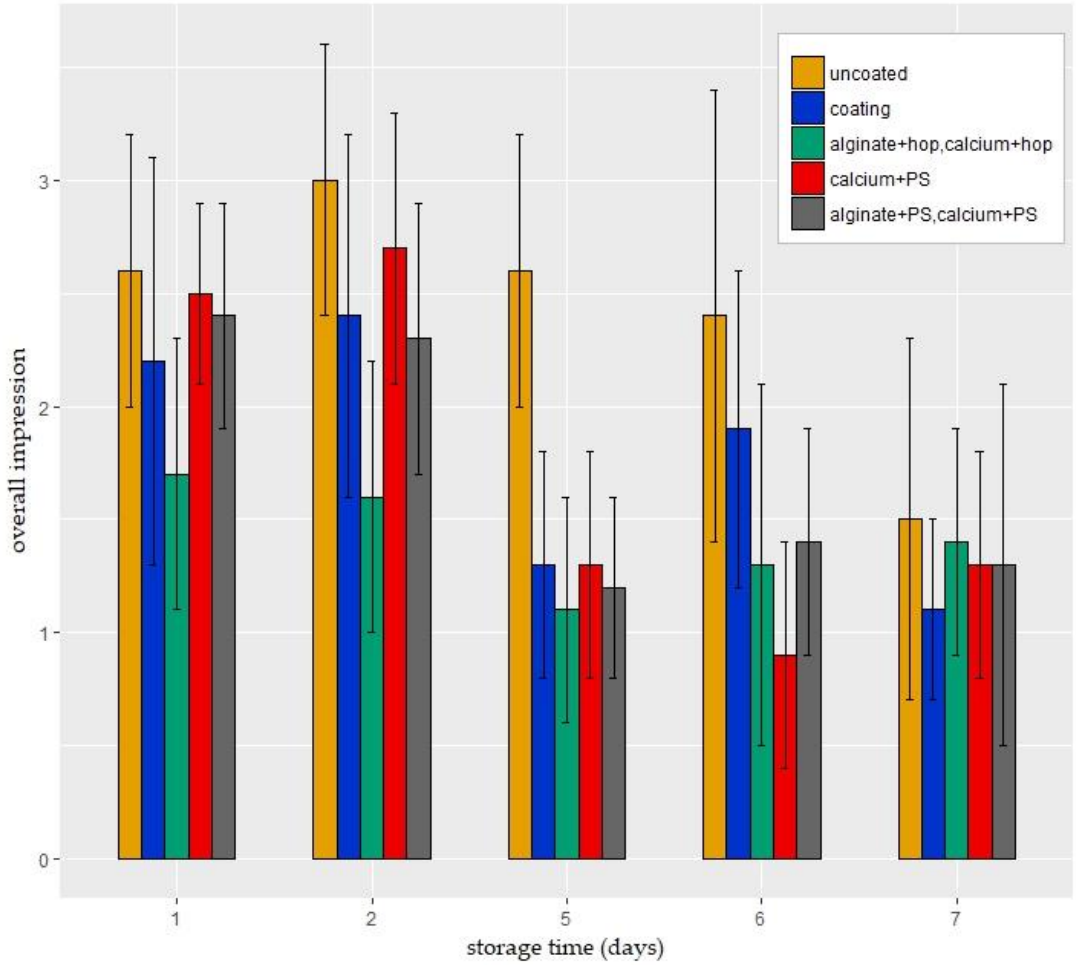

Figure 11. Overall impression of panelists according to five-points hedonic scale (i.e., **1**=dislike very much, **2**=dislike moderately, **3**=neither like nor dislike, **4**=like moderately, **5**=like very much). Alginate-based coating (1.25% alginate + 2% glycerol + 0.125% sunflower oil + 0.6% span 80 + 0.1% tween 40 and 2% calcium lactate (crosslinking agent), w/w). **Uncoated:** control; **coating:** hop and/or potassium sorbate were not incorporated; **alginate+hop, calcium+hop:** 625 μg/g Beta bio 40 was added to both coating and crosslinking solutions; **calcium+PS:** 625 μg/g potassium sorbate (PS) was added only to crosslinking solution; **alginate+PS,calcium+PS:** 625 μg/g potassium sorbate (PS) was added to both coating and crosslinking solutions.

As can be seen in Figure 12, lack of the adhesion ability of the alginate solution on the highly hydrophilic cut surfaces such as fresh-cut cantaloupe samples led to non-uniform coatings and even separation of the coating layer as a sheet. The low sensorial scores of coated cantaloupe samples might be related to coating layer separation. This issue was studied in Chapter VII in detail, and coating uniformity was achieved with the increased adhesion ability of the alginate-based solution.

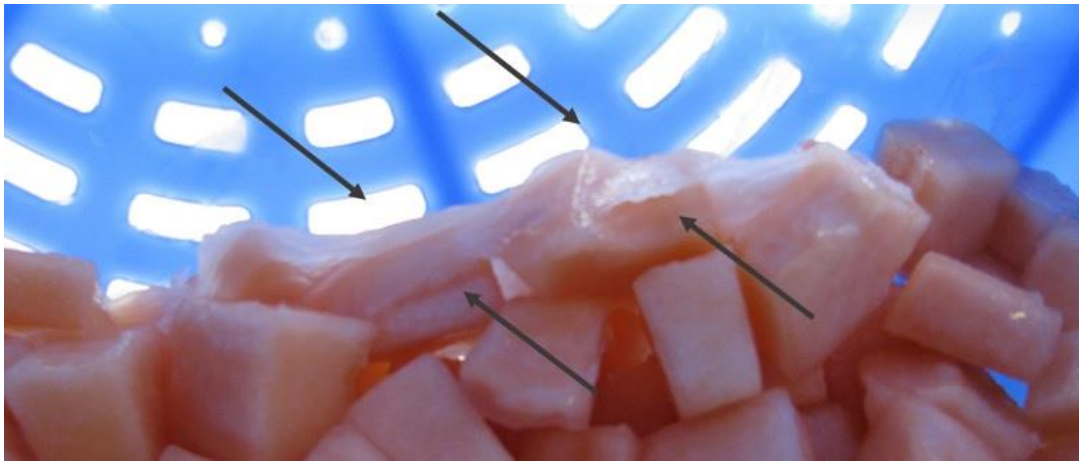

Figure 12. Images of coated cantaloupe pieces when the bulk amount of sample was dipped in coating and crosslinking solutions.

3.3 Conclusion and Consequences for the Aims of This Thesis

In the present chapter, the ability of an alginate-based coating to extend the shelf-life of fresh-cut cantaloupe as well as the effects on quality parameters of the food were studied. The results showed that shelf life was limited, especially by changes in sensory and microbial growth.

Studies in the present chapter have raised questions about the importance of distinct coating variables (immersion time, draining time, crosslinking time, etc.) that affect the coating amount adsorbed on the product surface (it can also be seen as an indicator of coating thickness). The determination of the amount of alginate coating applied is

essential for the evaluation of its protective function and for economic reasons (in industrial applications).

As seen from the photograph in Figure 12, inherently poor adhesion properties of the coating material and the coating defects were important shortcomings for the process. The attempts to achieve better adhesion properties (in other words, wettability) has been the second question brought up in this chapter. The efforts can have special focuses on (i) surface itself and (ii) coating solution.

Although alginate is a hydrocolloid material and does not target to control water vapor transport, results showed that the reduction of the water loss was the most important beneficial response to the coating process. Therefore, liquid water and water vapor permeability characteristics of the coating should be evaluated in detail.

It is necessary to emphasize that the questions raised in the present chapter were also linked to each other. For example, the reduction of water loss of the product is also dependent on the thickness of the edible coating present on the coated surface. Most likely, the coating parameters would affect the coated amount (therefore thickness) on the surface. In addition, increased adhesion properties on the surface and uniform thickness of the coating (lack of coating defects, holes, cracks, etc.) would improve the water transfer characteristics.

Table 5 lists the limitations, interesting observations, and the chapters they were investigated in this thesis.

Table 5. List of alginate-based coating process limitations and the chapters they were studied in.

• Insufficient technical information about the effect of dipping parameters and selection of adequate immersion and draining times *(Chapter IV)*
• Apparent lack of adhesion to the fruit surface *(Chapters V, VI, VII)*
• Effect of ingredients on the adhesion ability and stability of the coating *(Chapter VI)*
• Fresh-cut surface coating defects *(Chapter VII)*
• Reduction of water accumulation at the bottom of the fresh-cut fruits' packaging and inspection of the sinusoidal water loss curve *(Chapter VII)*

To sum up, the primary purpose of this chapter can be defined as the provision of general guidance for the following chapters.

Chapter IV.

Dipping and Vacuum Impregnation Coating Techniques

This chapter contains a peer-reviewed article "Effect of dipping and vacuum impregnation coating techniques with alginate based coating on physical quality parameters of cantaloupe melon". It is published in "Journal of Food Science" (Publication II). The author of this thesis is also the first author of the article. Authors' contributions were specified in the article under the names "Tugce Senturk Parreidt conceived, designed and performed the experiments and analyzed the data; Markus Schmid and Tugce Senturk Parreidt interpreted the results. Tugce Senturk Parreidt wrote the manuscript; and Markus Schmid and Kajetan Müller proofread the text".

Since the author of the published Wiley article was also the author of the present thesis, the full text of the published article could be reused as a part of this dissertation without any need to request permission. Nevertheless, a formal grant of license was downloaded from RightsLink Marketplace and presented in Appendix.

Summary of the Publication-II

Fresh food and food products are generally coated by dipping or spraying techniques, in which a thin film is formed on the surface that acts as a semipermeable membrane to control transfer processes.

Although the application time is very short, good adhesion on the hydrophilic cut surfaces may not be achieved well by the simple dipping method. Therefore, new coating techniques have been designed by the researchers to enhance the effectiveness of the coating application. Vacuum impregnation coating technique consists of the same dipping-draining steps; however, instead of dipping tanks, the samples are submerged into two airtight vacuum chambers connected to vacuum pumps. Subsequent to the vacuum application, products are subjected to atmospheric restoration while they remain immersed in the coating solution under atmospheric pressure.

The type of edible coating technique and the parameters used significantly affects the physical quality characteristics of coated food products. The present study aimed to compare two coating techniques (dipping and vacuum impregnation) and, in addition, to produce more technical information concerning these techniques. For this purpose, cantaloupe as a porous food material and sodium alginate as a coating solution were selected as a model system. The effects of various coating parameters (dipping time (30-

240 s); draining time (10-300 s); the time length of the vacuum period (5-15 min); vacuum pressure (50-150 mbar absolute pressure); atmospheric restoration time (2-30 min)) with several levels on physical quality parameters (percentage of weight gain, color, and texture) of coated samples were determined to define adequate coating process parameters to achieve a successful coating application. In this study, the dependent variable, i.e., weight gain was used as an indicator for the thickness of the coating, which is an important variable in mass transfer and barrier characteristics of the coating. Due to the application of only one coating formulation (the microstructure of the used coatings was the same), the relationship between the weight gain and the coating thickness was assumed linear.

Dipping and draining times of the simple dipping method were determined as 120 s and 60 s, respectively. Longer immersion into the coating solution did not increase the coating amount. Similarly, a linear relationship between coating variables and the coated amount on the product surface was also not observed for the vacuum impregnation process. In other words, increasing the amount of atmospheric restoration time or vacuum period or vacuum pressure did not necessarily increase the yield of the coating process. The highest weight gain results were achieved with 15 min atmospheric restoration time. Furthermore, the vacuum period had a significant effect on weight gain results; in particular, the highest weight gain results were achieved with a 10 min vacuum period.

The comparison of the results showed that both processes improved the firmness of the melon pieces. However, vacuum impregnation application had higher firmness, weight gain results, and had a significant effect ($p<0.05$) on color (lower luminosity, higher redness, yellowness, and chroma values). Experimental results affirm that the vacuum impregnation technique is a successful coating method; however, consumer responses to the alterations in quality parameters should be carefully assessed for each product.

Effect of Dipping and Vacuum Impregnation Coating Techniques with Alginate Based Coating on Physical Quality Parameters of Cantaloupe Melon

Tugce Senturk Parreidt, Markus Schmid, and Kajetan Müller

Abstract: Edible coating based on sodium alginate solution was applied to fresh-cut cantaloupe melon by dipping and vacuum impregnation coating methods. One aim of this work is to produce more technical information concerning these conventional and novel coating processes. For this purpose, the effect of various coating parameters (dipping time, draining time, time length of the vacuum period, vacuum pressure, atmospheric restoration time) with several levels on physical quality parameters (percentage of weight gain, color, and texture) of noncoated and coated samples were determined in order to define adequate coating process parameters to achieve a successful coating application. Additionally, the effects of dipping and vacuum impregnation processes were compared. Both processes improved the firmness of the melon pieces. However, vacuum impregnation application had higher firmness and weight gain results, and had significant effect ($P < 0.05$) on color (lower luminosity, higher redness, yellowness, and chroma values). Experimental results affirm that vacuum impregnation method can be used successively to improve mechanical and structural properties of food products.

Keywords: alginate, dipping, edible coating, melon, vacuum impregnation

Practical Application: Type of edible coating technique and the parameters used significantly affect the physical quality characteristics of coated food products. The work presented produced more technical information concerning dipping and vacuum impregnation coating techniques, along with evaluating the effects of various coating parameters with several levels. The results revealed that vacuum impregnation technique is a successful coating method; however the effects should be carefully assessed for each product.

Introduction

Edible coatings are defined as any type of material applied to the food surface and produce an extra physical barrier to reduce quality losses and improve appearance of the product (Han, 2003; Pavlath & Orts, 2009; Vu, Hollingsworth, Leroux, Salmieri, & Lacroix, 2011). The coatings produce thin layers (<0.3 mm) on the food products and can be consumed together with food or with further removal (Pavlath & Orts, 2009). Edible coatings can contend effectively with various challenges in the subject of retention of food quality such as being barriers to water vapor and gases thereby slow respiration, serving as protective coating for food ingredients, lessening migration of fats and oils, improving mechanical properties and structural integrity, and changing surface gloss (Krochta, Baldwin, & Nisperos-Carriedo, 1994; Nussinovitch, 2009). Edible coating can also be used as a vehicle for food additives, such as flavors, antimicrobial agents, antioxidants, nanoparticles and colors (Krochta et al., 1994; Nussinovitch, 2009; Skurtys et al., 2010). Moreover, edible coatings may be considered as an additional layer to the commercial packaging materials (for example, plastics) used for food products (Krochta et al., 1994).

Alginate (E400–E404) is an indigestible gum produced by brown seaweeds (*Phaeophyceae*, mainly *Laminaria)* (Skurtys et al., 2010). Due to being a component of dietary fiber, their addition to food product would increase the amount of fiber in consumers' diet and potentially has a positive effect on nutrition and health (Edwards & Garcia, 2009; Skurtys et al., 2010). Characteristic ion-binding properties of alginate are an attractive feature and represents the basis of the gelling capacity in presence of calcium (Draget, 2009; Skurtys et al., 2010). As a result of its unique colloidal properties such as thickening, stabilizing, suspending, film forming, gel producing, and emulsion stabilizing, alginate has a potential to form biopolymer film or coating component (Skurtys et al., 2010). Alginate, as many other hydrocolloids (gums), is hydrophilic and therefore edible films prepared from alginate has a natural limitation in terms of moisture-barrier properties. However, if the coatings are used in gel form (without drying), the gel acts as a sacrificing agent and by this way they can retard moisture loss (Nussinovitch, 2009). In our present study, alginate was selected due to its widespread usage in coating literature, and appropriateness to load additives such as antimicrobials and antioxidants.

The main techniques for the application of edible coatings are: dipping and spraying (Guilbert, Gontard, & Cuq, 1995; Krochta et al., 1994; Nussinovitch, 2009; Skurtys et al., 2010). Among

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doi: 10.1111/1750-3841.14091

them, sample immersion in the film-forming dispersions (dipping method) is the most common coating method to form a coating layer on the food product. This method consists of dipping the food product into the coating solution, then withdrawing the food and draining of the excessive solution covering the product. Due to the shortness of the process, evaporation of the water is generally neglected, and therefore characteristics of the solution like viscosity, surface tension, density, and so on, are considered as constant (Cisneros-Zevallos & Krochta, 2003). Recently, vacuum impregnation method (VI) started to be used to form a thicker, more effective coating that effectively incorporate solutes into porous solid matrices containing air, such as fruits and vegetables (Guillemin, Degraeve, Noël, & Saurel, 2008; Vargas, Chiralt, Albors, & González-Martínez, 2009). Due to the external pressure changes, structure and composition of the product are altered during VI treatment of porous food products (Fito, Andrés, Chiralt, & Pardo, 1996; Vargas et al., 2009). VI applications in fresh produce processing has several advantages such as enrichment of fruits and vegetables with minerals and vitamins, modifying product formulations when it is used as pretreatment before drying, freezing, canning, and frying processes, preserving natural flavor and many heat sensitive nutrients, preventing discoloration due to removal of oxygen, impregnating antimicrobial and antioxidant agents to the product for the retention of quality (Fito et al., 2001; Zhao & Xie, 2004).

The technical challenges involved in producing stable coated foods and lack of necessary technical information concerning coating process prevent the usage of edible coating from greater extend. Although the effects of various edible coatings/films on quality parameters and shelf life of food products had been studied extensively, almost all these studies, however, used predetermined conditions in the coating processes and not focus on the effects of the coating parameters on quality characteristics. Yet, the effects of coating process itself (dipping, VI, and so on) and the independent variables (such as time, pressure, and so on) used in the coating process have also strong effect on forming good quality coatings. Thus, the objective of this work was to evaluate the effect of different variables of two different coating processes on the physical attributes (weight gain/coating amount, color, texture) of the food product. Furthermore, the effect of a new coating method, VI was compared with conventional coating (dipping) method. For this purpose, melon as a porous food material and sodium alginate as coating solution were selected as model system.

Materials and Methods

Preparation of samples and coating materials

Whole cantaloupe melons *(Cucumis melo* var. *cantaloupensis)* were purchased from a local market in Freising (Germany) and transported directly to the laboratory. Cantaloupes were peeled and cut into 3 × 2 × 2 cm cuboid pieces (at about 8 g). Pieces were transferred into a large food container with lid and assigned to the treatments randomly.

Alginate based coating solution was prepared according to a previous study of Azarakhsh, Osman, Tan, Mohd Ghazali, and Mohd Adzahan (2012). Surface active agents and oil were incorporated into the coating formulation to improve adhesion of the coating on the product. 1.25 g of sodium alginate (Manugel GHB, FMC Biopolymer, Philadelphia, PA, U.S.A.) (viscosity 34.2 mPas at 0.5% and 595.7 mPas at 2% concentrations) was dissolved in distilled water while stirring at 70 °C. As alginate addition has been found to be a critical step to shorten solution preparation time, sodium alginate powder was added slowly to heated and continuously stirred solution. Two grams of glycerol (Sigma-Aldrich, Saint Louis, MS, U.S.A.) as plasticizer, 0.1 g Tween 40 (Sigma-Aldrich) and 0.6 g Span 80 (Sigma-Aldrich) as surfactants and 0.125 g sunflower oil (Rewe Bio, Rewe Markt Gmbh, Köln, Germany) as lipid source were added into the solution and total weight of the solution was increased to 100 g with distilled water. The mixture was homogenized with ultra turrax (Miccra D-8, ART modern Labortechnik GmbH, Müllheim, Germany) at 10500 min^{-1} for 5 min. The solution was put in ultrasonic bath (Transsonic 460/H, Carl Roth Gmbh Co. KG, Karlsruhe, Germany) at a frequency of 35 kHz for 10 min. To induce cross linking reaction, 2 g calcium L-lactate hydrate (Sigma-Aldrich) was dispersed in 100 g distilled water.

Dipping method

Coating of a surface with a hydrocolloid agent, which requires cation crosslinking to form a gel, compose of four steps: immersion of food into the coating solution, draining of the excessive hydrocolloid solution, second immersion of the hydrocolloid coated food product into the crosslinking bath to form a gel, and draining of the excessive gel (Nussinovitch, 2009).

Dipping method involved holding cantaloupe pieces with thin, metal rod with sharp point. It was noted that the metal part above the food was not immersed in the solution. Fruits were dipped into a solution by hand for various time intervals (seven levels between 10 s and 5 min) and then pulled back quickly and allowed to drain over the glass vessel containing coating solution. The glass vessel was on the top of an analytical balance (model MS6002SDR, Mettler Toledo GmbH, Greifensee, Switzerland) with a readability of up to 2 decimal places allowing recording of the coating solution over time. The amount of coating on the fruit at any time was the difference between the initial weight of the coating solution in the glass vessel and the weight recorded after the respective draining time. Samples were left for draining for 1 min.

It is assumed that holding metal rod was not covered with coating solution, damage on the fruit caused by puncture and its effect into solution were negligible. It is also assumed that evaporation of the solvent (water) does not take place during the process which is a very short time.

After the coating and draining processes, samples were directly transferred to APET containers (dimensions 125 × 125 × 77 mm^3) with a button lack closing systems (Vitembal Tarascon, Tarascon, France) at room temperature (20 ± 1 °C). Due to the small volume of the headspace in this closed system, it reached to equilibrium moisture content very quickly. Hence, drying (dehydration) of the coating and food product was prevented. The measurements were performed directly after the coating applications.

Vacuum impregnation method

For VI treatment, fresh cut cantaloupe cubes were immersed into coating solutions in two airtight vacuum chambers (designed by Fraunhofer Inst. for Process Engineering and Packaging IVV, Freising, Germany) connected to a vacuum pump (N740, 40 L/min flow rate and 10 mbar absolute vacuum, KNF Neuberger GmbH, Freiburg, Germany) and digital vacuum/barometer (GDH 200–14, Greisinger Electronic GmbH, Regenstauf, Germany). Samples were subjected to vacuum at 50, 100, and 150 mbar at room temperature (20 ± 1 °C) for 4, 10, and 15 min following atmospheric restoration for 2, 15, and 30 min. Samples

were left for draining for 1 min. And they were transferred to APET containers as described before.

Subsequent to the determination of the most efficient atmospheric restoration time (15 min), the effect of 3 level vacuum amount (50, 100, and 150 mbar) with 5 level of vacuum period (2.5, 5, 10, 15, and 30 min) on weight gain (%) values were evaluated again to verify the results of vacuum impregnation process.

Percentage of weight gain

The formula of the percentage of weight gain calculation was expressed by Eq. (1)

$$weight\ gain\ (\%) = \frac{|initial\ weight - final\ weight|}{initial\ weight} \times 100 \quad (1)$$

Color

CIE L*, a*, b*, C*, and h parameters which describe the intensity of lightness, color opponents red-green and yellow-blue colors, chroma and hue angle respectively were measured with computer controlled digital imaging system (DigiEye 2.8.0.3, VeriVide Ltd., Leicester, U.K.). DigiEye system consisted of illumination cabinet (VeriVide Ltd.) with D65 diffuse illumination, digital camera (Nikon D90 and Nikor AF Nikkor 35 mm 1:2D, Nikon Corporation, Tokyo, Japan), and a desktop computer (HP Inc., CA, U.S.A.). System was standardized and calibrated with the DigiEye Digitizer Chart. ΔE_{2000} values were calculated according to the equation described by Sharma, Wu, and Dalal (2005). The surface color of 10 fruit pieces per treatment was determined before and after each coating process.

Texture

The firmness of coated and uncoated melon samples were determined by using Texture Analyser (TA.XT.plus, Stable Micro Systems Ltd., Godalming, U.K.) with a 50 N load cell. The procedure was set up according to a previous study carried out also with fresh cut melon samples (Raybaudi-Massilia, Mosqueda-Melgar, & Martín-Belloso, 2008). A 5-mm diameter stainless steel cylindrical probe with a flat end was used and resistance strength of cylindrical samples (15 mm diameter and 20 mm height) against 10 mm penetration distance at a rate of 5.0 mm/s was measured as peak force (N). Measurements were carried out on 10 samples of each edible coating condition.

Statistical analysis

Results presented were means of separate replications ($n = 4$ to 10, which were stated for each analysis in results section) conducted at different time length, pressure, and so on. Means, standard deviations, graphics were performed with R 3.3.2 for Windows with packages ggplot2 (Wickham, 2009), plot3D (Soetaert, 2016), grid (R Core Team, 2016), extrafont (Winston, 2014). Data were analyzed using R 3.3.2 for Windows with packages car (Weisberg, 2011) and lsr (Navarro, 2015). ΔE_{2000} calculations were performed with Microsoft Excel 2010 (Microsoft Corp., Redmond, Wash., U.S.A.). Results were subjected to outlier analysis, N-factorial analysis of variance, and post hoc tests (Tukey Honest Significance Test (TukeyHSD) and Least Significant Difference (LSD) tests) were used to determine significant differences ($P \leq 0.05$) between treatments.

Results and Discussion

Percentage of weight gain

Alginate can form strong hydrogel or insoluble polymers through cross-linking with calcium ions. Due to the additional cross-linking step and complexity of evaluating the interaction of all variables, required draining times were determined as a first step of the study. Figure 1 shows the effect of draining time on the percentage of weight gain of the samples after alginate (120 s) and calcium lactate (120 s) dipping processes. To eliminate the difference in the sample sizes and its possible effect on the coated amount, results were expressed as percentage (%) of weight gain.

Response variable residuals of these two groups were not normally distributed, therefore, Kruskal Wallis test was conducted to compare the effect of draining times on percentage of weight change in 10, 30, 60, 120, 180, 240, and 300 s draining. There were significant effects of draining times of both alginate and calcium lactate on percentage of weight change at the $P < 0.000$ for the factor levels. Post hoc comparisons using the pairwise Wilcox test indicated that longer dipping times (≥60 s) in alginate coating solution did not significantly increase the weight gain of the samples. However, weight change results of calcium lactate draining time as short as 30 s were not significantly different than longer draining time results. 60 s was selected both for coating and crosslinking draining time for further experiments.

Studies on coating thickness have shown that the thickness of the deposited liquid film on the surface is increasing proportionally with higher viscosity, and withdrawal speed and decreasing proportionally with higher density, and surface tension of the coating solution (Cisneros-Zevallos & Krochta, 2003; Levich, 1962; Poirier, Fernando Fondeur, & Samuel Fink, 2006). The weight gain of the cantaloupe samples after dipping in alginate based coating solution was much higher than the weight gain after dipping in calcium lactate solution. The reason of higher weight gain was due to higher viscosity and lower surface tension and density characteristics of alginate based solution.

Scatter 3D plot in Figure 2 shows effects of dipping times of alginate solution (30, 60, 120, and 240 s) and calcium lactate solution (30, 60, 120, and 240 s) on weight gain (%) of samples. As stated above, residual solutions were allowed to drip off for 60 s. According to the output of the two-way ANOVA table, there was no evidence of a significant effect of dipping times of coating solution ($P = 0.1480$), cross linking solution ($P = 0.9317$), and interaction between them ($P = 0.7321$). Highest 3 weight gain percentages are 9.34%, 9.28%, and 9.17% for 4 min dipping in coating solution with 1 min crosslinking; 2 min dipping in coating solution with 2 min cross linking processes, and 4 min dipping in coating solution with 4 min crosslinking, respectively. However, Tukey HSD test showed that there was not any significant difference between these three groups.

Taken together, the amount of alginate coating is increased with increasing dipping time; however this increase stops after 2 min dipping. Longer dipping periods do not increase the coating amounts. The results agreed well with literature. Pavlath, Gossett, Camirand, and Robertson (1999) explained that two competitive reactions occurred during the immersion of alginate films in crosslinking solutions: (a) dissolution of alginate by the solution and (b) diffusion of the multivalent ions for the crosslinking and therefore insolubilization of the film. Olivas and Barbosa-Cánovas (2008) stated that insolubilization of the alginate-calcium film increase until 3 min dipping time, after that time solubilization of alginate increased. Rhim (2004) also denoted that thickness of the

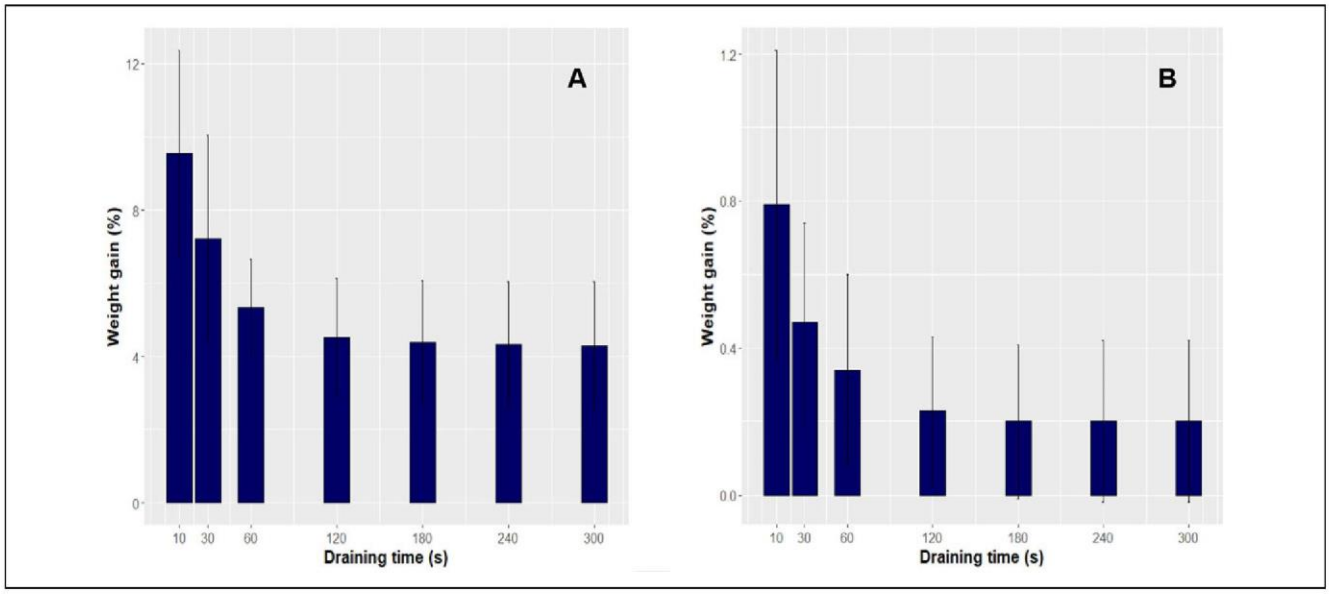

Figure 1–The effect of draining time on weight of coated samples (a) weight change (%) during draining after 2 min sodium alginate dipping (b) weight change (%) during draining after 2 min sodium alginate dipping, 1 min draining and 2 min calcium lactate dipping ($n = 10$). Error bars in the graphs represent standard deviations.

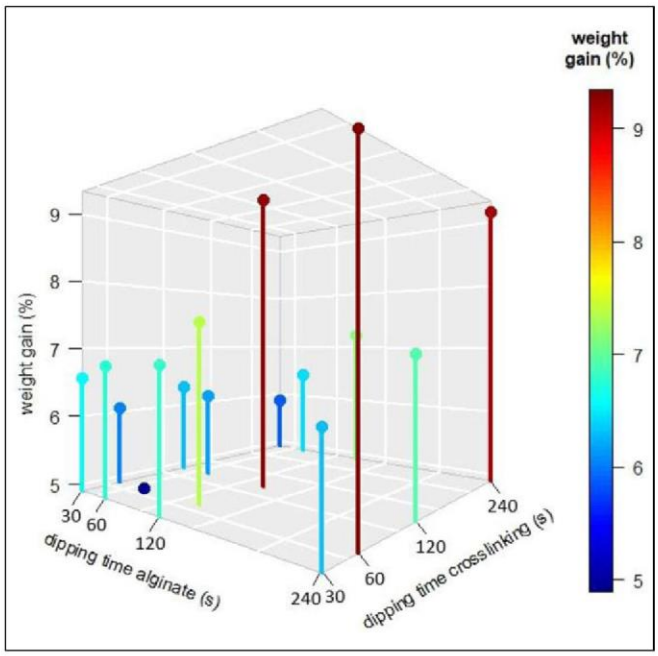

Figure 2–The effect of dipping times on weight gain (%) of coated samples. Dipping times in alginate solution is plotted in *x*-axis and calcium lactate solution in *z*-axis ($n = 4$).

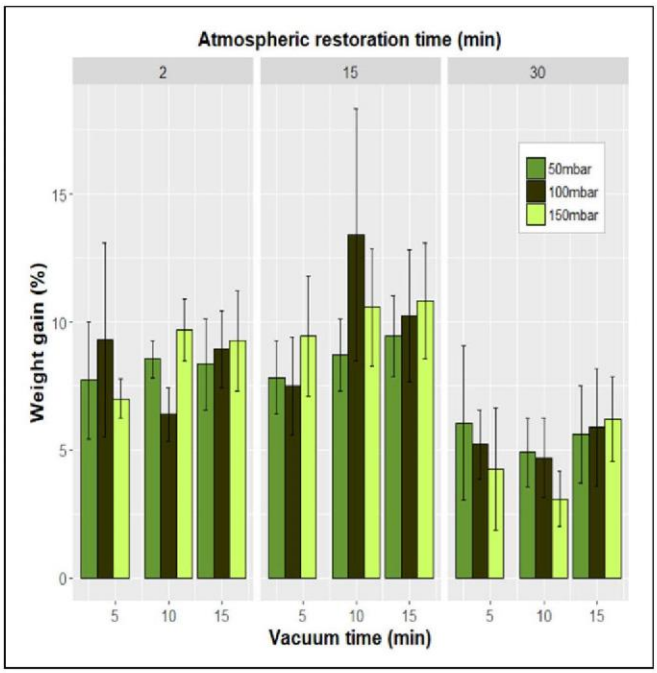

Figure 3–Effect of atmospheric restoration time, vacuum pressure and time length of vacuum period on weight gain (%) of melon ($n = 5$).

immersion films decreased due to the solubilization of alginate during soaking in calcium solutions.

Effect of VI technique to introduce coating material into the porous structure of cantaloupe tissues in a controlled way was examined. For this purpose, the impact of three factors was investigated: atmospheric restoration time (3 levels; 2, 15, 30 min), time length of the vacuum period (3 levels; 4, 10, 15 min) and vacuum pressure (3 levels; 50, 100, 150 mbar absolute pressure). MartÍNez-MonzÓ, MartÍNez-Navarrete, Chiralt, and Fito (1998), and Zhao and Xie (2004) pointed out that longer atmospheric restoration time (t_2) was necessary to have mechanical equilibrium and a remarkable impregnation of the coating solution, in case of usage of viscous impregnation liquids. The coating solution used in this study is a viscous liquid (approximately 200 mPas) therefore; a long atmospheric restoration time (30 min) was used as maximum level to take the effect of viscosity into the account. The results are shown in Figure 3. Outlier analysis was conducted to the multivariate data set. Highest weight gain results were achieved with 15 min atmospheric restoration time. Furthermore, it can be stated that increasing the amount of atmospheric restoration time or vacuum period or vacuum pressure do not increase the yield of coating process.

Table 1–Comparison of weight gain (%) of fresh cut melon samples, coated with vacuum impregnation method. Atmospheric restoration time is 15 min for all samples ($n = 6$).

	Time length of the vacuum period (min)				
Vacuum pressure (mbar)	2.5	5	10	15	30
50	$10.06 \pm 2.19_a$	$9.85 \pm 2.18_a$	$16.69 \pm 2.02_c$	$11.05 \pm 2.72_{ab}$	$12.38 \pm 1.65_b$
100	$13.00 \pm 1.66_a$	$10.55 \pm 1.38_a$	$15.44 \pm 1.33_c$	$11.13 \pm 2.04_{ab}$	$12.13 \pm 2.53_b$
150	$10.17 \pm 0.63_a$	$10.63 \pm 0.72_a$	$14.86 \pm 1.12_c$	$14.05 \pm 2.05_{ab}$	$14.38 \pm 0.95_b$

[1]For each parameter, similar small letters (subscript) in rows are not significantly different at $P \leq 0.05$.

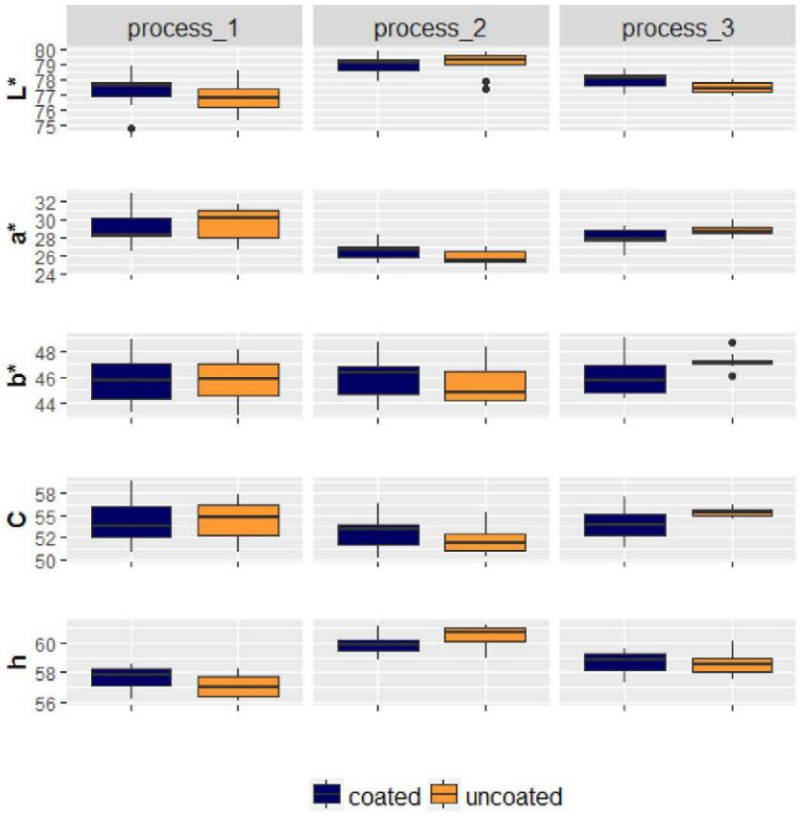

Figure 4–Effect of dipping coating method on color. Uncoated samples: no process application, process 1: sodium alginate: 240 s, calcium lactate: 60 s; process 2: sodium alginate: 120 s, calcium lactate: 120 s; process 3: sodium alginate: 240 s, calcium lactate: 240 s ($n = 10$).

Three-way ANOVA showed a significant effect of both atmospheric restoration time ($P < 0.0000$) and vacuum period ($P = 0.0328$), on the other hand vacuum pressure did not have significant effect ($P = 0.6737$) on weight gain. None of the two-way interactions had significant effect ($P > 0.05$) on weight gain, on the other hand, the three-way interaction effect was found significant ($P = 0.0235$).

To verify the results, the same experiment was conducted with 15 min fixed atmospheric restoration time (Table 1). The results correlated well with previous findings. There was no significant effect of vacuum pressures ($P = 0.2195$) and on the contrary, vacuum period had significant effect ($P < 0.0000$), as well as their interaction (vacuum period × vacuum pressure, $P = 0.0018$).

Chiralt et al. (2001) defined the required length of vacuum period as the necessary time to accomplish equal internal and external pressure, in other words mechanical equilibrium inside the product. Further analyses, which were presented in Table 1, showed that highest weight gain results were achieved once more with 10 min vacuum period. It can be stated that 10 min vacuum was the required period to achieve mechanical equilibrium in the present experimental setup. Longer vacuum periods did not increase the weight gain amounts. Findings were in good agreement with the study of Mújica-Paz, Valdez-Fragoso, López-Malo, Palou, and Welti-Chanes (2003), which stated that VI period had quadratic effect on melon, impregnated solution amount increased between 3 and 25 min period but then decreased for longer vacuum application time.

Color

The comparison of the color results of uncoated fresh cut melon pieces and alginate coated samples were made in terms of lightness (L*), red-green (a*), yellow-blue (b*), chroma or saturation (C*), and hue angle (h*) parameters. Boxplots in Figure 4 and 5 show distributional characteristics and comparison of the color values of uncoated control group and corresponding coated samples with dipping or VI methods, respectively. The mid-points of the data sets (medians) are indicated with lines that divides the box into two parts. Upper and lower whiskers represent the maximum and

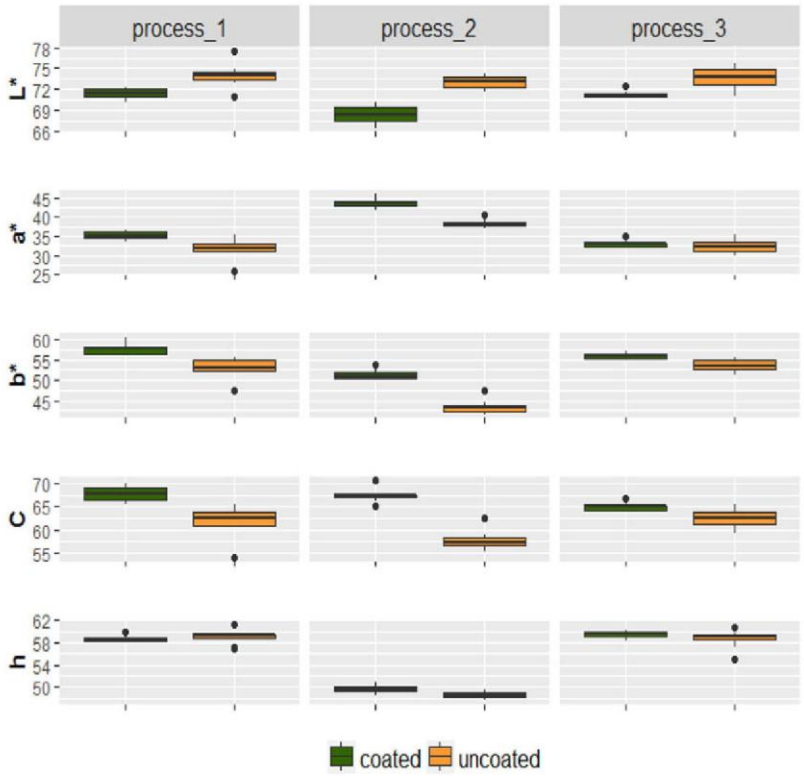

Figure 5–Effect of vacuum impregnation coating method on color. Atmospheric restoration time (t_{atm}) is 15 min for all processes. Uncoated samples: no process application, process 1: 10 min at 100 mbar; process 2: 15 min at 50 mbar; process 3: 10 min at 150 mbar ($n = 10$).

minimum values in the data set. Individual marks outside the whiskers show the outlier values.

In general, dipping application method did not cause any significant change in color parameters ($P > 0.05$). On the other hand, coating method with VI technique induced significant changes in L*, a*, b*, and C* values ($P < 0.05$). Luminosity values decreased significantly, while redness, yellowness and therefore chroma increased for vacuum applied coated products. This effect unlikely originates from oxidative reactions or enzymatic browning due to the low level of polyphenol oxidase enzyme activity and oxidizable phenol compounds of melon (And & Watson, 2001). Additionally, with the application of vacuum pressure; native gases including oxygen entrapped in the capillaries of the fruits, leave and therefore oxidative reaction rate slows down ((Derossi, De Pilli, & Severini, 2012; Xie & Zhao, 2003). Jost, Kobsik, Schmid, and Noller (2014) indicated that alginate films generated a strong impact on yellowness. In addition to that, Martinez-Monzo, Martinez-Navarrete, Chiralt, and Fito (2001, 1998) explained color change phenomenon in VI with the change in optical properties of the food product due to removal of the air from the pores and gas–liquid exchange. Researchers stated that VI treatment caused lower L* and slightly higher a* values but no significant effect on hue attributes. Vargas et al. (2009) observed significant increase in chroma and decrease in luminosity values after VI treatment of carrots.

ΔE is a single value for quantitative representation of perception of the color difference between two different samples by the human eye. Higher ΔE values indicate greater difference between two samples being compared. In our present study, the calculated difference between the color of samples was expressed as ΔE_{2000} (ΔE_{00}, CIE 2000), which is a mathematically expanded version of ΔE_{94} and recommended by ISO and International Commission on Illumination (CIE) due to its accurate formulation (Mokrzycki & Tatol, 2011; Qian and Kyan, 2014). In our study, ΔE_{2000} values were calculated according to the equation described by Sharma et al. (2005) and the results are showed in Figure 6.

The observer does not notice the color difference when $0<\Delta E<1$, only experienced observer can notice the difference when $1<\Delta E<2$, but even an unexperienced observer notices the difference when $2<\Delta E<3.5$, clear color difference is noticed when $3.5<\Delta E<5$, and $5<\Delta E$ shows two different colors (Mokrzycki & Tatol, 2011). According to this, dipping application caused a color change which cannot be noticed by consumers. On the contrary, vacuum application leads to greater color changes on coated products; the higher the vacuum pressure and vacuum period, the greater the difference between treated and untreated cantaloupes. Similarly, Martinez-Monzo et al. (2001) presented high ΔE values after VI treatment of fruits. Xie and Zhao (2004) stated that VI application of strawberries induced large color differences (ΔE^*), compared to fresh strawberries.

Texture

Firmness (hardness) of uncoated and coated cantaloupe pieces was determined by texture analysis and the results were expressed in Figure 7.

The results show that firmness of the melon samples increased significantly with both coating applications ($P < 0.05$). Moreover, VI coating application caused an increase in sample firmness due to the removal of oxygen through the pores of the melon and refilling these volume with coating solution (Park, Kodihalli, & Zhao, 2005). The highest firmness values were achieved with 10 min 100 mbar vacuum application process. These results were consistent with weight gain (%) experiment results, while the same process had the highest amount of coating on/in the products.

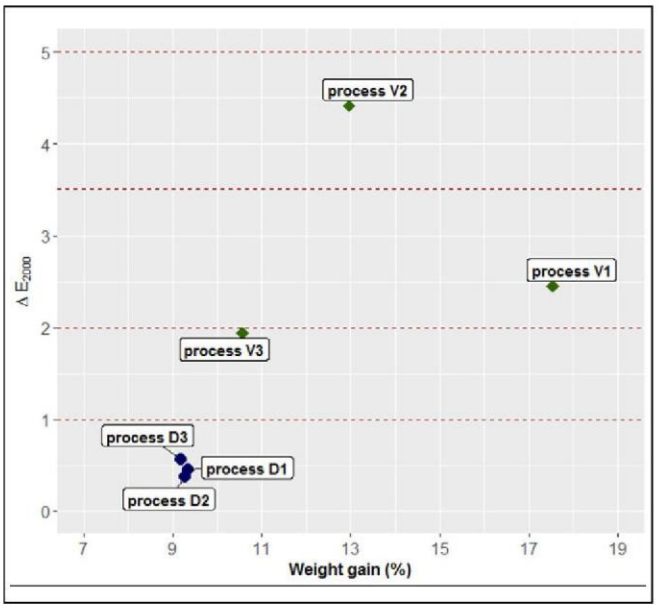

Figure 6–ΔE2000 color difference results of alginate coated samples compared to uncoated samples. process D1: coated with dipping method in sodium alginate: 240 s, calcium lactate: 60 s; process D2: coated with dipping method in sodium alginate: 120 s, calcium lactate: 120 s; process D3: coated with dipping method in sodium alginate: 240 s, calcium lactate: 240 s; process V1: coated with vacuum impregnation 10 min at 100 mbar; process V2: coated with vacuum impregnation 15 min at 50 mbar; process V3: coated with vacuum impregnation 10 min at 150 mbar. Atmospheric restoration time (t_{atm}) is 15 min for all vacuum impregnation processes ($n = 10$).

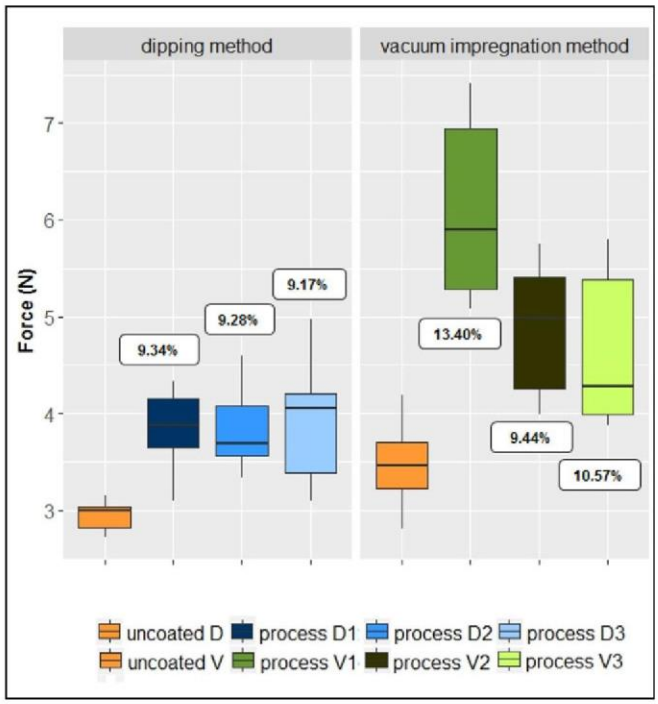

Figure 7–Firmness results of fresh cut melon pieces with/without edible alginate coating uncoated D: uncoated control sample; process D1: coated with dipping method in alginate: 240 s, calcium lactate: 60 s; process D2: coated with dipping method in alginate: 120 s, calcium lactate: 120 s; process D3: coated with dipping method in alginate: 240 s, calcium lactate: 240 s; uncoated V: uncoated control sample; process V1: coated with vacuum impregnation 10 min at 100 mbar; process V2: coated with vacuum impregnation 15 min at 50 mbar; process V3: coated with vacuum impregnation 10 min at 150 mbar. Atmospheric restoration time (t_{atm}) is 15 min for all vacuum impregnation processes ($n = 10$). The values inside the labels show weight gain (%) results of the groups.

The results are consistent with previous studies in the literature. Vargas et al. (2009) concluded that with the application of vacuum pulse fresh cut carrot samples maintained their mechanical stability and initial water content during storage compared to uncoated samples. Torreggiani and Bertolo (2001) presented arguments to emphasize that vacuum applied tissues had higher cellular integrity. Xie and Zhao (2004) observed also the increase in compression forces after vacuum treatment of strawberries.

Conclusion

This paper has described the selection of adequate immersion, draining times (for dipping method) and vacuum amount, vacuum time, atmospheric restoration time (for VI method), which are the critical steps in producing alginate-calcium coatings with different weight gains. Furthermore, with the comparison of two coating method for the same edible coating and for the same food product, this study investigated the usability of VI method as an alternative to conventional immersion method.

Our research suggests that longer immersion into the coating solution does not necessarily increase the coating amount; 4 and 2 min dipping times were not significantly different in terms of weight gain, color, and texture results. In fact, alginate is solubilized during longer immersion times in calcium lactate solution. Dipping method did not alter the optical characteristics and slightly increased the firmness of the cantaloupe pieces. On the other hand, the color change after the VI treatment was recognizable and the mechanical resistance (firmness) was promoted more than dipping treatment. The results of the vacuum impregnation experiments showed that the effect of vacuum application period and atmospheric restoration time are more effective then vacuum amount for increasing the amount of coating on the food product. This study had led us to conclude that VI method has higher impact on quality characteristics (color and texture) and may be an effective method for coating applications; however the consumer responses to the alterations in quality parameters should be evaluated carefully with sensory evaluations for each product.

Acknowledgments

The research was conducted as part of the IGF-project 95EN/1 under the CORNET initiative and was carried out under the auspices of the German Federation of Industrial Research Associations within the framework of the program to promote collaborative industrial re-search (IGF). It was financed by the German Federal Ministry of Economics and Technology (BMWi).

The authors gratefully acknowledge Dr. Carolin Hauser for her constructive comments.

Author Contributions

T. Senturk Parreidt conceived, designed and performed the experiments and analyzed the data; M. Schmid and T. Senturk Parreidt interpreted the results. T. Senturk Parreidt wrote the manuscript; and M. Schmid and K. Müller proofread the text.

Conflict of Interest

The authors have no conflict of interest to declare.

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Chapter V.

Surface Free Energy of Fresh Produce

This chapter contains a peer-reviewed article "Validation of a novel technique and evaluation of surface free energy of the food". It is published in the Open Access Journal "Foods" (Publication III). The author of this thesis is also the first author of the article. Authors' contributions were specified in the article under the names "Tugce Senturk Parreidt, Carolin Hauser, and Markus Schmid conceived and designed the experiments; Tugce Senturk Parreidt performed the experiments and analyzed the data; Carolin Hauser and Markus Schmid contributed reagents/materials/analysis tools; Tugce Senturk Parreidt wrote the paper; and Markus Schmid and Carolin Hauser proofread the text".

Summary of the Publication-III

The surface free energy (SFE) of a solid surface is an indicator of its adhesive properties. For any type of solid-liquid contact, a good knowledge of the SFE of solid and surface tension of the liquid allows us to determine the tendency for a coating formulation to spread on the solid surface (wetting). Better wettability leads to uniform physical protective barrier formation to retard the mass transport. Therefore, it is notably crucial for the optimization of the coating process. The key impediments for accurate determination of surface free energies and wettabilities of rough and irregular surfaces arise from the difficulty of measuring contact angles of probe liquids or coating solutions from unclear images taken by the conventional contact anglemeter (goniometer,i.e., drop shape analyzer (DSA)). Increasing the accuracy of contact angle determination would improve the accuracy of the calculations and consequently, the accuracy of the surface characteristics. Therefore, the main objective of the present paper is the evaluation of the usability of a novel contact angle measurement method on rough food surfaces. As case studies, the superficial characteristics of strawberry and endive salad were determined.

An extremely close-up photography stage was designed and used for taking macrophotographs of 3 µl droplets of test liquids (i.e. water, ethylene glycol, diiodomethane, glycerol) on plastics (i.e. polytetrafluoroethylene, biaxially-oriented polypropylene, polyethylene terephthalate-160 µm, and polyethylene terephthalate-12 µm) that had perfectly smooth, ideal surfaces. Contact angles and surface free energy results were determined both with a conventional goniometer and ImageJ software with DropSnake plugin. SFE components were calculated using the Owen/Wendt method to

achieve compatibility between the two measuring methods (i.e. DSA and ImageJ software with DropSnake plugin). Comparison of SFEs and polar-dispersive components of the plastic films enabled the validation of the system with the help of simple linear regression analysis.

As case studies, superficial characteristics of strawberry and endive salad were determined. The principal reason for the selection of these foods was their irregular, rough shapes (i.e., pitted structure with achenes for strawberry and wavy, curly shape of salad) and their hydrophobic surface characteristics. Even though the endive salad was not determined as a model food for this thesis, it was used as a supplementary substrate only for SFE studies. On the other hand, fresh-cut cantaloupe could not be used for SFE studies due to its wet surface; probe liquids could not form droplets/contact angles on the wet cantaloupe surface.

Determination of the superficial characteristics of the surfaces provides critical information in coating design studies. Strawberries have low energy surfaces (21 mN/m) with strong hydrophobicity (high dispersive forces (20 mN/m) and very low polar forces (1 mN/m)). Effective surface-active agents should be added to coating formulations to achieve higher wettability. In contrast, the effective spreading of coating solutions on the salad surface is relatively easy due to the higher polar (23 mN/m) and dispersive (20 mN/m) components.

This paper shows that the ImageJ program with the snake-based approach (in other words, spline curve, splinesnake or active contours) is an important tool for contact angle measurement of irregular and rough food surfaces.

foods

MDPI

Article

Validation of a Novel Technique and Evaluation of the Surface Free Energy of Food

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Academic Editor: Danyang Ying
Received: 6 March 2017; Accepted: 17 April 2017; Published: 20 April 2017

Abstract: Characterizing the physical properties of a surface is largely dependent on determining the contact angle exhibited by a liquid. Contact angles on the surfaces of rough and irregularly-shaped food samples are difficult to measure using a contact angle meter (goniometer). As a consequence, values for the surface energy and its components can be mismeasured. The aim of this work was to use a novel contact angle measurement method, namely the snake-based ImageJ program, to accurately measure the contact angles of rough and irregular shapes, such as food samples, and so enable more accurate calculation of the surface energy of food materials. In order to validate the novel technique, the contact angles of three different test liquids on four different smooth polymer films were measured using both the ImageJ software with the DropSnake plugin and the widely used contact angle meter. The distributions of the values obtained by the two methods were different. Therefore, the contact angles, surface energies, and polar and dispersive components of plastic films obtained using the ImageJ program and the Drop Shape Analyzer (DSA) were interpreted with the help of simple linear regression analysis. As case studies, the superficial characteristics of strawberry and endive salad epicarp were measured with the ImageJ program and the results were interpreted with the Drop Shape Analyzer equivalent according to our regression models. The data indicated that the ImageJ program can be successfully used for contact angle determination of rough and strongly hydrophobic surfaces, such as strawberry epicarp. However, for the special geometry of droplets on slightly hydrophobic surfaces, such as salad leaves, the program code interpolation part can be altered.

Keywords: contact angle; surface energy; edible coating; image processing; drop shape analysis; food

1. Introduction

The surface free energy (SFE) is one of the important thermodynamic quantities describing the state of equilibrium of atoms at the surface layer of materials [1]. The term is often used as a measure of the adhesive properties and is a characteristic quantity for each substance. In another definition, the surface free energy is the work necessary for creating a new surface unit, while separating two phases in equilibrium, in a reversible isothermal process [1].

The accurate determination of the SFE is one of the key parameters in controlling a wide range of phenomena, such as the precise characterization of a solid material surface (e.g., hydrophobicity), wettability, and effective spreading of a coating material on a solid surface. These aspects influence many industrial applications in which adhesive properties play an important role, such as adhesion, coating, printing, and lubrication [2–6].

Strategies to prevent microbial spoilage and quality loss in fresh foods for a longer period are important for the food industry [7–9]. Research on edible films and coatings has been intense in recent years due to these being environmentally friendly and an effective alternative to non-biodegradable plastic packaging [10,11]. Edible films and coatings are any type of material used for enrobing food and produce an extra physical barrier to extend shelf life, improve appearance and maintain the quality of the product [11–13]. The films and coatings can be eaten together with food with or without further removal [12]. Edible coatings and films must be designed taking into account the surface properties and wettability of coating emulsions in order to realize effective spreading of a coating solution on a food surface [14–17]. Studying the surface properties of products is one of the most important steps for effective formulation of edible coatings [17,18].

Contact angle measurements can be performed easily on a smooth and flat surface. In contrast, the surface energies of food products are very difficult to measure owing to the surface topography. Due to not having flat and reflective surfaces, differentiating the contact surface of the test liquid on food and determining the contact points of the droplet using a contact angle meter (contact angle goniometer) is usually not possible. The objective of the present study was to use a novel method, namely a snake-based ImageJ program, while presenting an experimental design described in detail to accurately measure the contact angles of rough and irregular shapes, such as food samples and, thus, accurately determine the surface energy of food materials. In order to achieve this goal, the contact angle data using the novel technique were first compared to the contact angle data using a conventional technique, namely using a drop shape analyzer device. Mathematical relationships between the two measurement methods were established.

Determination of the SFE: Theoretical Information

The surface energy and surface tension of a liquid are identical. Many techniques are available for measuring the surface tension of liquids [19]. However, measuring the surface energy of a solid is not straightforward. Surface energy values can be determined indirectly using various liquids of known surface energy and their components [6]. Drops of a series of liquids are placed on a solid surface and the contact angles are measured. For choosing the set of liquids, specific surface interactions, surface reactivities, and surface solubilities should be taken into consideration [20]. In addition to the lack of universally defined probe liquids, choosing a theory for converting contact angle data into surface energy data is the other critical step. Calculation methods for the surface free energy of solids have been reviewed by Zenkiewicz [5]. Based on the number of components, the most common surface energy theories are the one-component model—Zisman theory; two-component model—Owens/Wendt theory and Fowkes theory; and, lastly, the three-component model—Van Oss theory.

The contact angle meter used in this study converted the contact angle data into surface energy with the help of one of the most common methods for SFE calculation, the Owens/Wendt theory. Therefore, the same theory was used for the data acquired using contact angle evaluation software to ensure the compatibility of the results.

The Young equation (Equation (1)), which describes the phenomena of thermodynamic wetting (small or zero contact angle, θ, between the liquid and solid), is the basis of the method for calculating the SFE from contact angle data:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \quad (1)$$

Here, γ_{SV} is the surface tension on the solid-gas interphase, γ_{SL} is the surface tension on the solid-liquid interphase, γ_{LV} is the surface tension on the liquid-gas interphase, and θ is the equilibrium contact angle [21].

Owens and Wendt developed a two-parameter model—with a dispersive component (D) and a polar component (P)—for determining the surface energy of a solid, expressed by Equation (2a) and Equation (2b):

$$\gamma_L = \gamma_L^P + \gamma_L^D \quad (2a)$$

$$\gamma_S = \gamma_S^P + \gamma_S^D \tag{2b}$$

where γ_S is the SFE, $\gamma_S{}^P$ is the polar component of the SFE, and $\gamma_S{}^D$ is the dispersive component of the SFE. The polar component is the sum of polar, hydrogen, inductive, and acid-base interactions, while the dispersive component accounts for van der Waals and other non-site specific interactions [1,20–22].

In their study, Owens and Wendt [21] used Equation (3):

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_{SV}^D \gamma_{LV}^D} - 2\sqrt{\gamma_{SV}^P \gamma_{LV}^P} \tag{3}$$

Mathematically, the Owens/Wendt theory is based on two fundamental equations (Equation (1) and Equation (3)) In order to derive the solution, converting the equation into a linear fit to incorporate data for more than two liquids is the key [23]. After the necessary rearrangement to get the linear equation ($y = mx + n$), the following equation was obtained:

$$\frac{(1 + cos\,\theta)\,\gamma_L}{2\sqrt{\gamma_L^D}} = \sqrt{\gamma_S^P}\sqrt{\frac{\gamma_L^P}{\gamma_L^D}} + \sqrt{\gamma_S^D} \tag{4}$$

As is clear from Equation (4), the contact angle values of test liquids on the solid surface and the surface tension components of the liquids must be determined accurately in order to define the polar and dispersive components and, therefore, the surface free energy of a solid material. In other words, being able to determine the contact points of the test liquids on the solid and, hence, accurately measure the angles is the crucial step for determining the surface hydrophobicity. Determination of the contact points of test liquids on food samples using a conventional contact angle meter/goniometer is, however, not possible. The main aim of the present study was, therefore, to present an experimental procedure using a novel method for measuring the contact angles and surface free energies of rough and irregular-shaped food samples.

2. Materials and Methods

2.1. Materials

Validation of the contact angle measurement process was carried out on four different plastic films: polytetrafluoroethylene (PTFE) (thickness: 500 µm, SAHLBERG GmbH and Co. KG, Feldkirchen, Germany), biaxially-oriented polypropylene (BOPP) (thickness: 20 µm, Taghleef Industries GmbH, Holzhausen an der Heide, Germany), polyethylene terephthalate (PET-160 µm) (thickness: 160 µm, GEBA GmbH, Seewald, Germany), and polyethylene terephthalate (PET-12µm) (thickness: 12 µm, Mitsubishi Polyester Film GmbH, Wiesbaden, Germany). These plastic films were carefully selected to ensure a wide range of surface tension values.

Various test liquids, namely water for chromatography (Merck KGaA, Darmstadt, Germany), diiodomethane (Sigma-Aldrich, St. Louis, MO, USA), ethylene glycol (Sigma-Aldrich, St. Louis, MO, USA), and glycerol (Sigma-Aldrich, St. Louis, MO, USA), were used for the surface energy measurements.

Fresh endive salad *(Cichorium endivia)* and strawberries (*Fragaria ananassa*) were purchased from a local market (Freising, Germany). Samples were carefully selected to ensure uniformity of color, ripeness, and physical appearance based on visual analysis. Only the green parts of the endive salad leaves were used for the contact angle measurements. Before the measurements, the samples were left at ambient temperature (20 ± 1 °C). The samples (~3 cm × 2 cm) were cut into rectangular shapes.

2.2. Methods

2.2.1. Surface Tension of the Test Liquids

The surface tension of the test liquids (water, diiodomethane, ethylene glycol, and glycerol) and its polar and dispersive components were determined using the pendant drop method with a drop shape analyzer (DSA1 v1.90, Kruss GmBH, Hamburg, Germany) [24].

2.2.2. Validation of the Novel Method

The surface energy measurement of the four different plastic films was carried out by the contact angle (CA) technique with two different methods: The drop shape analyzer (DSA) (DSA1 v1.90, Kruss GmbH, Hamburg, Germany) and the ImageJ program with the DropSnake plugin [25].

In the first part of the analysis, both the CA (θ) and surface energy (γ_S) of the plastic films were determined with the DSA. Droplets of the test liquids (water, diiodomethane, ethylene glycol) were automatically placed with a 500 µL syringe (Hamilton, Switzerland) and 1.991 mm needle (Kruss GmbH, Hamburg, Germany). The device performed the CA measurement by the sessile drop technique and γ_S calculation using the Owens and Wendt (1969), Rabel (1971), and Kaelble (1970) theory [20].

In the second part of the study, photographs of droplets on the surfaces were taken with a Canon EOS 600D digital camera (Canon, Japan) fitted with auto extension tube set (Kenko, Japan). The photographs were taken in a dark room. Two yellow-colored light sources (35 W, 50/60 Hz, 220–240 V, 5400 K) were placed on two sides of the sample. The distances between the light sources and the samples and between the camera and the samples were fixed for all measurements and were 17 cm and 7 cm, respectively. At ambient temperature (20 ± 1 °C), small droplets (3 µL) of the test liquids (water, diiodomethane, ethylene glycol) were manually placed using a micropipette on the surface of the plastic films, which were fixed with adhesive tape so that horizontal, flat surfaces were obtained. As drop deposition has been found to be a critical step in previous work [8], the droplets were dispersed gently keeping the micropipette perpendicular to the surface. To avoid changes in the shape of the droplets due to gravitational force, the time between surface-liquid contact and photographic exposure was never longer than 7 s.

The contact angles at the left and the right margins of the droplet were determined using ImageJ software [25] with the DropSnake plugin [26]. This plugin was ideal for measuring asymmetric drops because no shape assumptions were used. Seven knots were manually placed along the contour of the drop and the contact angle was obtained by a polynomial fit [27]. The CA values of the drop were automatically calculated based on this fit. The surface energies of the plastic films were calculated by the theory of Owen/Wendt in Microsoft Excel 2010 (Microsoft Corp., Redmond, WA, USA) in order to achieve the compatibility of the two measuring methods.

2.2.3. Case Studies

The experimental design described in Section 2.2.2, was also used for determination of the surface free energy and its polar and dispersive components. Three microliter droplets of water, diiodomethane, and ethylene glycol were carefully placed on strawberries. However, glycerol was used instead of ethylene glycol for the endive salad experiments in order to have more apparent contact angles. The contact angle values of the droplets were determined using the ImageJ program with the DropSnake plugin with the help of high-resolution photos.

2.2.4. Statistical Evaluation

Fifteen measurements were performed for each condition (n = 15). The mean, standard deviation, regression analysis, fitting performance, and graphics were performed using R 3.3.2 for Windows with the packages ggplot2 [28], gridExtra [29], ggrepel [30], car [31], and lsr [32]. The R^2 statistic (coefficient of determination) and graphical residual analysis were used to evaluate the model fit.

3. Results

3.1. Surface Tension of the Test Liquids

The surface tension and the polar and dispersive forces of the test liquids are given in Table 1. The test liquids were measured periodically in order to track changes in their values. Throughout the experiments, no significant changes (>0.1 mN/m) were observed in the values indicated in Table 1. Therefore, the surface tension and component values are not specified with standard deviations. Water for chromatography, diiodomethane, ethylene glycol, and glycerol were chosen as the test liquids in order to span the whole range of fluids from dispersive to polar.

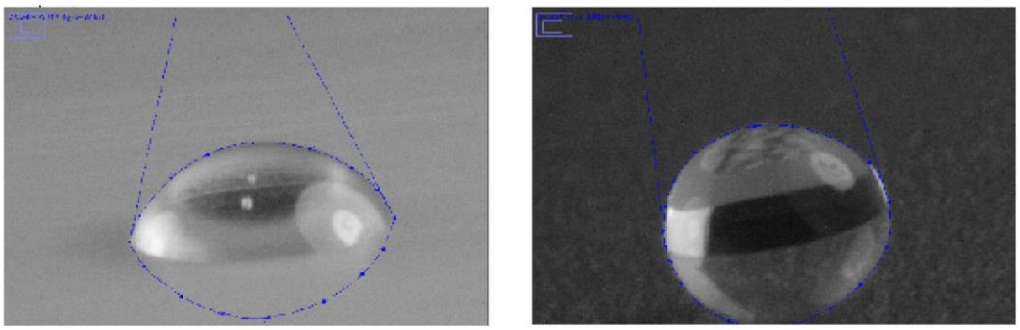
Table 1. Surface tension values of the test liquids used in this study in mN/m (T = 20 °C).

Liquids	Surface Tension (γ_L)	Polar Forces (γ_{LV}^{P})	Dispersive Forces (γ_{LV}^{D})
water	72.8	51.0	21.8
ethylene glycol	47.7	16.8	30.9
diiodomethane	50.8	0.7	50.1
glycerol	63.4	26.4	37.0

3.2. Validation of the Snake-Based Method

3.2.1. Contact Angle Measurement

The hydrophobicity and/or hydrophilicity of a surface can be specified by contact angle measurement. As recommended by Nguyen and Johns [33], pure liquids were selected according to two characteristics: their ability to form droplets on the surface ($\gamma_L > \gamma_C$, critical surface tension of the plastic films) and known dispersive and polar components. One non-polar liquid (diiodomethane) and two polar liquids (water and ethylene glycol) constitute a good set for CA and SFE measurements. Figure 1 shows screenshots of contact angle measurement of plastic films using the computer-based ImageJ program.



(**a**) (**b**)

Figure 1. ImageJ program screenshots of: (**a**) contact angle measurement of diiodomethane on PTFE; and (**b**) contact angle measurement of water on PET-160 μm.

The contact angle results and distribution characteristics of three test liquids (water, diiodomethane, and ethylene glycol) on PTFE, BOPP, PET-160 μm, and PET-12 μm surfaces are presented in a box plot diagram (Figure 2). Lines across the boxes indicate the medians and each outlier outside the whiskers is represented by an individual mark. The minimum and maximum values in the dataset are used as end points for the whiskers. The contact angle results of the two methods show the same increasing-decreasing pattern ($\theta_{water} > \theta_{e.glycol} \geq \theta_{d.methane}$). However, the differences in the medians and distributions of the two methods are worthy of further investigation. These

results demonstrate that the ImageJ program can be used as an alternative to DSA systems. However, the correlation between the results of the DSA system and ImageJ software should be expressed mathematically in terms of compatibility and reliability.

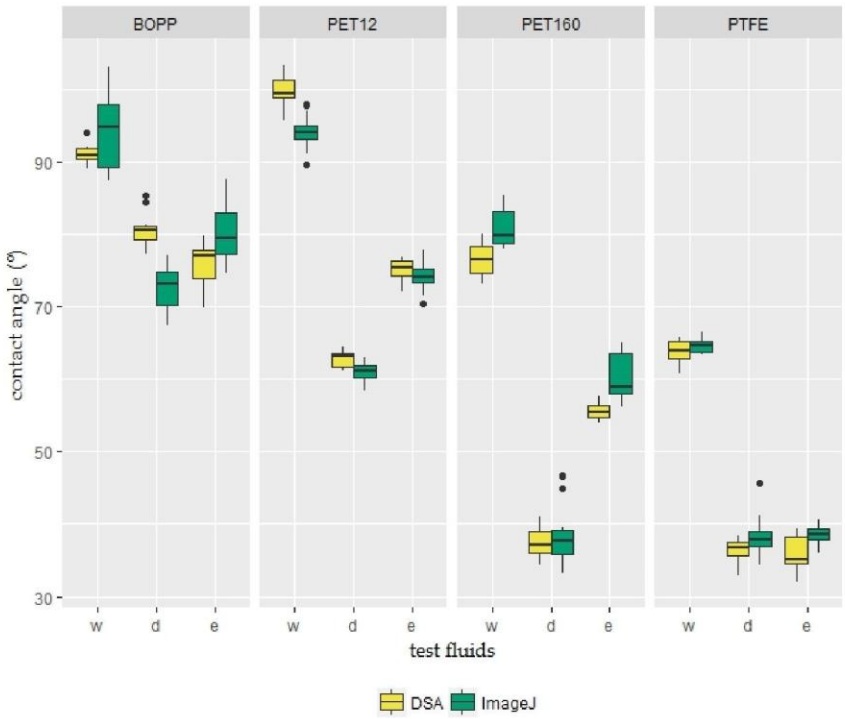


Figure 2. Box plot showing the variation of the contact angle of the test liquids (**w**: water; **d**: diiodomethane; **e**: ethylene glycol) using two different measurement methods (DSA and ImageJ) on plastic films (n = 15).

3.2.2. Surface Free Energy Measurement by the Polar—Dispersive Approach

The surface energy of a solid cannot be directly measured; values must be calculated from various liquid-solid contact angles using well-known theories. In the present study, the Owen/Wendt method was used in order to achieve compatibility between the two measuring methods. The relationships between the polar components (Figure 3a), dispersive components (Figure 3b), and surface energies (Figure 4) are illustrated in the graphs. Error bars, showing standard deviations, were only generated for the DSA results. The reason for this is that only one result for each surface energy component can be obtained from the linear regression plot of the Owens/Wendt theory with the aid of Equation (4). The total surface energy is the sum of the polar and dispersive components [19].

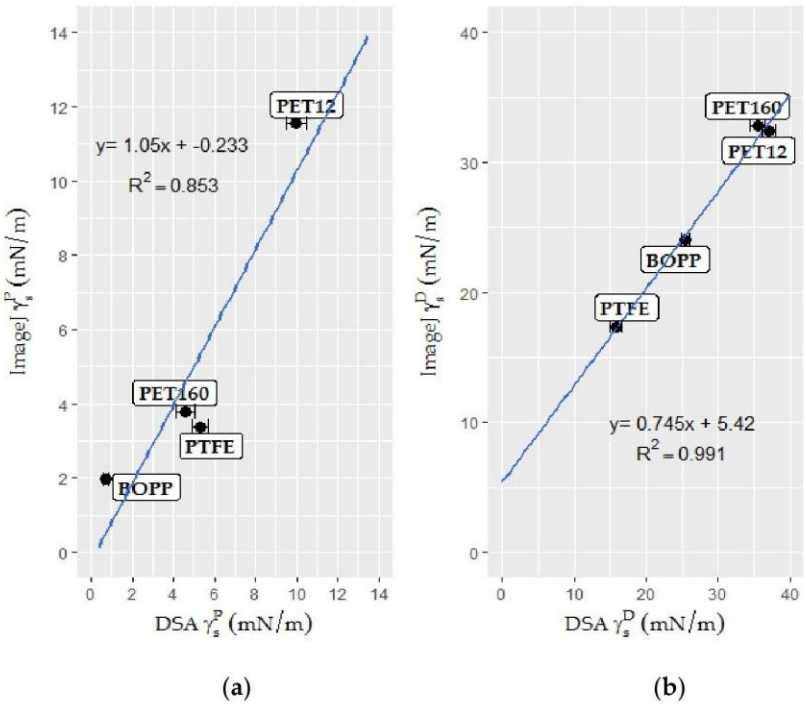


Figure 3. Scatterplots: (**a**) polar (γ_S^P) surface energy component of the novel method plotted as a function of the DSA results in mN/m for plastic films (n = 15); and (**b**) dispersive (γ_S^D) surface energy component of the ImageJ results plotted as a function of the DSA results in mN/m for plastic films (n = 15).

The graphs suggest that the results obtained using the novel method change linearly with the results of the conventional DSA. Therefore, simple linear regression models allowed us to study the relationship between these two measurement methods.

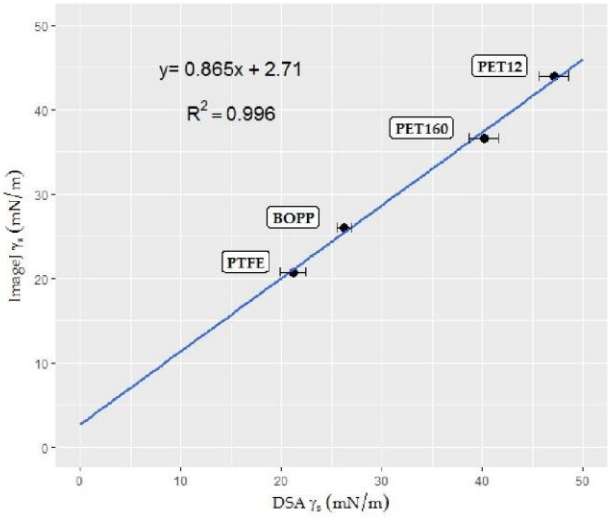


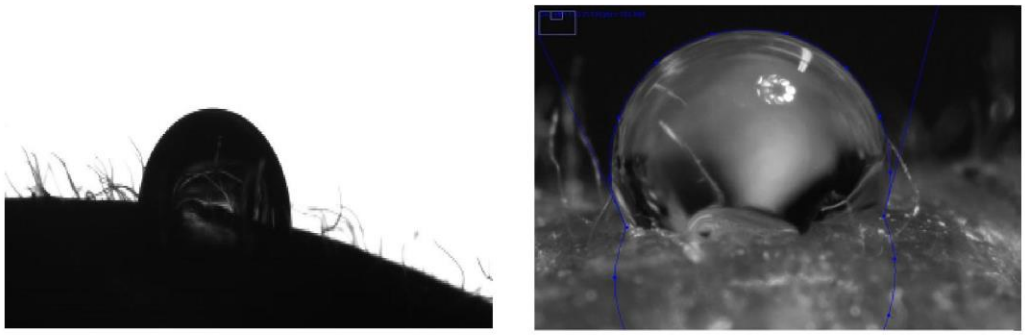
Figure 4. Scatterplot of the surface free energy (σ_S) results of the ImageJ program plotted as a function of the DSA results in mN/m for plastic films (n = 15).

The scatterplots show a fairly strong and reasonably linear relationship between the two variables. All of the models, visually, gave a good fit of the data. The validity of the models was checked with both graphical residual analysis and numerical R^2 statistics (coefficient of determination). The R^2 values were found to be high ($R^2 > 0.85$) for all datasets. Moreover, residuals appeared to behave randomly in generated residual graphs, suggesting that linear regression models fit the data well. The method validation confirms that with the aid of a defined mathematical relationship the novel contact angle measurement tool is suitable for determining the SFE of rough and irregular surfaces, such as the surfaces of fruit and vegetables. The models were, therefore, used for determining the SFE of food products.

3.3. Case Studies

3.3.1. Strawberry

The surface energy of the strawberry epicarp has been described in the literature before [7]. However, CA measurements were performed using a face contact angle meter. Due to the insufficient light source for the angle meters and rough, pitted, and round food samples, defining the contact points of the liquids on the strawberry surfaces was not easy. Figure 5 shows screenshot photos taken with the DSA system and a digital camera as part of the drop shape evaluation process. Accurately estimation of the angles of the contact points of the test liquids is extremely difficult using the widely-used contact angle meter. However, with the help of more powerful and portable light sources, angles could be determined in the photos taken with a high-zoom camera.



(**a**) (**b**)

Figure 5. Screenshot photos of 3 μL water droplets on strawberry epicarp: (**a**) taken with DSA system; and (**b**) taken with a digital camera in the drop shape evaluation process.

The special geometry of strawberry reveals the necessity of paying particular attention to some critical details when taking the photos and the calculation processes. The camera was aligned perpendicular to have a horizontal surface of the substrate. The droplets were placed carefully away from seed (achene) holes. However, due to the irregular, convex shape of the strawberry, the surface had small angle slopes (maximum of 10°) in some cases. However the effect which caused by gravitational force was calculated and found to be very small and negligible. Furthermore, the photographs were carefully selected and both left and right contact points of the droplets on the surface were clearly visible.

When considering the attractive forces on a strawberry surface, the contact angle data of test liquids on the surface and the surface tension values (overall, polar, dispersive) of the liquids have to be known and plotted in an Owens-Wendt graph (linear Equation (4)). The CA of water, diiodomethane, and ethylene glycol on strawberry skin was found to be 103.7 ± 2.8, 71.8 ± 3.6, and 80.5 ± 5.7, respectively. No mild or extreme outliers were found in the datasets. The resultant Owens-Wendt plot is shown in Figure 6.

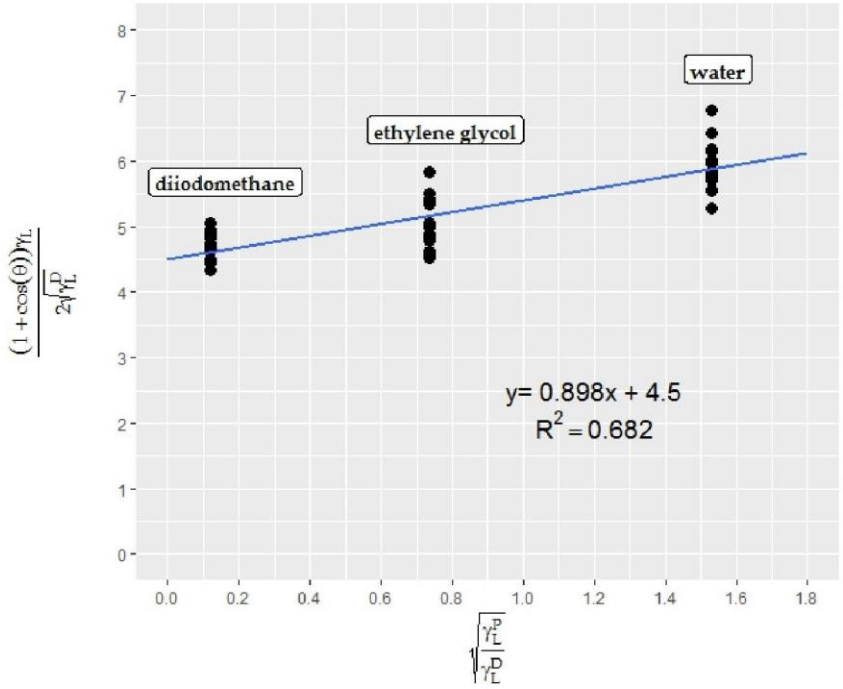


Figure 6. Owens-Wendt plot for strawberry epicarp (n = 15).

The superficial characteristics of strawberries are not uniform through the surface. Different parts of the fruit exhibit different surface free energy. Therefore, droplets of the same liquid have different contact angles on different parts of the fruit. In the present study, the contact angles from different parts of different strawberries were plotted in order to denote the entire surface. Nevertheless, using the whole surface led to lower R^2 results.

The superficial properties of strawberry epicarp were calculated with the help of the equation ($y = 0.8978x + 4.5041$) obtained from the Owens-Wendt plot for strawberry epicarp (Figure 6). According to the calculations, the strawberry surface is a low energy surface with a surface free energy of 21.10 mN/m, and polar and dispersive components of 0.81 and 20.29 mN/m, respectively. The program results were also converted into widely-used contact angle meter (DSA) results with the help of linear regression models obtained from Figure 3a,b, and Figure 4 and are presented in Table 2.

Table 2. Superficial properties of strawberry epicarp. y: results obtained with the novel method, linear regression models obtained from Figure 3a,b and Figure 4, and x: results calculated using the drop shape analyzer.

Superficial Properties	Novel Method (mN/m)	Linear Regression Models	DSA (mN/m)
Surface free energy	21.10	$y = 0.865x + 2.71$	21.26
Polar component	0.81	$y = 1.05x - 0.233$	0.99
Dispersive component	20.29	$y = 0.745x + 5.42$	19.96

3.3.2. Endive Salad

The CA of water, diiodomethane, and glycerol on endive salad was found to be 55.65 ± 9.61, 61.40 ± 5.87, and 58.34 ± 5.14, respectively (for a screenshot see Figure 7). Glycerol was used instead of ethylene glycol in order to have higher and, therefore, more apparent contact angles on endive leaves.

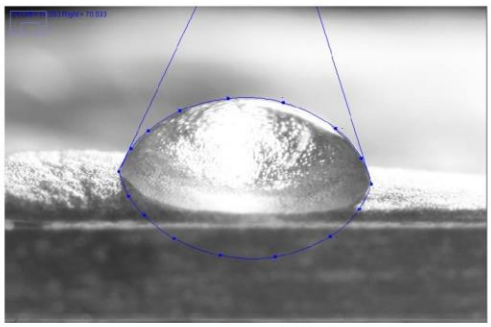


Figure 7. Screenshot photo of a 3 µL diiodomethane droplet on the endive salad surface taken with a digital camera as part of the drop shape evaluation process.

No mild or extreme outliers were found in the datasets. The resultant Owens-Wendt plot is shown in Figure 8.

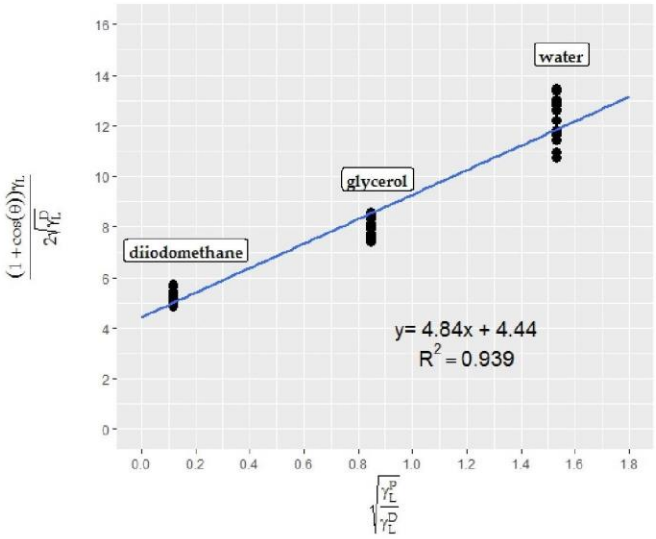


Figure 8. Owens/Wendt plot for endive salad epicarp (n = 15).

The superficial properties of endive leaves were calculated with the help of the equation ($y = 4.8358x + 4.4407$) obtained from the Owens-Wendt plot for endive salad. According to the calculations, endive salad has a relatively high energy surface (43.11 mN/m) with polar and dispersive components of 23.39 and 19.72 mN/m, respectively. The results of the program were also converted into widely-used contact angle meter (DSA) results with the help of linear regression models obtained from Figures 3a, b and 4 and are presented in Table 3.

Table 3. Superficial properties of endive salad epicarp. y: results obtained with the novel method, linear regression models obtained from Figures 3a, b and 4, and x: results calculated using the drop shape analyzer.

Superficial Properties	Novel Method (mN/m)	Linear Regression Models	DSA (mN/m)
Surface free energy	43.11	$y = 0.865x + 2.71$	46.71
Polar component	23.39	$y = 1.05x - 0.233$	22.50
Dispersive component	19.72	$y = 0.745x + 5.42$	19.19

4. Discussion

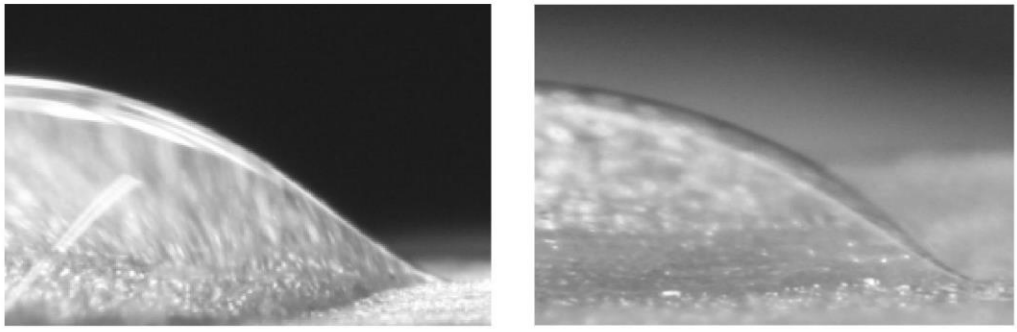
Most fruit and leafy vegetables that exhibit strong hydrophobicity have surface roughness with microstructures and nanostructures comprising unwettable wax crystals [34]. In the present study two different food materials were carefully selected for their irregular, rough shape. Due to their round shape, pitted structure with seeds (achenes), and hairs attached to the achenes, strawberries are a challenge for accurate contact angle measurement. Similarly, due to the wavy, curly shape of the leaves, surface energy characterization of endive salad is also challenging. A novel method using the ImageJ program with the DropSnake plugin was used to define contact angles for non-axissymmetric drops from digital photographs with high resolution. As a first step, the novel method was validated with the aid of four plastic films, comparing the measured contact angles with those obtained using the widely-used DSA device. The measured SFE with its polar and dispersive components are summarized in Table 4 along with the literature data. The results from this study agree well with those in the literature. The values of the surface free energy and its components increased with the decreasing thickness of the PET film.

Table 4. Summary of the SFE and its polar and dispersive components measured on plastic films in the present study along with literature data in mN/m.

Study	Plastic Film	Polar Component (γ_S^P)	Dispersive Component (γ_S^D)	SFE (γ_S)
Present study	BOPP	0.71	24.03	26.23
Guimond et al. [35]	BOPP	~0.5 [1]	~24.5 [1]	~25 [1]
Present study	12 µm PET	9.98	37.12	47.10
Present study	160 µm PET	4.58	35.55	40.13
Wang et al. [36]	10 µm PET	-	-	45.6 [1]
Present study	PTFE	5.31	15.82	21.13
Jun and Qunji et al. [37]	PTFE	3.93	28.42	-

[1] Units were converted to mN/m.

With the help of linear regression models, mathematical relationships were determined between the results of two different measurement techniques. However, the dispersive forces which were determined using the ImageJ program were biased compared to the DSA results. The difference between the results may originate from the contact angle interpolation skim of the program. Figure 9 shows the unusual, bell shapes of sessile drops of water and glycerol on endive salad surfaces. In the study of Kako et al., bell-shaped droplets on hydrophilic/hydrophobic surfaces were well documented [38]. As the contact angle results are obtained by a piecewise polynomial fit of the program [26], further research is needed to improve the curve fitting for bell-shaped droplets.



(**a**) (**b**)

Figure 9. (**a**) Bell-shaped water droplet on an endive salad leaf and (**b**) bell-shaped glycerol droplet on an endive leaf.

The surface free energies of strawberry and endive salad surfaces were determined with the help of high-accuracy contact angles. The results of the present study showed that the strawberry surface is a low energy surface (21.26 mN/m) with high dispersive forces (19.96 mN/m) and very low polar forces (0.99 mN/m). These results agree with the findings of Ribeiro et al. who found the surface tension of strawberries to be 28.94 mN/m, with polar and dispersive components of 5.95 and 22.99 mN/m, respectively [7]. On the other hand, Velasquez et al. measured surface energy values of strawberry samples using the acid-base approach and found a value of ~40 mJ/m^2 (40 mN/m) [39]. The difference between the results may be due to differences in the methods used for surface free energy calculation.

High dispersive forces with low or zero polar forces indicate that the surface is strongly hydrophobic, meaning that polar liquids, such as water-based coatings, cannot uniformly spread and wet the surface [22,40,41]. It is clear that high solid surface free energy and low liquid surface free energy favors wettability [21]. Therefore, different formulations of edible coatings with effective surfactants should be evaluated for higher wettability of the strawberry surface.

The surface energy of endive salad, which has not been previously described in the literature, was found to be 43.11 mN/m. However, the higher polar (23.39 mN/m) and dispersive (19.72 mN/m) components indicate that higher surface wettability can be achieved with coatings having a relatively high surface tension. Although, as in the strawberry study, different parts of different endive salad leaves were used for the contact angle measurements, the contact angle results did not show drastic scatter (unlike the results for strawberries), implying the green endive salad leaves have a more uniform surface structure.

5. Conclusions

In the present work, accurate contact angles of test liquids on rough-shaped food samples and, hence, actual surface free energy values, were measured. The novel method that was used was validated by comparing the data with the results obtained using a contact angle meter. The latter is frequently used for flat surfaces in the literature and for industrial applications. Linear regression models and linear equations were defined to represent the mathematical relationship between the two measurement methods. This part of the work will be particularly useful for comparing results obtained using these two measurement methods in future studies.

Strawberries and endive salad were chosen due to their rough and irregular shapes. The surface energies, as well as the polar and dispersive components, were determined using the more accurate contact angles. According to the results, strawberries have a low energy surface (21.26 mN/m) with strong hydrophobicity (high dispersive forces (19.96 mN/m) and very low polar forces (0.99 mN/m)). Effective surface active agents should be added to coating formulations to achieve higher wettability. In contrast, effective spreading of coating solutions on salad surface is relatively easy due to the higher polar (23.39 mN/m) and dispersive (19.72 mN/m) components.

The results show that the ImageJ program with the snake-based approach is an important tool for contact angle measurement of irregular and rough food surfaces. The concept presented in this paper can be used as a guideline for designing coating materials with improved surface wettability, with the help of more accurate contact angle measurements. The program can be developed further to prevent biased data and to obtain better polynomial fitting for bell shaped droplets.

Acknowledgments: The research was conducted as part of the IGF-project 95EN/1 under the CORNET initiative and was carried out under the auspices of the German Federation of Industrial Research Associations within the framework of the program to promote collaborative industrial re-search (IGF). It was financed by the German Federal Ministry of Economics and Technology (BMWi).

Author Contributions: Tugce Senturk Parreidt, Carolin Hauser, and Markus Schmid conceived and designed the experiments; Tugce Senturk Parreidt performed the experiments and analyzed the data; Carolin Hauser and Markus Schmid contributed reagents/materials/analysis tools; Tugce Senturk Parreidt wrote the paper; and Markus Schmid and Carolin Hauser proofread the text.

Conflicts of Interest: The authors declare no conflict of interest.

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Chapter VI.

Effect of Ingredients in Sodium Alginate-Based Edible Coatings

This chapter contains a peer-reviewed article "Effect of presence and concentration of plasticizers, vegetable oils, and surfactants on the properties of sodium-alginate-based edible coatings". It is published in the Open Access Journal "International Journal of Molecular Sciences" (Publication IV). The author of this thesis is also the first author of the article. Authors' contributions were specified in the article under tha names "Tugce Senturk Parreidt conceived, designed and performed the experiments and analyzed the data; Markus Schmid and Tugce Senturk Parreidt interpreted the results. Tugce Senturk Parreidt wrote the manuscript; and Markus Schmid and Kajetan Müller proofread the text".

Summary of the Publication-IV

The properties of the components in the coating solution, as well as the final formulation, are very important factors that affect the quality characteristics of the coated food product. Therefore, the objective of the present work was to assess the usability and effectiveness of the gradually-built formulations in terms of surface tension values and their polar and dispersive components, emulsion droplet size and optical appearance at the microscopic scale. For this purpose, various concentrations of gelling agent (0-3.5%, w/w), plasticizers (glycerol and sorbitol, 0-20%, w/w), surfactants (tween 40, tween 80, span 60, span 80, lecithin, 0-5%, w/w) and vegetable oils (sunflower oil, olive oil and rapeseed oil, 0-5%, w/w) were incorporated into different formulations. Alginate is the main gel-forming hydrocolloid, while plasticizers were added to overcome brittleness. Vegetable oils were incorporated as lipid elements (to enhance moisture barrier properties) and surface-active agents were added to improve the adhesion properties of the coatings.

Results showed that the viscosity was the limiting factor for determining the alginate concentration in the formulation. It increased exponentially with the increasing concentration of alginate. With the help of the optimal curve fitting (with smoothing method), it was found that vegetable oils and surfactants formed similarly descending curves (i.e., rational functions, $y=f(x)=(a+cx)/(1+bx)$ $R^2 \geq 0.9$), but the slopes were different for each component. Moreover, interactions between the surfactants as well as the sunflower oil and surfactants were also analyzed. Once the formulations were optimized,

the stabilities of the formulated emulsions, as well as the wettability characteristics of the selected food product (strawberry) were determined.

The results obtained showed that 1.25% sodium alginate, 2% glycerol, 0.2% sunflower oil, 1% span 80, and 0.2% tween 40 or tween 80 could be used in formulation to obtain an effective coating for hydrophobic food surfaces. Three formulations were designed, and their stability (emulsion droplet size, optical characteristics, and creaming index) and wettability tests on strawberry showed that they could be successfully used in coating applications.

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Effect of Presence and Concentration of Plasticizers, Vegetable Oils, and Surfactants on the Properties of Sodium-Alginate-Based Edible Coatings

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Received: 31 January 2018; Accepted: 1 March 2018; Published: 6 March 2018

Abstract: Achieving high quality of a coated food product is mostly dependent on the characteristics of the food material to be coated, the properties of the components in the coating solution, and the obtained coating material. In the present study, usability and effectiveness of various components as well as their concentrations were assessed to produce an effective coating material. For this purpose, different concentrations of gelling agent (sodium alginate 0–3.5%, w/w), plasticizers (glycerol and sorbitol (0–20%, w/w), surfactants (tween 40, tween 80, span 60, span 80, lecithin (0–5%, w/w), and vegetable oils (sunflower oil, olive oil, rapeseed oil (0–5%, w/w) were used to prepare edible coating solutions. Formulations were built gradually, and characteristics of coatings were evaluated by analyzing surface tension values and its polar and dispersive components, emulsion droplet size, and optical appearance in microscopic scale. The results obtained showed that 1.25% sodium alginate, 2% glycerol, 0.2% sunflower oil, 1% span 80, and 0.2% tween 40 or tween 80 can be used in formulation to obtain an effective coating for hydrophobic food surfaces. Three formulations were designed, and their stability (emulsion droplet size, optical characteristics, and creaming index) and wettability tests on strawberry showed that they could be successfully used in coating applications.

Keywords: edible coating; sodium alginate; plasticizer; vegetable oil; surfactant; surface tension; coating stability

1. Introduction

The development of new packaging materials for the food industries, particularly due to increased health and environment-consciousness, is a rapidly growing area. Hence, there has been an increased amount of research on renewable, sustainable materials to use for packaging [1]. One of these approaches is edible films and coatings, which are biodegradable packaging formulated from edible components such as various animal or vegetal origin substances [1,2]. Edible coatings and films have great advantage over conventional plastic packaging, as they can be a complete food coating or incorporated between food components such as baked pastry in a pie and ingredients in a pizza [1,3,4]. Edible coatings and films provide a fortification layer to decrease the mass transfer (water migration, gas transfer, migration of aromatic compounds and solvents, etc.) between the product and the surrounding medium, provide mechanical stability, and become a barrier against

light [1]. Free-standing edible films have enough integrity that they can be cut and placed on food surfaces [5,6]. Conventionally, film solution is deposited on an inert surface, uniformly spread, and various techniques like solvent removal, thermal gelation, and melting followed by solidification are applied to obtain the stand alone wrapping material. On the other hand, edible coatings are applied on the surface of the food product by dipping, spraying, spreading, and vacuum impregnation methods, and are created as a thin layer on the surface [5–7].

The main gel-forming substances are classified according to their structural materials: hydrocolloids (i.e., proteins and polysaccharides), lipids, or a combination of them (i.e., composites) [2,8]. Among these, alginate is an extensively used polysaccharide that is quite abundant in nature. Alginate (alginic acid sodium salt) is a structural component in marine brown algae (Phaeophyceae, mainly Laminaria) and soil bacteria [9,10]. Food grade sodium alginate (E401) is affirmed as "Generally Recognized as Safe" (GRAS) and used as emulsifiers, stabilizers, thickeners, and gelling agents [11]. In Europe, alginic acid and its salts are listed as European Commission (EC)-approved additives [9,12]. Although alginate-based coatings produce rigid gel instantaneously in the presence of calcium or a bivalent ion, due to their hydrophilic nature, they exhibit poor water resistance [10,13]. As a rule of thumb, lipids are coating biopolymers, used for reducing water transmission. On the other hand, lipid-based films which contain hydrophilic polymers have durability and structural integrity [14]. Lipid elements can be included in the formulation to form composite coatings and to enhance the moisture barrier properties [3,15,16]. Lipids such as waxes (paraffin wax, beeswax, carnauba wax, candelilla wax, etc.), vegetable oil, mineral oil, acetylated monoglycerides, and sucrose esters of fatty acids can be used as coating materials [16,17].

Unplasticized coatings are brittle and not applicable for coating applications. Plasticizers such as glycerol, sorbitol, monoglycerides, polyethylene glycol, glucose, etc., are commonly used to overcome edible coating brittleness and improve flexibility and elongation of polymeric substances [2,16,18].

Surfactants are surface active agents, whose major characteristic is to be at higher concentration at the surface (liquid–solid, liquid–liquid, or liquid–air interface) than in the bulk of the liquid [19]. Based on the chemical structure of hydrophilic groups and the charge type of the surface active part, surfactants can be classified as anionic (negatively charged), non-ionic (no charged group), cationic (positively charged), and amphoteric (can be positively or negatively charged, or both, depending on the circumstances) [19]. Adhesion of the coating material to the surface of the product can be promoted by adding surfactants to the formulation due to reducing surface tension [3]. Sorbitan esters (spans) and their ethoxylates (tweens) are non-ionic surfactants with food approval [20,21]. Addition of multi-ether groups to the structure (ethoxylation) increases the water solubility of the surfactant. Moreover, water solubility feature increases with larger amounts of ethylene oxide [19]. They have many functional benefits: they can be also used as emulsifier, dispersant, and wetting and foaming agents [19,22]. They are stable over a wide pH range and they are electrolyte-tolerant [22]. Tweens are hydrophilic and are soluble or dispersible in water; on the other hand, spans are partly soluble in water [22]. Tweens are compatible with other surfactants and the synergistic effect between the surfactants are well known [19]. Phosphatidylcholine (PC), which are phospholipids with choline head group, is an important component of soybean lecithin and gives the natural surfactant characteristic to it [23]. Although the biggest concern about lecithin is its allergenicity, the Food Allergy Research and Resource Program (FARRP) at the University of Nebraska–Lincoln pointed out that soy lecithin does not contain sufficient soy protein residues to cause allergic reactions [24].

Functional properties and effectiveness of edible coating emulsions are strongly correlated with the wetting and uniform spreading ability of the coating on the targeted food product [25–27]. These concepts depend on the balance between adhesion (W_a) and cohesion forces (W_c), surface tension of the coating liquids, and surface characteristics (i.e., surface free energy) of the product [26]. Song and Springer introduced a digital-image-processing-based method to estimate the surface and interfacial tension of systems using the profile of a pendant drop [28,29]. However, determining the surface energy of the solids is not as straightforward as liquids. It can be measured indirectly with the

help of various liquids with known values of surface tension and components. Additionally, there have been different theories to calculate surface free energy of a solid from contact angle data. One of these theories is the Owens, Wendt (1969), Rabel (1971), and Kaelble (1970) method (OWRK), which is based on a two-component model: polar and dispersive forces [30–32]. Similarly, polar and dispersive components of the liquid can be measured indirectly with the help of a solid with a well-known surface free energy and its components [33,34]. With the help of the contact angle created by the coating emulsion on the solid product surface, and surface tension of the coating emulsion, the wettability (W_S) characteristic of the food product can be calculated [35].

Composition, preparation method, and the droplet size have strong effect on stability of the emulsions [36]. Generally, droplet sizes larger than 1 μm are affected by gravitational forces [36]. Creaming index (CI) values can be used to predict the behavior of the edible coating solution during storage [37].

Even though the effects of various edible coating formulations based on alginate gel matrix on quality parameters and shelf life of food products have been studied in detail, there has been less literature about the creation of the coating formula; the very initial step in alginate-based coating design was not extensively investigated and well-documented. Additionally, previous works have focused on a limited number of components in the design of coating formulations.

Therefore, the main aim of the present work was to design and optimize sodium-alginate-based edible coating formulations. This study investigated the formulation preparation step broadly and built the formulation gradually with experiments. Concurrently, the influence of the presence and the concentration of components to the physical properties (surface tension, as well as the polar and dispersive components) of alginate-based edible coatings were elucidated. Additionally, the relationship between surface tension and droplet characteristics of coating solutions were examined. Once the formulations were optimized, the stabilities of the formulated emulsions as well as the wettability characteristics on the selected food product (strawberry) were presented.

2. Results

2.1. Surface Tension of the Coating Solutions

The effect of dissolved sodium alginate concentration on the surface tension of the solution is shown in Figure 1a. The results indicated a statistically insignificant decrease in surface tension when alginate concentration was increased ($p > 0.05$, Kruskal–Wallis test). However, the limiting factor, which determined the concentration of the alginate to be used in the formulation, was viscosity of the solution. Viscosity increased exponentially with the increased concentration, as shown in Figure 1b. Alginate concentration had a significant effect on the viscosity of the coating gel ($p \leq 0.05$, Kruskal–Wallis test). The 3.5% (w/w) is selected as the highest concentration due to the high gel viscosity. According to the studies in the literature, coating thickness has been increasing proportionally with higher viscosity [38,39]. A thick coating on the food product is not a preferred feature in the coating process. The viscosity of the alginate solution increased drastically for the concentrations higher than 2%. On the other hand, a decent amount of gelling agent was required in order to achieve gel formation. Therefore, 1.25% (w/w) alginate was selected as the highest alginate concentration in the formulation with low effect of viscosity. Lower concentrations were not selected due to being able to observe the effects of alginate in the subsequent experiments.

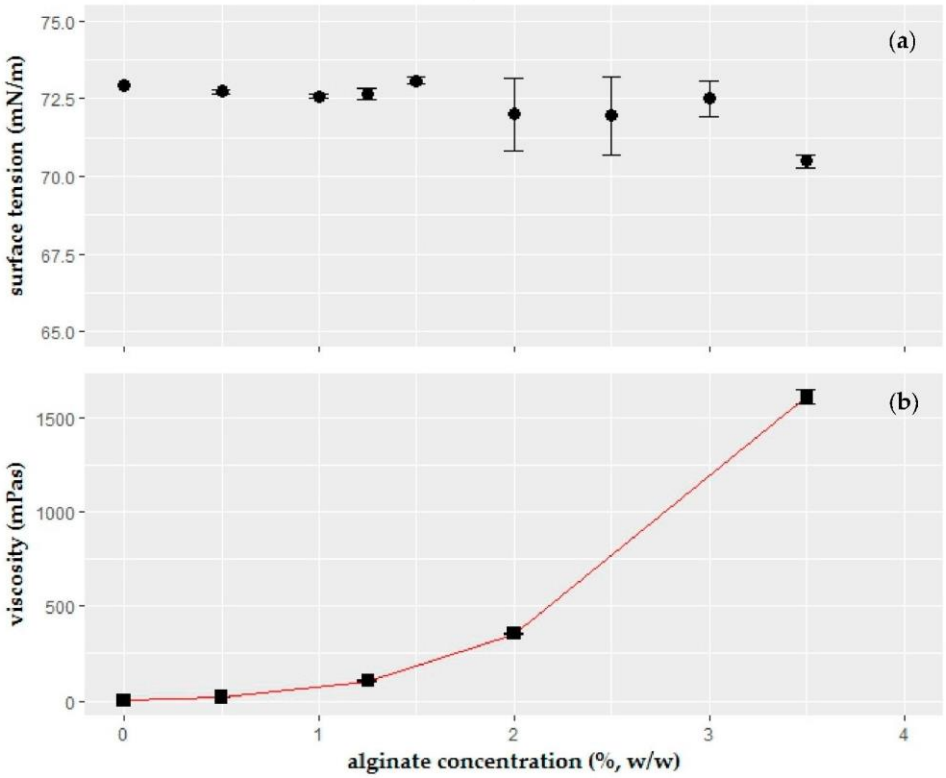

Figure 1. Effect of sodium alginate concentration (%, w/w) on (**a**) surface tension (mN/m); (**b**) viscosity (mPa·s) of the coating solution ($n = 3$).

As a second step, the presence and influence of two different plasticizers (0–20%, 6 levels) on surface tension of the coating solution were investigated (Figure 2a,b). A two-way analysis of variance (ANOVA) test was run on the results. Both main and interaction effect analysis as well as TukeyHSD post hoc test showed that only 20% (w/w) glycerol-added solution had significantly different effects on surface tension values ($p \leq 0.05$), and additionally there was no significant difference between glycerol and sorbitol. Sorbitol is a sweetener that is used to replace sucrose in the food products [40]. Hence, glycerol was chosen as plasticizer to obtain a natural taste in the edible coating.

Fresh-cut fruits and vegetables have high water activity on the surface. This characteristic enables the water-based edible coatings to spread easily on the coating surface, and water barrier properties should be taken into consideration in order to prevent water loss. Tapia, et al. [41] investigated the effects of glycerol concentration (1–2%, w/v) on barrier functionality of alginate-based edible coatings and concluded that glycerol concentrations higher than 1.5% (w/v) enhanced the water vapor resistance (WVR) of the alginate coating on papayas. Therefore, 2% glycerol concentration was selected for the formulation.

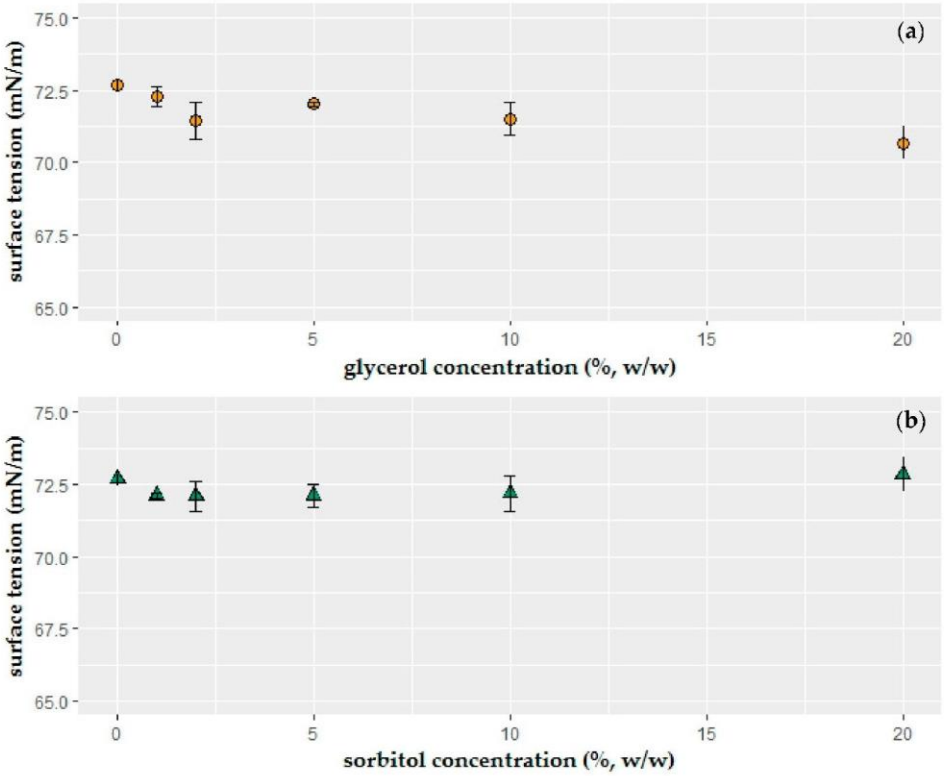

Figure 2. Effect of plasticizer (**a**) glycerol, (**b**) sorbitol concentration (%, *w*/*w*) on surface tension (mN/m) of the coating solution. Glycerol or sorbitol was incorporated into 1.25% (*w*/*w*) sodium alginate solutions ($n = 3$).

Vegetable oils were added as a lipid source to the 1.25% sodium alginate and 2% glycerol dissolved coating formulations. It was no surprise that oil did not reduce the surface tension drastically (Figure 3). Formulations of 100% sunflower oil, olive oil, and rapeseed oil had 32.68 ± 0.60 mN/m, 31.75 ± 0.25 mN/m, and 32.44 ± 0.27 mN/m surface tension, respectively. According to the separate Kruskal–Wallis tests results, oil type and concentration had a significant effect ($p \leq 0.05$) on surface tension. Surface tension results of olive oil-added solutions were significantly different from sunflower- and rapeseed oil-added samples. The pairwise Wilcoxon rank sum post hoc test indicated that higher concentrations (>0.2% oil) do not significantly decrease the surface tension results.

The simplest fitting function to data points were found as rational function $y = f(x) = (a + cx)/(1 + bx)$ for all three vegetable oils with fairly low number of variables. The goodness of fits was quantified by R^2 (R-squared) values, which determine how close the data is to the fitted regression lines. The variables in the functions (a, b, and c) were very close, and goodness of fit values of the curves were high ($R^2 \geq 0.90$).

Despite the lower surface tension results, olive oil has certain drawbacks (i.e., having darker color compared to sunflower oil, being more expensive and having a strong, distinguishable odor and flavor). Due to the small differences in surface tension results, sunflower oil was selected as the lipid source for the formulation.

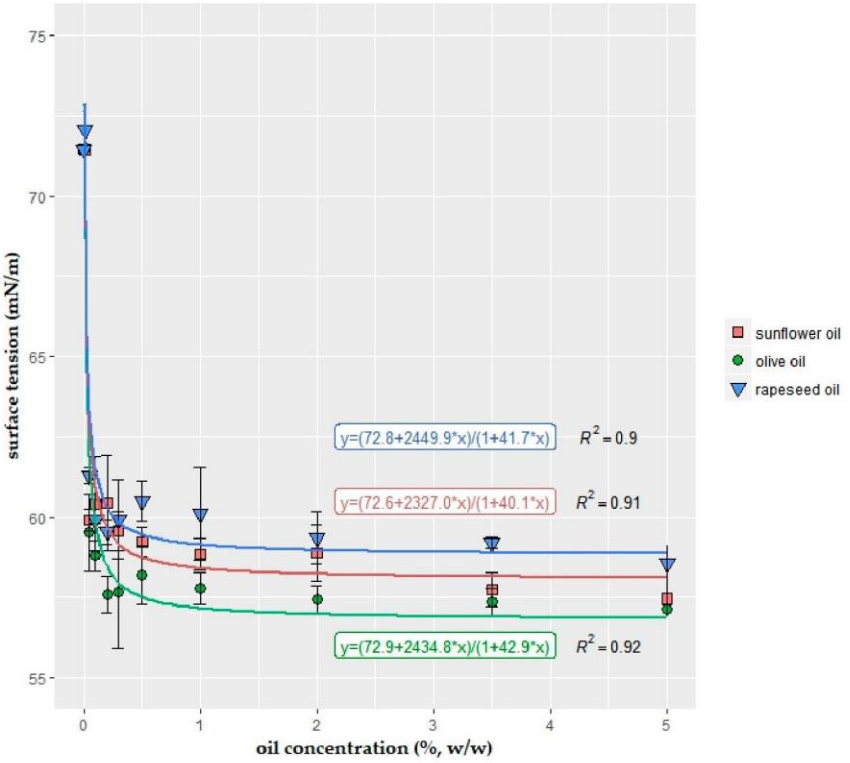

Figure 3. Variation of the surface tension (mN/m) of the solution with the concentration (%, *w*/*w*) of vegetable oils: sunflower, olive, and rapeseed oil. Each concentration was added into 1.25% sodium alginate + 2% glycerol solutions (n = 3 replications).

Intact fruits and vegetables have low energy and hydrophobic surfaces. Porter [19] stated that non-ionic surfactants were adsorbed in higher amounts on non-polar or hydrophobic surfaces than polar surfactants. Therefore, non-ionic surfactants such as tween 40, tween 80, span 60, and span 80 were used in the present study. Additionally, soy lecithin was also included to the trials due to its emulsification effect and widespread usage in the industry. The effects of surfactant type and concentration on surface tension values are shown in Figure 4. Although the surfactants formed similar descending curves, the slopes were quite different. Yet, all reached their saturation point around 1%. Statistical evaluations showed that surfactant type, concentration, and their interaction had significant effect (two-way ANOVA, $p < 0.05$). For the lower surfactant concentrations (<0.5%), tween 40 and tween 80 were more effective in decreasing surface tension. However, for concentrations above 0.5%, span 80 was the most effective. The results showed that tween concentrations could be kept low; on the other hand, span 80 must be used in higher amounts (~1%) to reduce the surface tension to the utmost degree.

It was very interesting that the same rational function [y = f(x) = (a + cx)/(1 + bx)], which determined the descending curves of change in surface tension with increasing oil concentration (Figure 3), also constructed good fits to the surface tension versus surfactant concentration data points (Figure 4). The variable "a" is approximately the same for each equation (~71) due to starting at the same surface tension value in zero concentration (i.e., solutions containing only 1.25% alginate and 2% glycerol, without surfactant and oil addition). The "b" and "c" variables in the functions of tween 40 and tween 80 were very close to each other, as expected. However, it was found to be interesting that spans had also very similar "b" and "c" values despite being located quite far from each other in the graph. Apart from "c", the change in the "b" value was particularly important in this distribution difference.

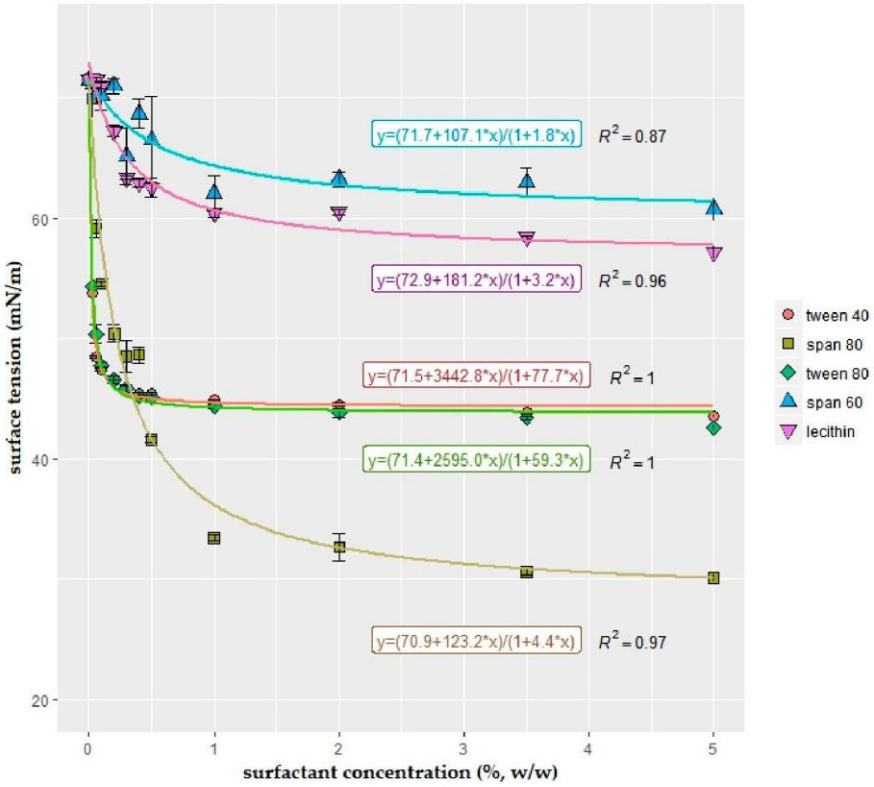

Figure 4. Variation of the surface tension (mN/m) of the solution with the concentration (%, *w*/*w*) of surfactants: tween 40 (polyoxyethylenesorbitan monopalmitate), tween 80 (polyoxyethylenesorbitan monooleate), span 80 (sorbitan monooleate), span 60 (sorbitan monostearate), and soy lecithin. Each surfactant concentration was incorporated into 1.25% sodium alginate + 2% glycerol solutions (n = 3).

2.2. Polar and Dispersive Components of the Coating Solutions

The calculated dispersive ($\gamma_L{}^D$) and polar ($\gamma_L{}^P$) components of surfactants (tween 40, tween 80, span 60, span 80, lecithin) and oil (sunflower) are presented in Figure 5. Surface energy and dispersive and polar components of the polytetrafluoroethylene (PTFE) film used in the calculation were 14.24 ± 0.52 mN/m, 14.18 ± 0.50 mN/m, and 0.06 ± 0.03 mN/m, respectively.

Error bars, showing standard deviations, were not generated due to the usage of mean values of all variables (i.e., contact angle, liquid surface tension, polar and dispersive components of PTFE film surface energy) in the calculations.

Polar forces of surfactants and sunflower oil decreased with increasing concentration. On the contrary, dispersive forces increased with the higher concentration. Besides this, dispersive forces of relatively more effective surfactants (i.e., tween 40, tween 80, and span 80) had higher values compared to their polar counterpart. On the other hand, relatively less effective surfactants and sunflower oil had higher polar forces compared to their dispersive components.

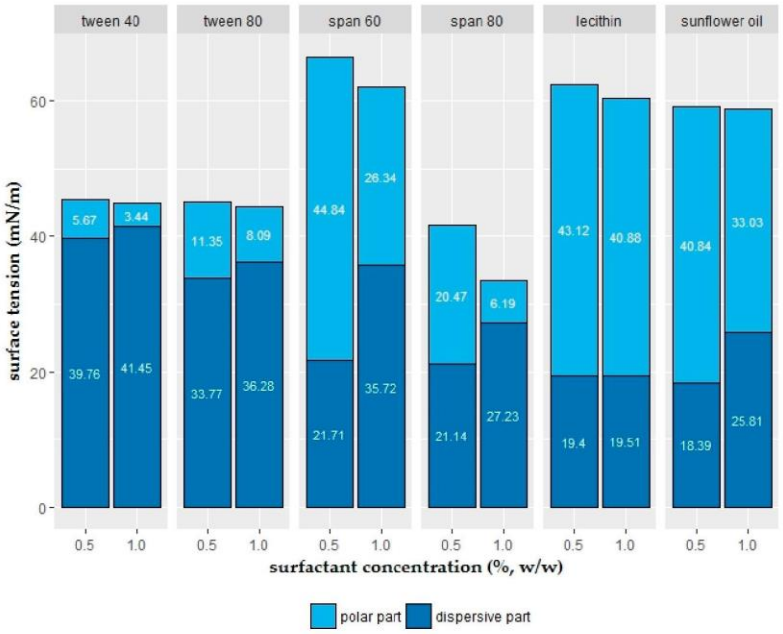

Figure 5. Effect of surfactant and oil type and concentration on polar ($\gamma_L{}^P$) and disperse ($\gamma_L{}^D$) part of the surface tension of coating solution. Each surfactant concentration was incorporated into 1.25% sodium alginate + 2% glycerol solutions (n = 3).

2.3. Interaction of Surfactants

Subsequent to the determination of single effects formed by each individual surfactant, synergistic properties of mixtures should also be evaluated. The interaction between the most effective surface agents are presented in Tables 1 and 2. A 2k three-factorial design setup was applied, in which each factor took two levels (low and high). These levels were determined according to the results presented in Figures 3 and 4. The lowest value was the lowest concentration of the component which had statistical decrease in surface tension values. Similarly, the highest value was taken as the concentration where the surfactant saturation was reached; in other words, surface tension remained constant with increasing surfactant concentration.

As presented previously in Figure 4, the surface tension reduction effect of tween 40 and tween 80 were very similar. For this reason, the interaction of span 80 with each tween compound was analyzed separately in a small trial shown in Table 1. For statistical evaluations, the population distributions of low and high concentrations of tweens were compared among themselves. Results showed that there was not any significant difference between tween-40- and tween-80-added solutions (Mann–Whitney–Wilcoxon test, $p > 0.05$).

Table 1. Interaction effect of surfactants on surface tension (γ_L) values of coating solutions. Each formulation (each row) was incorporated into 1.25% sodium alginate + 2% glycerol + 0.05% sunflower oil solutions (n = 3).

Span 80 (%)	Tween 40 (%)	Tween 80 (%)	γ_L (mN/m)
0.06	0.03	-	55.42 ± 0.66^{A}
0.06	-	0.03	54.64 ± 0.14^{A}
1	-	1	38.05 ± 0.30^{B}
1	1	-	37.75 ± 0.27^{B}

For each formulation, different superscripts in column are significantly different ($p \leq 0.05$).

Since no significant difference between tween 40 and 80 was found, the interaction effects between oil, span 80, and tween 40 were examined more detailed in Table 2. Data transformation was applied because the data was positively skewed (right skewed distribution) to get normal distribution. Three-way ANOVA was run to examine the interaction effect between oil, tween 40, and span 80 concentrations on surface tension values. Results showed that all two-way as well as three-way interactions have significant effect ($p < 0.05$).

Table 2. Interaction effect of components on surface tension (γ_L) values of coating solutions. Each formulation (each row) was incorporated into 1.25% sodium alginate + 2% glycerol solutions ($n = 3$).

Sunflower Oil	Span 80 (%)	Tween 40 (%)	γ_L (mN/m)
0.05	0.06	0.03	55.42 ± 0.66^{A}
1	0.06	0.03	50.10 ± 0.25^{B}
0.05	0.06	1	43.72 ± 0.42^{C}
1	0.06	1	43.13 ± 0.05^{C}
0.05	1	0.03	33.63 ± 0.60^{D}
1	1	0.03	34.99 ± 0.28^{E}
0.05	1	1	37.75 ± 0.27^{F}
1	1	1	37.16 ± 0.12^{F}

For each formulation, different superscripts in column are significantly different ($p \leq 0.05$).

2.4. Emulsion Stability Measurements

2.4.1. Emulsion Droplet Size Determination and Optical Evaluations

The effect of presence and concentrations of surfactants and sunflower oil on emulsion size distributions were investigated. The droplet sizes of sunflower oil and lecithin solutions are given as surface area mean diameter (Sauter mean) in Table 3. The effects of any noise, bubbles, or agglomerations at the higher end of the data range were removed with modification of the results. During the analysis in Mastersizer, the liquid sample was placed in a stirred sample cell, which was filled with demineralized water. The device took the sample automatically from the stirred cell and sent it to the analyzer beam. Hence, the measurement of surfactants such as tween 40, tween 80, and low concentrations of lecithin was impossible due to their dilution in the sample cell. Additionally, particle size distributions of span 60 and span 80 did not overlap during the measurements of the parallels. Therefore, the results were not shown in the table. Interestingly, almost all concentrations of span components formed two peaks with similar frequencies. Span solutions have larger particles (>10 μm), which indicated that they could not be successfully integrated into the emulsion alone, and the process should be improved.

Table 3. Surface area mean diameter (Sauter mean) of droplets of components at specified concentrations. Each component was incorporated into 1.25% sodium alginate + 2% glycerol solutions ($n = 3 \times 2$).

Component	0.25%	0.5%	0.75%	1%	3.5%
Sunflower oil	$2.31 \pm 0.09_{a}$	$2.08 \pm 0.21_{a}$	$2.08 \pm 0.30_{a}$	$2.06 \pm 0.16_{a}$	$2.06 \pm 0.43_{a}$
Lecithin	-[1]	-[1]	$0.53 \pm 0.01_{b}$	$0.44 \pm 0.01_{c}$	$0.41 \pm 0.01_{d}$

[1] Measurements cannot be performed due to the dilution of the samples in sample cell of the Mastersizer. or each component, different subscripts in rows are significantly different ($p \leq 0.05$).

Droplet sizes of lecithin solutions decreased significantly with increasing concentration (Kruskal–Wallis test, $p < 0.05$). However, the reduction was insignificant for droplet sizes of sunflower oil emulsions (Kruskal–Wallis test, $p > 0.05$).

Solutions of 1.25% sodium alginate + 2% glycerol + surfactant (0.25–3.5%, 5 levels) were optically examined to determine the agglomeration, micelle formation, as well as the homogeneity of the coatings (Figure 6). Due to the water solubility of tweens, components were dissolved in the coating solution (Figure 6a). However, during optical evaluation of tween-added solutions (both tween 40 and tween 80), 10-µm-long gel-like particles were observed in the 0.5% and higher concentrations (Figure 6b). These structures were not detected in any 0.25% tween-incorporated samples. Sorbitan esters (spans) were not soluble in water, which could possibly cause the formation of particles with different sizes as seen in Figure 6c. In the images of higher span 80 concentrations (>1%), a translucent ring formation which surrounded the droplets could be observed (Figure 6d). Lecithin and span 60 produced carpet-like continuous structures which had an increasing intensity with increasing concentration (Figure 6e,f).

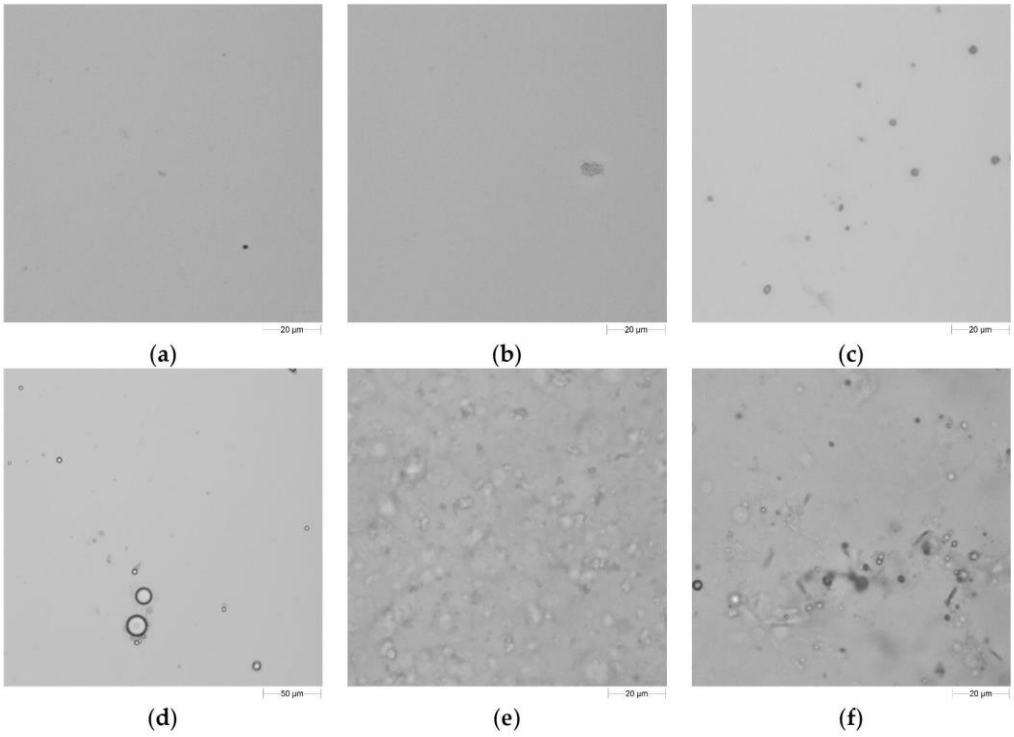

Figure 6. Microscope images of surfactant added coatings: (**a**) 0.25% tween 40; (**b**) 1% tween 40; (**c**) 0.25% span 80; (**d**) 1% span 80; (**e**) 0.25% lecithin; (**f**) 0.25% span 60. Surfactants listed in letters, incorporated into 1.25% sodium alginate + 2% glycerol solutions. Solutions were not diluted.

So far, the experiments were conducted to determine the individual effects of the components. According to the results obtained, three formulations were designed. All three formulations contained sunflower oil and span 80. Additionally, tween 40 and tween 80 were incorporated into second and third formulations, respectively.

Droplet sizes of the created formulations are presented in Figure 7. Formulation 1 (oil + span 80) and Formulation 3 (oil + span 80 + tween 80) were found significantly different (one-way ANOVA, TukeyHSD test, $p < 0.05$). Addition of sunflower oil into the span 80 solution increased its reproducibility.

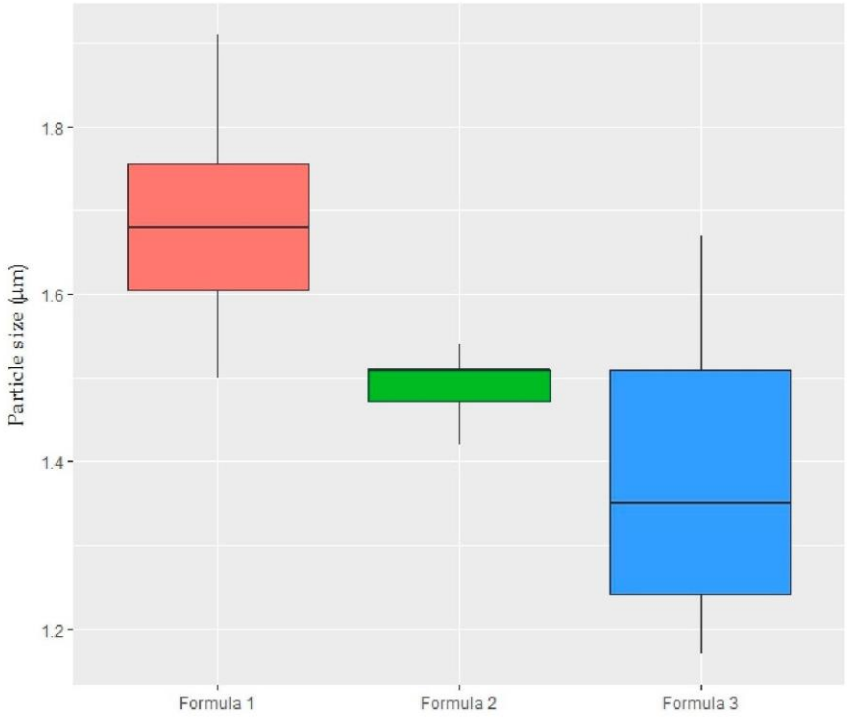

Figure 7. Box plot shows the emulsion droplet size (µm) as surface mean area diameter of the formulations. Formula 1: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80; Formula 2: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 40; Formula 3: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80 (n = 6). Medians are shown with lines across the boxes. Minimum and maximum values (excluding outliers) are represented by whiskers ($n = 3 \times 2$).

Formulations, which were designed based on surface tension and droplet size results, were also examined under microscope (Figure 8). All solutions had agglomerations, and agglomerations in tween 40-added solutions were greater in size and amount compared to the others.

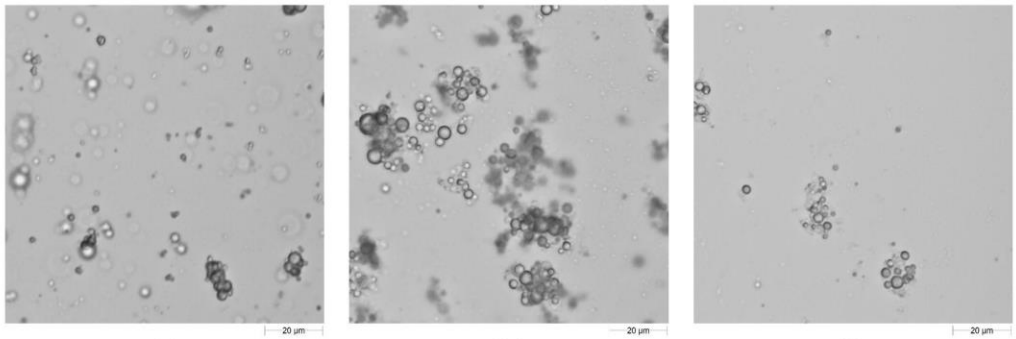

Figure 8. Digitized microscope images obtained from different formulations: (**a**) Formula 1: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80; (**b**) Formula 2: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 40; (**c**) Formula 3: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80. Solutions were not diluted.

2.4.2. Creaming Index

Stability of the formulated emulsions was monitored for 26 h ($n = 3$). Phase separation or creaming was not observed in any test group.

2.5. Wettability

The wettability parameter should also be taken into account during optimization and comparison of the coating solutions. Superficial characteristics were measured on a low-energy strawberry surface. Table 4 summarizes surface tension, contact angle, adhesion coefficient (work of adhesion per unit area), cohesion coefficient (work of cohesion per unit area), and the wettability (spreading coefficient) data for the designed coating formulations determined above.

The third formulation (with tween 80) had the highest amount of work of adhesion, which caused the spreading of the coating on the surface (Welch test, Games–Howell post hoc test, $p < 0.05$). Despite that, work of cohesion, which induced the contraction of the coating, was lowest in first formulation (only with span 80). The highest wettability was achieved with first formulation (Welch test, Games–Howell post hoc test, $p < 0.05$). Nevertheless, wettability values were very close to each other.

Table 4. Surface tension (γ_L), contact angle θ (°), adhesion coefficient (W_a), cohesion coefficient (W_c), and wettability (W_S) data of formulations. Formula 1: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80; Formula 2: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 40; Formula 3: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80 ($n = 20$).

Formulation	γ_L (mN/m)	θ (°)	W_a (mN/m)	W_c (mN/m)	W_S (mN/m)
Formula 1	31.80 ± 0.09^{A}	66.39 ± 5.98^{D}	45.83 ± 2.29^{F}	63.60^{H}	-17.77 ± 2.29^{L}
Formula 2	36.26 ± 0.51^{C}	72.62 ± 5.31^{E}	47.05 ± 3.05^{FG}	72.52^{K}	-25.47 ± 3.18^{N}
Formula 3	35.41 ± 0.27^{B}	65.99 ± 8.28^{D}	49.68 ± 4.64^{G}	70.82^{I}	-21.14 ± 4.64^{M}

For each variable, different superscripts in columns are significantly different ($p \leq 0.05$).

3. Discussion

Surface tension is one of the principal representatives to characterize a surfactant and has been used to measure adsorption phenomenon of the coating solution [19]. Since we formulate the edible coating for hydrophobic surfaces such as surfaces of fruits and vegetables with natural protection layer, reduction of the surface tension of the coating solution is crucial for our study.

In the present work, the effects of the components on surface tension characteristics were assessed one after another, starting with the base material (sodium alginate). Therefore, the formulation has been gradually developed. By this means, their standalone effect as well as their interaction with the other components were observed.

The 3.5% sodium alginate was determined as the highest alginate concentration due to the rapid increase in the viscosity. Alginate did not change the surface tension values significantly, which indicated that the component did not have any adsorption activity in the liquid–vapor interface. Since the coating thickness of the deposited liquid on the food product increased proportionally with increasing viscosity [38,39,42], 1.25% alginate solution with 105.67 ± 1.63 mPa·s viscosity was selected as a gelling structure of the solution.

Glycerol and sorbitol did not modify the surface tension of the liquids. Additionally, the results showed that there was no significant difference between the glycerol and sorbitol results. Only 20% glycerol concentration caused statistically different results in surface tension measurements. Rodríguez, et al. [43] also observed that starch and glycerol did not affect the surface tension of the solutions.

Addition of an oil source to alginate-based coating has many advantages: reducing moisture content, water transmission, and permeability of the coating [44], and being a solvent for oil-soluble surfactants. The results showed that sunflower, olive, and rapeseed oils also decreased the surface tension even in low concentrations such as 0.2%. Higher concentrations did not cause any further reduction of surface tension. Bearing in mind that coating formulation would be designed for fresh-cut fruits and vegetables, the addition of higher oil concentrations would also be disadvantageous in terms of consumer acceptance due to increasing calorie and energy uptake. Furthermore, the size of the bubbles increased with increasing oil concentrations, which would cause a creaming effect and phase separation. Designing a transparent, clear coating is beneficial in terms of higher acceptance and usability in a larger range in the food industry.

Curve fitting and their mathematical functions were constructed to have better data visualizations. In the present study, the smooth functions, which fit the data quite well ($R^2 \geq 0.87$), were defined to be used for interpolation for the data points to infer values where no data are available.

The highest surfactant concentration used in the study is 5% due to observing no decrease in surface tension with increased concentration. Also, Rodríguez, Osés, Ziani and Maté [43] emphasized that surfactants (for soy lecithin, tween 20, and span 80) concentrations above 5% do not allow to produce a uniform starch-based edible film. Porter [19] additionally explained that viscosity of the coating solution increased drastically at higher surfactant concentrations after reaching saturation, which led to the production of a gel-like structure due to the formation of lamellar or cylindrical micelles.

Surfactants formed similar decreasing curves with different slopes [$y = (a + cx)/(1 + bx)$]. Differences in the slope arose from the different sizes and shapes of hydrophobic and hydrophilic groups of the surfactants [19]. Without exception, surface tension values decreased rapidly as the concentrations of the surfactant increased until certain points (~1%, w/w). Decrease of surface tension slowed down at higher concentrations. This phenomenon was explained with the adsorption characteristics of surfactants by Porter [19]. When low concentration of surfactant was added to a solution, the majority of the surfactant molecules were adsorbed on the air–liquid interface, and by increasing the surfactant concentration, they continued to be adsorbed at the surface. This situation would continue until the saturation point, and when the saturation was reached, the surface tension became almost constant. After this point, increasing surfactant concentration would not decrease the surface tension, while the surfactant molecules would remain in the bulk of the solution. The collected information with optical evaluations was consistent with this theory. The differences in the surface tension curves (Figure 4) of surfactants could be elucidated with optical evaluations (Figure 6). When the surfactant solutions, which had statistically lower surface tension results, were examined under microscope, very few particles could be detected in the bulk solution. On the contrary, numerous particles with bigger sizes could be detected in surfactant solutions with higher surface tension results. This difference was especially noticeable in span 80 and span 60.

The results of tween 40 and tween 80 correlate favorably with Wan and Lee [45], who studied the effect of various polysorbates (tweens) on the surface tension, despite the fact that researchers found a slightly higher reduction in tween 40-added samples compared to tween 80. However, Ribeiro, Vicente, Teixeira and Miranda [27] found that the saturation point of tween 80 was 0.02% (w/v) in carrageenan solution, which was very low compared to our study. Rodríguez, Osés, Ziani and Maté [43] showed that span 80 was more effective than lecithin or tween 20 to reduce surface tension of starch-based edible films.

During solution preparation, span components caused foam formation on the top of the solution. Foam formation was more intense in span 60 compared to span 80. Thick foam formation on the surface of the coatings was explained in the literature in that these surfactants were strongly adsorbed at the air–liquid interface [19]. Figure 6c,d confirms with this theory. Even at the high concentration ($\geq$1%), span 80 could not be optically detected in the solution. However, the same theory could not be verified for span 60 (Figure 6f). As observed in the photographs taken from different concentrations,

span 60 particles were embedded in a translucent, gel-like structure, which did not accumulate on the liquid–air interface, but was found in high amounts in the bulk solution. The melting of span 60 during coating preparation process could be a reason for the formation of these structures.

Span 60 and span 80 can be distinguished from each other by the length and structure of their hydrocarbon chains; span 80 has double bonding in its acyl chain, while span 60 has a longer chain without any double bonding [46]. The surface tension difference of span 60 and span 80 could be caused by the double bond in the molecular structure of span 80, which decreases the hydrophobic nature of the surfactant [47]. In addition to that, the arrangement ability of the longer hydrocarbon chain in span 60 causes smaller surface area per molecule compared to span 80, which has larger molecular areas [47].

Determination of the polar and dispersive parts of liquid is not a straightforward process. Subsequent to the measurement of surface tension values, the dispersion force component of the liquid can be calculated with the help of a solid that has a completely nonpolar surface, such as PTFE film [33]. Dipole-dipole and hydrogen bonding interactions are polar interactions; Van der Waals type of interactions are dispersive interactions [48]. On the condition that only dispersion forces operate, the liquid or solid is nonpolar [30]. In the present study, coating was intended to design for fruits and vegetables, both fresh-cut and intact products with hydrophobic (in other words, nonpolar) surfaces. Therefore, relatively nonpolar liquids with higher dispersive and lower polar components would serve better as coating material. Tween 40, tween 80, and span 80 suited well to these circumstances (Figure 5) due to having relatively higher dispersive and lower polar forces.

The effects of tween 40 and tween 80 in mixtures of sodium alginate, glycerol, oil, and span 80 were compared in Table 1. It was apparent from the table that there was no significant difference between the same amount of tween 40- and tween 80-incorporated samples. Hence, both can be used in the edible coating formulation.

The interaction effects between sunflower oil, span 80, and tween 40 were identified in more detail in Table 2. The results correlated well with previous findings in Figures 3 and 4. Concentration increase of all three components significantly reduced the surface tension. Span 80 had the highest reduction effect, followed by tween 40, and sunflower oil. The two-way and three-way interactions had significant effect on surface tension, which indicated that there were synergistic effects between surface active components.

Droplet size is an important agent of emulsion stability and, additionally, it affects many characteristics of solution such as viscosity, texture, and optical appearance [2,36]. In droplet size determination experiments, the focused concentration area was determined as 0–1% surfactant concentrations since the major surface tension decrease occurred within this concentration range (Figures 3 and 4). In contradiction with earlier findings of Fernandez, André, Rieger and Kühnle [36], which stated that the type of droplet size distribution changed with concentration, in the present study, concentration increase did not cause a drastic change in droplet size distribution for the same type of surfactant. Distribution type changed only with surfactant type.

It has been suggested that droplet sizes between 0.01 and 10 μm were suitable emulsions. Droplet sizes smaller than 1 μm were referred to as molecular dispersions, while those larger than 1 μm were considered as coarse dispersions [49]. According to this definition, tweens and soy lecithin formed true solutions (molecular dispersions); on the other hand, spans and oils generated coarse dispersions. Translucent rings were formed around the span 80 droplets (Figure 6d). This ring could cause a scattering effect during the measurements in laser diffraction system, which could have affected the results of droplet size determination experiment.

It was very interesting that, oil and span mixtures had smaller particle sizes than oil and span formed alone, respectively, in alginate–glycerol solutions (Table 3 and Figure 7). Furthermore, particle sizes were significantly decreased with the addition of tween 80 to the system (Figure 7).

Aggregates of different sizes were embedded into the bulk solution of designed formulations (Figure 8a–c). Captured images showed that tween 80 could be incorporated successfully into the formulation and result in smaller aggregates with less intensity in the bulk solution.

Emulsions can have various instabilities, which cause creaming behavior. Considering the commercial importance of edible coating, visual creaming behavior was monitored as a function of storage hours. Since the designed solutions would be used for coating material, and would not be stored for long time, creaming was monitored only for a day, not longer. No phase separation was observed during this time interval.

Wettability is one of the important phenomena that have a strong impact on the effectiveness of formulated edible coating on food products [25,50]. The highest wettability result (-17.77 ± 2.29 mN/m) was achieved by Formulation 1 (1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80). However, considering the particle size, tween 80-incorporated Formulation 3 (1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80) with -21.14 ± 4.64 mN/m wettability could also be successfully used. Ribeiro, Vicente, Teixeira and Miranda [27] found wettability on strawberry surfaces as -44.61 ± 3.05, -45.28 ± 0.88, and -38.89 ± 2.83 for starch-, carrageenan-, and chitosan-based formulated coatings, respectively.

4. Materials and Methods

4.1. Materials

Sodium alginate (Manugel GHB, FMC Biopolymer Co., Philadelphia, PA, USA), glycerol (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), sorbitol (Acros Organics, Geel, Belgium), sunflower oil, olive oil, colza (rapeseed) oil (Rewe Bio, Rewe Markt Gmbh, Köln, Germany), tween 40 (polyoxyethylenesorbitan monopalmitate) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), tween 80 (polyoxyethylenesorbitan monooleate) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), span 80 (sorbitan monooleate) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), span 60 (sorbitan monostearate) (Merck KGaA, Darmstadt, Germany), and lecithin (made from GMO-free soybeans) (Carl Roth GmbH Co. KG, Karlsruhe, Germany), were used in coating formulations. Glycerol and sorbitol were employed as plasticizer. Tween 40 (hydrophilic–lipophilic balance, HLB = 15.6), tween 80 (HLB = 15.0), and span 80 (HLB = 4.3) were viscous liquid formed surfactants, while span 60 (HLB = 4.7) was in beige flakes and soy lecithin (HLB = 8.0) was in light brownish powder form.

Polytetrafluoroethylene (PTFE) (thickness: 500 µm) was purchased from SAHLBERG GmbH and Co. KG (Feldkirchen, Germany).

Fresh strawberries (*Fragaria ananassa*) were purchased from a local market (Freising, Germany). Samples were carefully checked to ensure uniform size and absence of any defects. Before measurements, samples were left at ambient temperature (~21 °C). Samples were cut into rectangular shapes (~3 cm × 2 cm) to reduce the slope of the surface.

4.2. Preparation of Coating Solutions

The amounts of components (i.e., gelling agent, plasticizers, oils, surfactants) were adjusted to achieve the specified amount in 100 g final solution.

Sodium alginate (0–3.5% (*w*/*w*), 9 levels) was dissolved in hot distilled water at 70 °C with continuous stirring (magnetic stirrer (500 rpm)) until complete dissolution was achieved and a clear solution was obtained. Plasticizers (glycerol and sorbitol (0–20% (*w*/*w*), 6 levels) were added to the solutions. Subsequently, surfactants (tween 40, tween 80, span 60, span 80, lecithin (0–5% (*w*/*w*), 11 levels) and vegetable oils (sunflower oil, olive oil, rapeseed oil (0–5% (*w*/*w*), 10 levels) were incorporated into the formulations. Hydrophobic surfactant (Span 60) was prepared according to the previous study of Villalobos et al. [51]. Span 60 was melted at 60 °C in distilled water with continuous stirring and added into the solution. The final weight of the emulsion increased to 100 g upon adding distilled water, and the mixture was continuously stirred with a magnetic stirrer to achieve dissolution

of the surfactants. Afterwards, the mixtures were homogenized and emulsified using an ultra-turrax homogenizer (Miccra D-8, ART modern Labortechnik GmbH, Müllheim, Germany) at 10,500 min^{-1} for 5 min. The solutions were put in ultrasonic bath (Transsonic 460/H, Carl Roth GmbH Co. KG, Karlsruhe, Germany) at a frequency of 35 kHz for 5 min.

4.3. Surface Tension Measurements

Surface tension (γ_L) of coating solutions was measured at room temperature (~21 °C), using the pendant drop method and Laplace–Young equation [28,29,52] with a drop shape analyzer (DSA1 v1.90, Kruss GmBH, Hamburg, Germany). Characteristic "pear shape" droplets were formed with a 500 µL syringe (Hamilton, Switzerland) and 1.991 mm needle (Kruss GmbH, Hamburg, Germany). Three replications were prepared for each solution and 10 measurements were taken on each replication.

Surface free energy (γ_S) of PTFE film was determined by the sessile drop technique by a drop shape analyzer. For this purpose, water for chromatography (Merck KGaA, Darmstadt, Germany), diiodomethane (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), and ethylene glycol (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were used as test liquids by placing 15 droplets of each test liquid on the PTFE film. Photographs were taken no longer than 5 s after surface–liquid contact. Surface tension values of the test liquids was given in the previous study of Senturk-Parreidt, Schmid, and Hauser [53]. The OWRK method was used for the calculation of γ_S of the PTFE film.

Determination of the polar and dispersive components of surface tension of liquid was carried out on PTFE film by using sessile drop arrangement with tangent method. Three replications were prepared for each solution and 10 measurements were taken on each replication.

4.4. Wettability Measurements

Wettability measurements were conducted according to the set up developed by Senturk-Parreidt, Schmid, and Hauser [53]. Droplets of 3 µL of the coating solutions were manually placed on strawberry epicarp, using a micropipette, which were kept perpendicular to the surface. Photographs were taken no longer than 5 s after surface–liquid contact. Twenty droplets of each coating solution were dispersed on the surface of the strawberry. Contact angle values of the droplets were measured with using ImageJ software [54] with the DropSnake plugin [55]. Adhesion coefficient (W_a), cohesion coefficient (W_c), and spreading coefficient (W_s) were calculated as stated in the previous studies of Ribeiro, Vicente, Teixeira and Miranda [27] and Casariego, Souza, Vicente, Teixeira, Cruz and Díaz [50]. The derived equations can be summarized as:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV} \times (1 + \cos\theta) \quad (1)$$

$$W_c = 2 \times \gamma_{LV} \quad (2)$$

$$W_s = W_a - W_c \quad (3)$$

4.5. Viscosity Measurements

Physica MCR 301 rheometer (Anton Paar GmbH, Graz, Austria) using a measuring system (CC27) with measuring cup (diameter 28.913 mm) and measuring bob (diameter 26.656 mm and length 40.025 mm) was used to measure the dynamic viscosity of the approximately 15 mL aliquots of coating solution at room temperature (~21 °C). Three measurements were performed for each solution with constant shear rate.

4.6. Emulsion Stability Measurements

4.6.1. Droplet Size Measurement with Laser Diffraction System

Three replications of 0.25–3.5% (5 levels) surfactants/oil-added 1.25% alginate + 2% glycerol samples were prepared. The air, which was present in the solutions, was removed with vacuum application. For this purpose, solutions were transferred into 20 mL glass vials and placed in an airtight vacuum chamber (designed by Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany) connected to a vacuum pump (N740, 40 L/min flow rate and 10mbar absolute vacuum, KNF Neuberger GmbH, Freiburg, Germany) and digital vacuum/barometer (GDH 200-14, Greisinger Electronic GmbH, Regenstauf, Germany).

The droplet size measurement was carried out with a Malvern Mastersizer S long bench model MSS, Software version 2.19, with the small sample dispersion unit MS 1 (volume max. 150 mL) and the 300 mm RF lens (Malvern Instruments Ltd., Worcestershire, UK). For the calculation of the droplet size, a polydispersity distribution was chosen as analysis model, and Mie Theory with the optical density for the wet phase, 1.33, and for the disperse part, 1.46, were set (Software Model: 3NHD). To arrange the sample concentration, the obscuration, which denotes the amount of laser light that has been lost by passing through the sample, was adjusted between 10% and 30%. The measurement was started after 2–3 min of dispersion time. The mean values of the droplet sizes were calculated as mean of three samples which were measured twice.

4.6.2. Optical Evaluation

Samples, which were prepared for droplet size measurements (0.25–3.5%, 5 levels) were used also in optical evaluations. A droplet was prepared between glass slides and examined in Morphologi G3 S microscope model 2410 (magnification: ×20 and ×50) with Software 8.11 (Malvern Instruments Ltd., Worcestershire, UK). Diascopic light was used with an intensity of 70–80%. The device can measure the particle size from 0.5 µm to 1000 µm. Optical microscope images with length scale were taken.

4.6.3. Creaming Index

Immediately after preparation, 25 mL coating solutions were placed in transparent, graduated cylindrical plastic tubes (diameter: 25 mm, height: 110 mm) and sealed with their plastic lids. Three replications were prepared for each coating solution. After a gentle agitation, tubes were left for 26 h at room temperature (~21 °C) without moving. Photos were taken at 0, 6, 12, 20, and 26 h with Nikon D3300 digital camera (Sendai Nikon Co., Tokyo, Japan) and Tokina 100 mm F2.8 Macro lens (Kenko Tokina Co., Ltd., Tokyo, Japan). The distance between the camera and the tubes was fixed for all measurements at 18.5 cm. Creaming was characterized by calculating creaming index (CI):

$$\mathrm{CI}\ (\%) \ = \ 100 \ \times \ \frac{H_S}{H_E} \tag{4}$$

where H_S is the height of serum layer and H_E is the total height of the emulsion [37].

4.7. Statistical Evaluations

Means and standard deviations were performed with Microsoft Excel 2010 (Microsoft Corp., Redmond, WA, USA). Graphics, statistical evaluations, etc. were performed with an open source program, R 3.3.2 for Windows. ggplot2 [56], grid [57], gridExtra [58], plyr [59], graphics [57] extrafont [60] packages for graphics; car [61], lsr [62], userfriendlyscience [63] packages for statistical analysis were used. One dimensional roots were found with rootSolve package during determination of dispersive components of liquid surface tensions [64,65]. The best fitting curves and their functions were determined with Table Curve 2D v5.01 (Systat Software Inc., San Jose, CA, USA).

5. Conclusions

In the present study, the effects of various coating components, as well as their concentrations on surface tension, and emulsion droplet size were investigated in order to design an effective edible coating with high wettability on hydrophobic nonpolar food surfaces. The results showed that addition of different sodium alginate and plasticizer (i.e., glycerol and sorbitol) concentrations did not alter the surface tension results. However, vegetable oils (i.e., sunflower, olive, rapeseed oils) and surfactants diminished the surface tension.

Surfactants are the most important factor affecting surface tension, and in this way the wettability of the coating solution on food products. The presence, type, and concentration of surfactants affected surface tension, size, as well as distribution of emulsion droplets differently. Span 80, tween 80, and tween 40 were found as the most effective surface active agents, respectively.

As a compromise between achieving maximum reduction of surface tension and using minimum amount of coating component, the use of 1.25% sodium alginate, 2% glycerol, 0.2% sunflower oil, and 1% span 80 in the formulation was recommended. The results previously presented have led us to conclude that the addition of tween 80 into the formulation decreased the droplet size and amount in the bulk solution.

This study provided an important methodology for the edible coating/film formulators. The findings might have many implications for edible coating/film research and industry applications. The constructed curves and functions enables coating formulators to conduct interpolation for the data points to infer values where no data are available. Further studies may concentrate on investigating the effects of suggested formulations on achieving uniform coating, coating thickness, and transport mechanisms.

Author Contributions: Tugce Senturk Parreidt, Michael Schott, and Markus Schmid conceived and designed the experiments; Tugce Senturk Parreidt performed the experiments and analyzed the data; Michael Schott, Markus Schmid, and Kajetan Müller contributed reagents/materials/analysis tools; Tugce Senturk Parreidt wrote the paper; and Michael Schott, Markus Schmid, and Kajetan Müller proofread the text.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; and in the decision to publish the results.

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Chapter VII.

Water Barrier Properties

This chapter contains a peer-reviewed article, "The development of a uniform alginate-based coating for cantaloupe and strawberries and the characterization of water barrier properties". It is published in the Open Access Journal "Foods" (Publication V). The author of this thesis is also the first author of the article. Authors contributions were specified in the article as: "Conceptualization: Tugce Senturk Parreidt, Markus Schmid and Kajetan Müller; investigation: Tugce Senturk Parreidt, Martina Lindner, and Isabell Rothkopf; methodology: Tugce Senturk Parreidt and Martina Lindner; supervision: Markus Schmid, and Kajetan Müller; writing—original draft: Tugce Senturk Parreidt and Martina Lindner; writing—review & editing: Tugce Senturk Parreidt; Martina Lindner; Isabell Rothkopf; Markus Schmid; Kajetan Müller".

Summary of the Publication-V

The transport of water in solid food materials inevitably causes deterioration of the overall quality of the food. The detrimental effect of water can vary with regard to the food itself, such as textural, organoleptic, chemical, or microbial changes.

As stated by the fruit producers, water leakage from the tissues of the fresh-cut fruits (e.g., fresh-cut melon, watermelon, pineapple, etc.) and its accumulation at the bottom of the package is a very important problem that decreases the demand for the product and its sellability.

The aims in this chapter were twofold, and each interrelated with the other: The first part of this paper shed new light on uniform, continuous alginate coating layer either on a very hydrophilic or a hydrophobic surface. The previously formulated sodium alginate-based coating solution (1.25% sodium alginate, 2% glycerol, 0.2% sunflower oil, 1% span 80, 0.2% tween 80, (w/w)) was used in this study. A uniform edible film formation was achieved (with a thickness of 0.187±0.076 mm and 0.235±0.077 mm for cantaloupe and strawberries, respectively) with an additional immersion step into a calcium lactate solution at the very beginning of the coating process. Cross-section images of alginate-coated fruits evidenced the achieved coating uniformity by the novel coating method.

The second aim was to investigate the effects of coating on the water barrier characteristics of fresh-cut cantaloupe and strawberries. For this purpose, various moisture barrier tests (weight loss (%), water desorption as a means of mass loss during

RH decrease, water activity, water vapor resistance) were conducted. The coating application significantly reduced the water loss of the cantaloupe pieces. However, no significant effect was observed in water vapor resistance (WVR) results and weight change measurements in a climate chamber (80% → 60% RH at 10 °C). It is an interesting observation that alginate-based edible coating reduced water loss of hydrophilic surfaces when the fruit pieces were stored in bulk storage (piles in the packages). However, the effect could not be observed when a detailed evaluation was conducted on each small piece. Different water transport mechanisms were influential for single pieces and pieces in a pile. It might be explained by the lack of homogeneity of the hydrophilic surfaces of cut pieces, which had water channels oriented outwards. Most likely, water loss did not originate from water vapor transmission but the transport of liquid water in combination with the contact pieces. Due to forming porous but not fully coherent film, other effects such as mechanical pressure, energy and capillary effects directed the liquid water transfer. Therefore, the current experimental setup of the WVR and climate chamber tests should be revised.

External packaging conditions (closed, perforated, open packages) were not significantly effective on water activity (a_w) values of cantaloupe but effective on strawberry values. In general, the coating application promoted the water loss of strawberry samples. The pronounced negative impact can be explained by the adverse effect of the water-based coating on the surface waxes of strawberries.

In the last step of the study, the transfer of water vapor through the stand-alone film (prepared using the same coating formulation) was investigated. Due to the complexity of the multi-component food systems, measuring the water barrier characteristic of the stand-alone film could give a researcher the chance to observe the effect in relatively ideal conditions. The water vapor transmission rate (WVTR) of the stand-alone film was determined (2131 g·100μm/(m²·d·bar) under constant environmental conditions (23 °C, 100% → 50% RH).

In conclusion, alginate-based coating treatment shows a promising effect on hydrophilic cut surfaces, especially on porous food samples, but the effect on waxy surfaces should be investigated in more detail. Moreover, future studies should attempt to develop relatively more complex models for porous-hydrophilic, or waxy outer layered-hydrophobic surfaced food samples to include the effects on the surface characteristics and other water transport factors such as gravity, capillary forces, etc.

foods

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Article

The Development of a Uniform Alginate-Based Coating for Cantaloupe and Strawberries and the Characterization of Water Barrier Properties

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Received: 25 May 2019; Accepted: 5 June 2019; Published: 11 June 2019

Abstract: Water loss, gain or transfer results in a decline in the overall quality of food. The aim of this study was to form a uniform layer of sodium alginate-based edible coating (1.25% sodium alginate, 2% glycerol, 0.2% sunflower oil, 1% span 80, 0.2% tween 80, (*w*/*w*)) and investigate the effects on the water barrier characteristics of fresh-cut cantaloupe and strawberries. To this end, a uniform and continuous edible film formation was achieved (0.187 ± 0.076 mm and 0.235 ± 0.077 mm for cantaloupe and strawberries, respectively) with an additional immersion step into a calcium solution at the very beginning of the coating process. The coating application was effective in significantly reducing the water loss (%) of the cantaloupe pieces. However, no significant effect was observed in water vapor resistance results and weight change measurements in a climate chamber (80%→60% relative humidity (RH) at 10 °C). External packaging conditions (i.e., closed, perforated, and open) were not significantly effective on water activity (a_w) values of cantaloupe, but were effective for strawberry values. In general, the coating application promoted the water loss of strawberry samples. Additionally, the water vapor transmission rate of stand-alone films was determined (2131 g·100 µm/(m^2·d·bar) under constant environmental conditions (23 °C, 100%→50% RH) due to the ability to also evaluate the efficacy in ideal conditions.

Keywords: edible coating; edible film; sodium alginate; fruits; coating uniformity; dipping; water loss; water activity; water vapor resistance; water sorption

1. Introduction

Fruits and vegetables supply dietary fibers, vitamins, minerals, and phytochemicals that have functions, such as phytoestrogens, antioxidants, anti-inflammatory agents, etc. [1,2]. Fruit and vegetable consumption must be increased to optimize nutrition uptake, promote health due to the strong link between fruit and vegetable intake, and decrease risk of cancer, heart disease, stroke, cataracts, diverticulosis, chronic obstructive pulmonary disease, and hypertension [3]. Due to the increasing demand of consumers for fresh, healthy, additive-free, and ready food products with reduced preparation time, the fresh-cut fruits and vegetables market has grown perpetually in the

European Union (EU) [4,5]. According to the 2015 market research report presented by Euromonitor International [6], a 19% per capita volume growth for fresh-cut fruit in Western Europe was recorded. Fresh-cut produce are fruits and vegetables that have been cleaned, peeled, cored, chopped, sliced, diced, and packaged. As a result of these physical processes, fresh-cut products are more perishable and susceptible to physiological–biochemical changes and microbial degradation [7,8]. On top of these limitations, consumers expect fresh-cut products to maintain characteristics such as fresh-like appearance, taste, and flavor longer without the use of preservatives [9].

A natural alternative to maintain the quality characteristics, diminish the undesired physicochemical changes, and prolong the shelf-life of fresh-cut produce during the storage period, is the usage of edible barrier materials (i.e., polysaccharides, proteins, and lipids) [10,11]. Lipids constitute the most resistant edible coatings against moisture transfer owing to their hydrophobic character [12,13]. However, due to the presence of consumer concerns about lipid consumption and the creation of waxy mouth-feel [14], lipid-based coatings are not preferred as a base material for the coating of fresh-cut fruits and vegetables.

Alginate is a marine-origin polysaccharide extracted from brown algae [15,16]. It is classified as a GRAS (generally regarded as safe) substance by the US Food and Drug Administration (FDA), listed as an authorized food additive by the European Commission (EC), and used as an emulsifier, stabilizer, thickener, and gelling agent in the food sector [17,18]. Since alginate is a polyuronide, a natural ion exchanger, the addition of certain bivalent cations (e.g., Ca^{2+}, Sr^{2+}, Ba^{2+}) into an alginate solution induces conformational changes such as the formation of the egg-box model [19] and leads to a gel formation through the bounding of bivalent ions between two chains of alginate and the formation of divalent salt bridges [20–23]. The immersion of an alginate film/coating into a calcium solution initiates two type of reactions: (i) insolubilization of the alginate film, which is induced by the diffusion of multivalent ions and the formation of linkage; (ii) the dissolution of alginate by the solution [24,25]. The dominancy of the dissolution process is suppressed by increasing the concentration of the bivalent ion [24]. Moreover, the application method of the bivalent ion has an impact on film thickness; for instance, the immersion of the alginate gel into a crosslinking solution leads to thinner film formation compared to the direct addition of the crosslinking agent into the alginate solution [26]. Alginate-based coatings and films crosslinked with Ca^{2+} preserve the quality characteristics and extend the shelf life of the food products by acting as a barrier to flavor volatiles and gases, impeding the loss of moisture, preventing microbial contamination and fat oxidation, maintaining textural stability, and preventing surface discoloration [27–30].

Recently, composite or multicomponent films have been designed as bilayers or emulsions to benefit from the complementary advantages of hydrophilic and hydrophobic compounds together [10,31]. Due to the requirement of four preparation stages (i.e., two casing and two drying stages), bilayer films have not been frequently focused on. On the other hand, there are numerous studies on the preparation of emulsion systems with hydrocolloidal components and dispersed lipid components such as vegetable oils, waxes, or fatty acids [31].

Water is a predominant component and constitutes 70–90% of the weight of fruits and vegetables [32]. The water contents of cantaloupe and strawberries were determined to be 92.8% w.b. (wet basis) and 90.7% w.b., respectively [33–35]. There are three states of water in food products: (i) free water (acts as a solvent or dispersing agent), (ii) adsorbed water (is held tightly), and (iii) water of hydration (bound chemically) [36]. The microbial stability, chemical and enzymatic reaction kinetics, textural properties, and physical stability of food are strongly related to the gain or loss of moisture in the food system and consequently end up with a reduction in shelf-life [14,37]. In other words, water loss, which is mainly caused by transpiration, is the major cause of food deterioration as a result of inducing an unappealing appearance (wilting, shriveling, etc.), textural alterations (softening, crispness, etc.), and a loss of nutritional quality and marketable weight [38,39]. Transpiration is a mass transport process, i.e., water vapor transfer from the food surface to the surrounding air [39]. When there is a water activity (a_w) gradient between the food product and its environment, moisture transfer

(transfer of liquid water and vapor) can occur from higher water activity (i.e., fruits) to lower water activity (i.e., packaging environment) until the thermodynamic equilibrium is reached [13,14,40,41]. Three phenomena occur during the mass transfer of water in foods. These are: (i) water transport within the product; (ii) water vapor transport between the surface of the product and the surrounding environment; and (iii) equilibrium between the water content of the food and the water content of the surrounding environment [42].

The rate of transpiration is directly proportional to the partial pressure gradient and transfer areas but inversely proportional to the surface resistances [39]. When viewed from this aspect, edible barriers such as coatings and films enhance the surface resistance of the produce. It is, therefore, necessary to understand the effect of an edible coating on water loss to select the most suitable coating formulations, conditions for packaging, and storage life.

Fruit manufacturers state that water accumulation at the bottom of the fresh-cut fruits' packaging is a very important problem, decreases the value of the product, and discourages customers from buying. The fruit leakage can be observed especially in fresh-cut melon, watermelon, pineapple, etc. The objective of this study is to evaluate the efficacy of the previously optimized alginate-based coating formulation [43] based on the water barrier properties of coated fresh produce, i.e., strawberry and fresh-cut cantaloupe. To this end, coating uniformity was achieved with the addition of an extra immersion step into a calcium lactate solution initially before the coating step. To the best of the authors' knowledge, this application method has not been utilized so far for the products that could not be uniformly coated with an alginate-based edible coating due to the high moisture content of their surface (hydrophilic surface, fresh-cut cantaloupe). In addition to this, the uniform gel-forming performance of the coating was also tested on a very hydrophobic surface (i.e., strawberry). Afterwards, the water loss, water activity, water vapor resistance characteristics of coated (with the new method, the extra immersion in calcium lactate solution) and uncoated products were measured and compared throughout the storage to identify whether the coating prevents the fruit from drying out. Furthermore, the differences in the mass losses of coated and uncoated products caused by a gradual decrease in relative humidity (RH) were monitored. Additionally, the water vapor transmission rate (WVTR) of stand-alone alginate films was measured for the assessment of barrier properties under ideal conditions.

2. Materials and Methods

2.1. Materials

Sodium alginate (Manugel GHB, FMC Biopolymer Co., Philadelphia, PA, USA), glycerol (Sigma–Aldrich Chemie GmbH, Steinheim, Germany), sunflower oil (Rewe Bio, Rewe Markt Gmbh, Köln, Germany), tween 80 (polyoxyethylenesorbitan monooleate) (Sigma–Aldrich Chemie GmbH, Steinheim, Germany), span 80 (sorbitan monooleate) (Sigma–Aldrich Chemie GmbH, Steinheim, Germany), calcium L-lactate hydrate (Sigma–Aldrich Chemie GmbH, Steinheim, Germany) were used in coating formulations.

Whole cantaloupe (*Cucumis melo* var. *cantalupensis*) and strawberries (*Fragaria* × *ananassa* D.) were purchased from Krohns Obst-Gemüse-Express (Berlin, Germany), Schweiger Obst-und Gemüsehandel (Freising, Germany), and a local market in Freising (Germany). Samples were transported directly to the laboratory.

2.2. Preparation of Food Sample

Fruits with no external defects were selected for the experiments. Experiments were conducted always at the same day of the fruit purchase and samples were stored at 4 °C room until used.

Cantaloupes were peeled, cut into two halves, the seeds were removed, and the remaining fruits were cut into pieces in accordance with the requirements of the experiments. Due to the large number of samples (in water loss (%) and water activity determination), or the easiness of capturing good stereomicroscope images (in thickness determination), cuboid pieces (14.1 ± 1.1 g, $n = 20$, ≈4 × 2 ×

2 cm^3) were prepared. For the experiments (i.e., water desorption as a means of mass loss during RH(%) decrease and water vapor resistance tests) in which special geometry was necessary for the experimental setup, ease of calculations and/or specified devices, cylinder pieces were cut as described in the relevant sections.

Strawberries were not hulled, cored or cut, but used as whole fruit. They were assigned to the experiments in accordance with the requirements of the associated experiments; e.g., due to the small sampling cups of the automated water sorption analyzer, strawberries with similar, small volumes were chosen. Pieces were transferred into a large food container with a lid and assigned to the treatments randomly.

2.3. Preparation of Edible Coating

Coating solution was prepared according to a previous study by Senturk Parreidt, Schott, Schmid, and Müller [43]. Sodium alginate (1.25%, *w*/*w*) was dissolved in distilled water with continuous stirring (magnetic stirrer (500 rpm)) at 70 °C until complete dissolution and a clear solution was achieved. Two percent glycerol (*w*/*w*) was added into the formulation to increase coating flexibility. Surface active agents (1% span 80 (*w*/*w*) and 0.2% tween 80 (*w*/*w*)) were incorporated into the coating formulation to improve adhesion of the coating on the product. Sunflower oil (0.2%, *w*/*w*) was added as a lipid source to increase water barrier characteristics. The concentration of oil was kept low since target food materials are fruits and consumer acceptance against high oil-incorporated fruit may be low. Subsequent to the continuous stirring with a magnetic stirrer (IKA Werke GmbH & Co. KG, Staufen, Germany) to achieve the dissolution of ingredients, mixtures were homogenized and emulsified using an ultra-turrax homogenizer (Miccra D-8, ART modern Labortechnik GmbH, Müllheim, Germany) at 10,500 min^{-1} for 5 min. The solutions were degassed at room temperature (~20 °C) in an ultrasonic bath (Transsonic 460/H, Carl Roth GmbH Co. KG, Karlsruhe, Germany) at a frequency of 35 kHz for another 5 min.

To induce the gelling mechanism and crosslinking reaction, 2% calcium lactate was dispersed in distilled water.

2.4. Coating Application

2.4.1. Conventional Alginate Coating

Coating applications were performed according to the process parameters (i.e., dipping and draining periods) stated by Senturk Parreidt, Schmid, and Müller [28] and illustrated in Figure 1a. Fruits were immersed into the alginate solution for 2 min and the excessive hydrocolloid solution was drained for 1 min. Afterwards, coated samples were immersed into a 2% calcium lactate solution for 2 min to achieve gel formation, and the residual solution was allowed to drip off for 1 min. Subsequent to the coating process, strawberries were dried at room temperature (~20 °C) for 35 min. However, coated fresh-cut cantaloupe pieces were not allowed to dry to keep their juicy surface image. Preliminary sensorial evaluations showed that consumers preferred to see watery, juicy fresh-cut cantaloupe samples instead of a cut surface covered with a relatively dry gel formation.

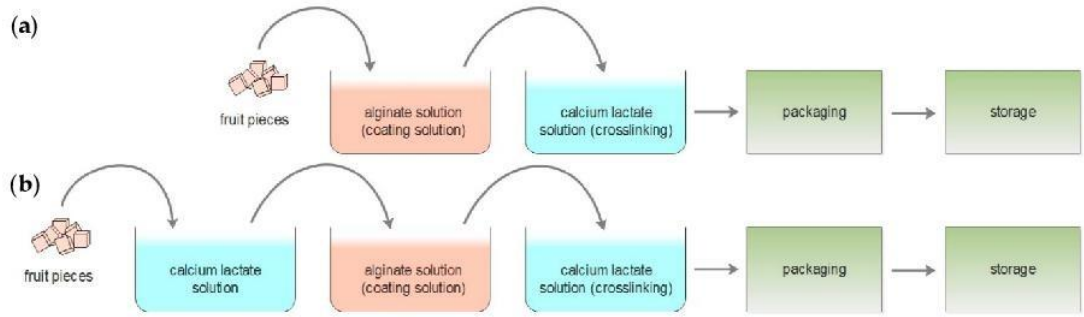

Figure 1. Schematic illustration of coating methods: (**a**) conventional dipping method to coat food products with alginate-based coatings; (**b**) novel dipping method with the incorporation of an extra immersion step into a calcium lactate solution.

2.4.2. Novel Alginate Coating

To achieve a uniform coating layer, additional dipping and draining processes were included initially before the conventional coating process (Figure 1b). Fruits were dipped in a calcium lactate solution for 2 min and the residual solution was allowed to drip off for 1 min. Afterwards, the same coating procedure, which was described in the conventional alginate coating section, was applied.

It is important to note that a novel coating method was used to test water barrier characteristics.

2.5. Coating Uniformity and Thickness

Coating uniformity, adherence to the fruit surface, and coating thickness were monitored using a stereomicrograph (Leica MZ16, Leica Mikrosysteme Vertrieb GmbH, Bensheim, Germany) by randomly taking five measurements at different points of the cross section of 10 samples ($n = 10 \times 5$). The coating uniformity of samples, which were coated with conventional and novel alginate coating methods, and coating thicknesses were determined and compared.

2.6. Storage Conditions

Wills, McGlasson, Graham, and Joyce [2] and Jiang and Fu [44] reported that a RH of 90% is often considered as the best compromise condition for the storage of fruit. In the present study, a 90% RH level was chosen as the storage condition. The storage temperature was set to 10 °C, the minimum operating temperature for 90% RH storage in a constant climate chamber (APT.Line KBF, WTB Binder Labortechnik GmbH, Tuttlingen, Germany).

2.7. Weight Loss (%)

Fruits after coating and dripping were packed in aPET (amorphous polyethylene terephthalate) transparent boxes with an attached lid (250 mL, 117.25 mm × 112.5 mm × 41 mm, thickness = 250 µm, item no. 80,441, Meier Verpackungen GmbH, Hohenems, Austria). Coated and uncoated fresh-cut cantaloupe and strawberries were kept on shelves inside a constant climate chamber at 10 °C and 90% RH over a storage period of 14 days. Weighing was done using an analytical laboratory scale (Sartorius Lab Instruments GmbH & Co. KG, Goettingen, Germany) with 0.001 g sensitivity. To neutralize the static electricity at the work area, which originated from plastic packaging, and to increase the accuracy of the results, an ionizing blower (18 V, AC, 2 W, Sartorius Lab Instruments GmbH & Co. KG, Goettingen, Germany) was used during packaging and weighing.

Weight loss was determined in each package at different sampling dates by a percentage of weight loss (Equation (1)) with respect to day 0 ($weight_{initial}$). Measurements were performed in four replicates ($n = 4$). Weight loss graphs were plotted with respect to time. Since a comparison was made using both

coated and uncoated samples from the same batch, the contribution of the respiration rate to weight loss could be neglected.

$$Weight\,loss\,(\%) = \frac{Weight_{initial} - Weight_{final}}{Weight_{initial}} \times 100 \quad (1)$$

2.8. Water Desorption as a Means of Mass Loss During Relative Humidity Decrease

The percentage of the mass change of coated and uncoated food samples was measured as a function of time by means of an SPSx-1μ automated water sorption analyzer (ProUmid GmbH & Co. KG, Ulm, Germany). Subsequent to the removal of the thick rind (exocarp) and seeds, cantaloupe cylinders were prepared from fleshy mesocarp using a metal pastry cutter (diameter = 4.19 cm, height = 1.9 cm). In the case of strawberries, relatively similar sized cone-shaped samples were chosen. Samples were placed in individual aluminum weighing trays (diameter = 64 mm) on the sample carousel arranged in a circle and equilibrated at 80% RH and 10 °C. Afterwards, the relative humidity of the chamber was gradually decreased (5%) while the temperature was kept constant. Every next humidity decrease was induced when equilibrium was reached. Equilibrium was defined by less than 0.01% mass change per 75 min (equals 5 weighing cycles). The weight of the samples was recorded at 15 min intervals during 236 h with 0.001 mg sensitivity until 60% RH was reached.

2.9. Water Activity (a_w)

Subsequent to the fruit coating (in the case of strawberry, also drying), fruits were packed in (i) closed, (ii) perforated, and (iii) open aPET transparent boxes. Perforation was provided by punching nine holes on the top surface of the packages using a sewing needle (diameter = 2 mm, Prym Consumer Europe GmbH, Stolberg, Germany).

The water activity of the samples was measured at 20 ± 0.2 °C using a dew point water activity meter (Aqualab 4TEV, METER Group AG, Munich, Germany) with the accuracy of ±0.003. The device was calibrated using two standards (i.e., 6.0 Molal NaCl in H_2O (a_w = 0.760) and 0.5 Molal KCl in H_2O (a_w = 0.984)). After calibration, samples were cut in the form of plastic sample cups and placed inside the measuring chamber.

2.10. Water Vapor Resistance (WVR)

The WVR of coated and uncoated strawberries and fresh-cut cantaloupe pieces was evaluated gravimetrically as described by Poverenov et al. [45] using Equation (2). Subsequent to the removal of the thick rind (exocarp) and seeds, cantaloupe cylinders were prepared from fleshy mesocarp using a metal pastry cutter (diameter = 4.19 cm, height = 1.9 cm). In the case of strawberries, relatively similar sized cone-shaped samples were chosen (diameter = 2.6 ± 0.3 cm, height = 3.0 ± 0.2 cm, n = 20). Water vapor resistance is defined as follows:

$$WVR = \left[\frac{\left(a_w - \frac{\%RH}{100}\right) \times p_{WV}}{R \times T}\right] \times \left(\frac{A}{J}\right) \quad (2)$$

where WVR is s/cm, a_W is the water activity of strawberries or fresh-cut cantaloupe pieces, $\%RH$ is the relative humidity of the climatic chamber (=90%), p_{WV} is the saturated water vapor pressure at 10 °C (9.21 mmHg [46]), R is the specific gas constant for water vapor (461.5 J kg^{-1} K^{-1} = 3461.544 mmHg cm^3 g^{-1} K^{-1}), T is the temperature of the climatic chamber (283.15 K), A is the surface area of the food products (38.8 cm^2 for cantaloupe and 13.3 ± 2.0 cm^2 for strawberry), and J is the slope of weight loss in food product versus storage time (g/s). The area of cantaloupe pieces was assumed as cylinders, while the shapes of strawberries were assumed as cones. J and a_w were measured using devices that were previously defined in Sections 2.8 and 2.10.

Coated and uncoated pieces were placed in the middle of individual, plastic trays (diameter = 9 cm) and placed on shelves inside a constant climatic chamber (APT.Line KBF, WTB Binder Labortechnik GmbH, Tuttlingen, Germany) at 10 °C and 90% RH over a storage period of 14 days. The RH and temperature of the climatic chamber were also recorded over time via portable data logger to monitor the environmental conditions.

Control tests with uncoated fresh-cut cantaloupe and strawberries were performed to determine the resistance factor of the uncoated fruits to water vapor. Since comparison was made using both coated and uncoated samples from the same batch, the contribution of respiration rate to weight loss could be neglected.

2.11. Water Vapor Permeability (P) of Alginate Films

Aqueous alginate solutions were prepared with the same method and ingredients as previously described in Section 2.3. Different amounts of solutions (10, 15, 20, 30 g solution/plate) were cast on various sizes of glass and plastic Petri plates, and subsequently, a calcium lactate solution was sprayed on them. From that, films were obtained following the drying at 23 °C and 50% RH for 30 days in a climate chamber. Since RH was kept at a constant level in the chamber, films did not dry during measurements.

Water vapor transmission rate (WVTR) was measured with the gravimetric method according to DIN 53122-1 and using the modified ASTM method E 96–95 [47,48]. Cups were filled with distilled water, then stored in a climate chamber (Binder GmbH, Tuttlingen, Germany) at 23 °C and 50% RH. The initial weight of the cups and the weight during storage (each 1 h) was measured (Mettler H315; Mettler–Toledo GmbH, Gießen, Germany) until the weight gain stagnated. Three replicates of each of the seven specimens in different thicknesses (52–122 µm) were tested. The WVTR was calculated using the following Equation (3):

$$WVTR = \frac{24}{\Delta t} \cdot \frac{\Delta m}{A} \cdot 10^4 \qquad \left(\frac{\text{g}}{\text{m}^2 \cdot \text{d}}\right) \tag{3}$$

where Δt (h) is the time between two weight measurements of which Δm is calculated, Δm (g) is the weight difference of two successive weight measurements, and A (cm^2) is the sample area. To make these values comparable for different film thicknesses (d), the WVTR is multiplied with the thickness of the sample (Q_{100}):

$$Q_{100} = WVTR \cdot d \qquad \left(\frac{\text{g} \cdot 100\,\mu\text{m}}{\text{m}^2 \cdot \text{d}}\right) \tag{4}$$

As other researchers measured the $WVTR$ at different partial pressure differences (Δp), this information is further transformed into the permeability values p:

$$P = \frac{Q_{100}}{\Delta p} \qquad \left(\frac{\text{g} \cdot 100\,\mu\text{m}}{\text{m}^2 \cdot \text{d} \cdot \text{hPa}}\right) \tag{5}$$

Strictly speaking, this transformation is not valid, as the law of Henry does not apply for such polar polymers for water vapor but is accepted as a simplification [49].

2.12. Statistical Evaluation

All experiments were performed in quadruplicate (n = 4). The mean and standard deviation were determined in Microsoft Excel 2010 (Microsoft Corp., Redmond, WA, USA). Graphics and statistical evaluations were performed using R 3.3.2 for Windows with the packages ggplot2 [50], grid [51], gridExtra [52], car [53], and lsr [54]. The types of statistical tests applied to the results were denoted individually in the relevant results and discussion sections.

3. Results

3.1. Coating Uniformity and Thickness

Figure 2a–f illustrates the stereomicroscope images of uncoated and coated (both conventional and novel coating method) products, which generally allows for a qualitative evaluation of coating uniformity. As can be seen in Figure 2b, the conventional coating method formed thicker gels especially on the edges/corners and thinner structures on the middle. This issue is most likely caused by a lack of the adhesion ability of the alginate solution on the highly hydrophilic cut surface. Figure 2e shows that the conventional coating method had better adhesion on the strawberry epicarp, thus, the coating spread more uniformly compared to the surface of the cantaloupe. However, as can be easily realized in Figure 2f, initial immersion into a calcium solution led to a gel formation that completely covers the low and high points (e.g., seed (achene) holes), forming a smoother gel surface.

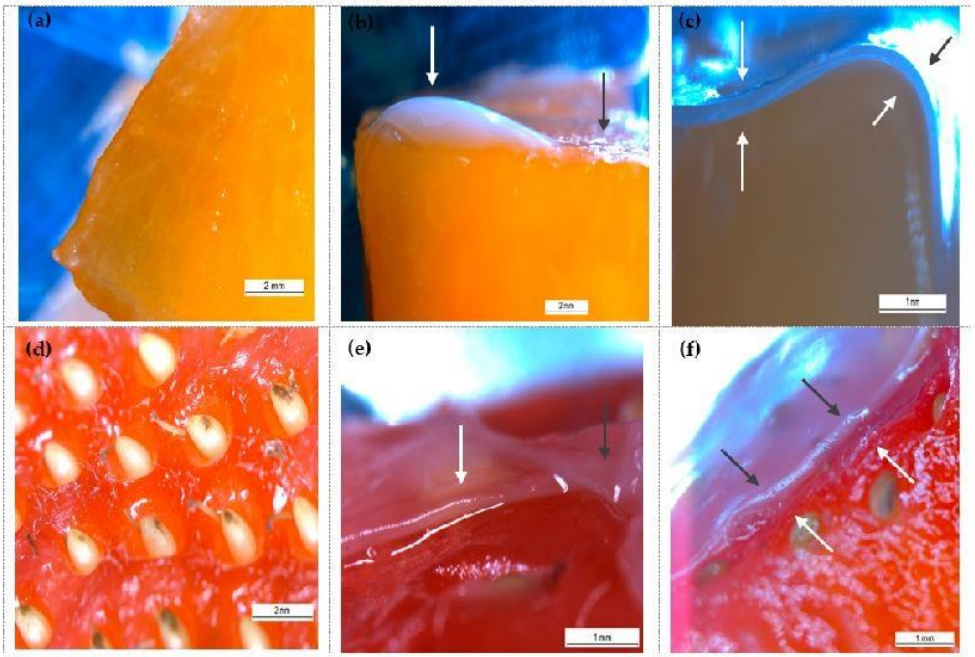

Figure 2. Stereomicroscope images of uncoated and coated fruits: (**a**) surface of uncoated cantaloupe; (**b**) cantaloupe surface coated with conventional method; (**c**) cantaloupe surface coated with novel method; (**d**) surface of uncoated strawberry; (**e**) strawberry surface coated with conventional method; (**f**) strawberry surface coated with novel method. Coating solution: 1.25% alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80. Gel formation was accomplished with a 2% calcium lactate solution. The color of the arrows does not designate anything and was only changed to increase visibility.

Cross-sections of alginate-coated cantaloupe (Figure 2c) and strawberry images (Figure 2f) evidence the achieved coating uniformity by the novel coating method. The initial dipping into the calcium lactate solution generates a thin calcium lactate layer on the surface of the cut cantaloupe. In this way, alginate molecules can interact directly with calcium and form a gel on the surface. As is evident from the figures, the addition of an extra immersion step into a calcium solution led to thicker and more homogeneous gel formation. Average thicknesses of applied alginate coatings were measured as 0.187 ± 0.076 mm and 0.235 ± 0.077 mm for cantaloupe and strawberries, respectively.

3.2. Relative Weight Loss during Storage at 10 °C, 90% RH

Variations in water loss values of coated and uncoated products during 10 °C, 90% RH storage are presented in Figure 3. To eliminate the difference in the sample sizes, results were expressed as a percentage (%) of weight loss.

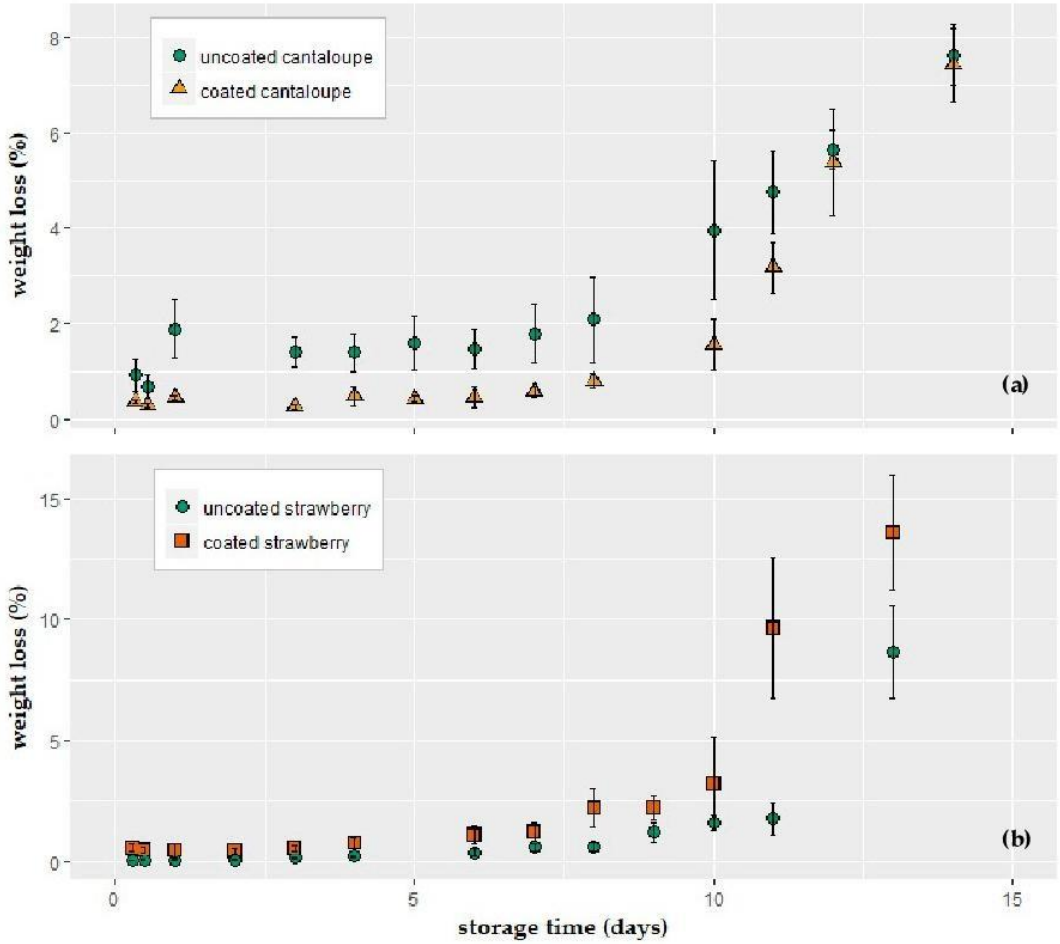

Figure 3. Weight loss of (**a**) fresh-cut cantaloupe; (**b**) strawberry fruits coated with an alginate-based solution (1.25% alginate + 2 glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80 and 2% calcium lactate (crosslinking agent)) during storage at 10 °C and 90% relative humidity (RH).

The pattern of water loss increase was similar for all experimental groups; the weight loss (%) of cantaloupe and strawberry samples increased with storage time. According to the conducted two-way ANOVA tests, coating application, storage time, and their interactions all had significant effects ($p < 0.05$) on the amount of water loss in both the cantaloupe and strawberry samples.

The coating process decreased the weight loss of the fresh-cut cantaloupes significantly compared to uncoated samples (Figure 3a). Post-hoc comparisons using the Tukey HSD (Honestly Significant Difference) test indicated that from day 0 to day 8, there were no significant differences between the samples in the same treatment group ($p > 0.05$).

In contrast to the cantaloupe application, two-way ANOVA tests revealed that the coating process significantly increased the water loss in the strawberry samples. Particularly after 10 days of storage, the difference in water loss increased drastically.

3.3. Water Desorption as a Means of Mass Loss During Relative Humidity Decrease

The relationship between the time and mass loss (%) of the samples obtained with and without coating application during 80%→60% RH is given in Figure 4. It is a similar experiment to those presented in the previous section. In theory, the sorption measurement device enables one to examine each sample piece individually, allows one to observe the effect of variable RH, and provides a comparison with the previous results.

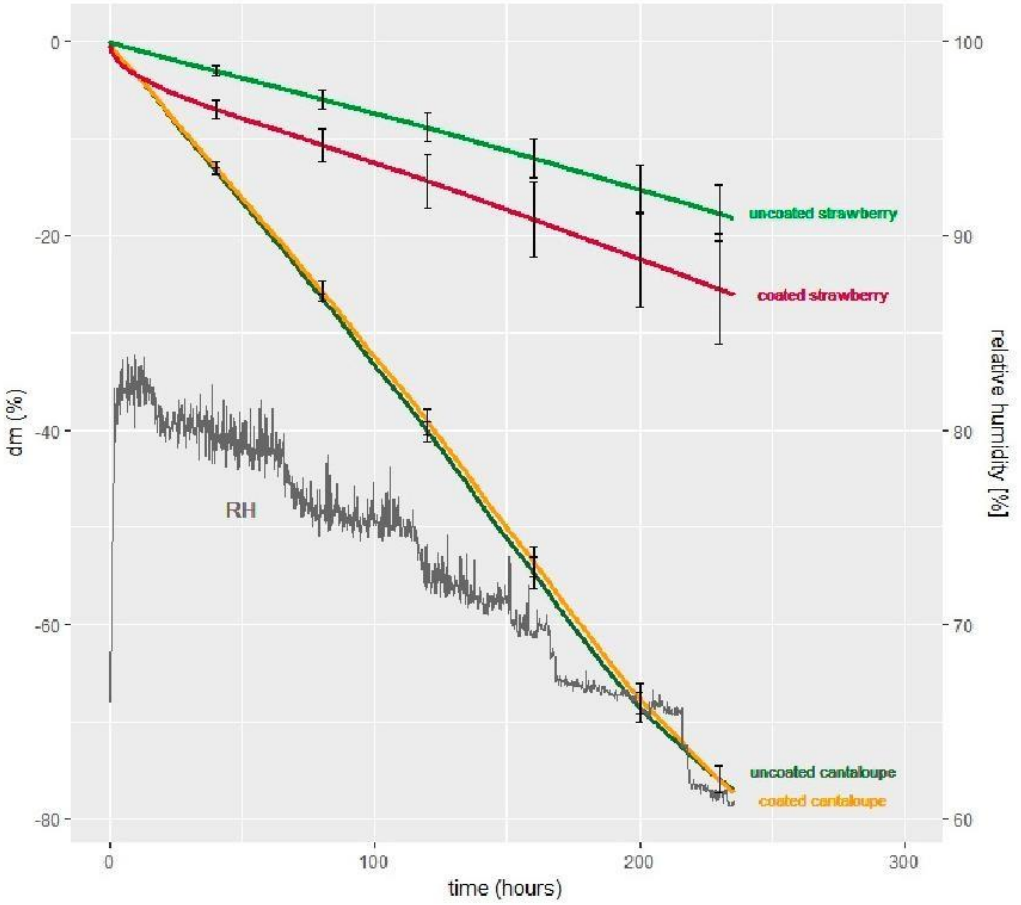

Figure 4. Mass loss (dm, %) of coated and uncoated strawberries and fresh-cut cantaloupes at 10 °C during gradual RH decrease (80%→60% RH) (n = 4). (Coating solution: 1.25% alginate + 2 glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80 and 2% calcium lactate (crosslinking agent)).

The masses of the strawberry samples (independent of being coated or not) decreased linearly with time. However, the slope of the decreasing functions of the coated sample was smaller than the uncoated samples ($m_{coated} < m_{uncoated} < 0$). It is interesting to note that at the very beginning of the experiment (<20 h), coated strawberries showed a drastic decrease in mass loss followed by a relatively linear decrease, while uncoated samples had a linear decrease throughout the entire process.

According to Figure 4, there is, however, no distinguishable differences between coated and uncoated cantaloupe samples. On the contrary, it can be clearly seen from the graph that coated strawberries had higher mass loss compared to uncoated samples. This is also in agreement with Figure 3. To perform statistical evaluations, the curves presented in Figure 4 were assumed linear, and the average drying speed ($|dm/dt|$, $\%{\cdot}h^{-1}$) was calculated using the boundary conditions (i.e., t_1 = 0 h and t_2 = 235 h) presented in Table 1. The Kruskal–Wallis rank–sum test and pairwise comparisons using the Wilcoxon rank–sum test revealed that there was no statistical difference between uncoated

and coated cantaloupes; however, both coated and uncoated strawberry samples were significantly different ($p < 0.05$).

Table 1. Average drying speed (|dm/dt|, %·h^{-1}) (boundary conditions; $t_1 = 0$ h and $t_2 = 235$ h) of coated and uncoated strawberries and fresh-cut cantaloupes at 10 °C during gradual relative humidity (RH) decrease (80%→60% RH) ($n = 4$). (Coating solution: 1.25% alginate + 2 glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80 and 2% calcium lactate (crosslinking agent)).

Drying Speed [1,2] (|dm/dt|) (%·h^{-1})			
Fresh-Cut Cantaloupe		Strawberry	
Uncoated	Coated	Uncoated	Coated
0.33 ± 0.01 $_a$	0.33 ± 0.01 $_a$	0.08 ± 0.01 $_b$	0.11 ± 0.02 $_c$

[1] For average drying speed calculations, the curves (dm (%) versus time, Figure 5) were assumed linear. [2] For each group, similar small letters (subscript) in rows were not significantly different $p \leq 0.05$.

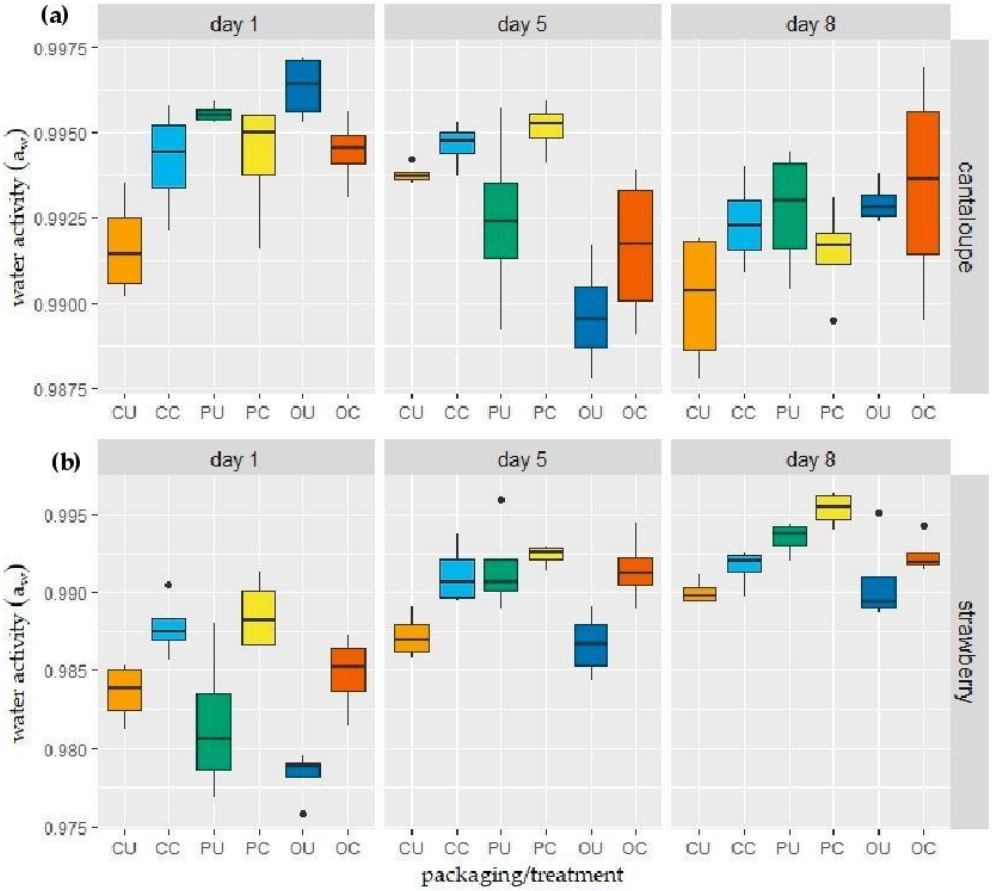

Figure 5. Box and whisker plots (median, min/max values, outliers) of water activity values of uncoated and coated (**a**) fresh-cut cantaloupe; (**b**) strawberry samples during storage at 10 °C and 90% RH. Alginate-based coating solution consists of 1.25% alginate + 2 glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80 and 2% calcium lactate (crosslinking agent). CU: closed package–uncoated; CC: closed package–coated; PU: perforated package–uncoated; PC: perforated package–coated; OU: open package–uncoated; OC: open package–coated.

3.4. Water Activity (a_w)

Throughout the duration of moisture transfer between a food and its environment, water activity as well as the moisture content of the product become a function of time [14]. Hence, the water activity values of coated and uncoated fresh-cut cantaloupe and strawberry samples, packed in closed, perforated, and open aPET transparent boxes were determined on the 1st, 5th, and 8th storage days (Figure 5).

For fresh-cut cantaloupes (Figure 5a), statistical evaluations (two-way ANOVA) revealed that the difference in packaging applications did not cause a significant change between a_w results ($p > 0.05$); however, storage time and the interaction of the type of packaging × storage time had a significant effect on a_w results ($p < 0.05$). The water activity values of cantaloupe samples on day 1 were significantly higher than day 5 and day 8. It can be concluded that the amount of water in the food product that can take part in chemical and physical reactions slightly decreased.

For strawberries (Figure 5b), results showed an increasing pattern as the storage period prolonged. Despite the drying of coated products, coating increased the available, unbound water amount. Two-way ANOVA results revealed that both the time, type of packaging, and their interaction had significant effects on a_w results ($p < 0.05$). Moreover, the samples stored in perforated packages showed a drastic increase.

3.5. Water Vapor Resistance (WVR) of Edible Coating

Table 2 compares the results obtained from the WVR analysis of coated/uncoated fresh-cut cantaloupe and strawberry samples. The WVR of the fruit surfaces decreased significantly after the second day of storage.

Table 2. Water vapor resistance (WVR) (s/cm) of uncoated and coated fresh-cut cantaloupe and strawberry samples throughout a 10-day storage period ($n = 4$). (Coating formulation: 1.25% alginate, 2% glycerol, 0.2% sunflower oil, 1% span 80, 0.2% tween 80).

Experiment Day	Fresh-Cut Cantaloupe [1,2]		Strawberry [1,2]	
	Uncoated	Coated	Uncoated	Coated
Day 2	7.05 ± 0.39^{A}	6.77 ± 0.33^{A}	$14.61 \pm 3.36^{C}_{a}$	$6.28 \pm 0.76^{C}_{b}$
Day 4	2.79 ± 0.56^{B}	2.86 ± 0.84^{B}	$6.12 \pm 1.91^{D}_{a}$	$4.64 \pm 1.59^{D}_{b}$
Day 6	2.40 ± 0.18^{B}	2.66 ± 0.23^{B}	$6.64 \pm 2.07^{D}_{a}$	$3.92 \pm 0.98^{D}_{b}$
Day 8	2.43 ± 0.12^{B}	2.93 ± 0.40^{B}	$7.71 \pm 1.32^{D}_{a}$	$3.44 \pm 0.76^{D}_{b}$
Day 10	2.31 ± 0.19^{B}	2.82 ± 0.12^{B}	$4.97 \pm 0.30^{D}_{a}$	$3.89 \pm 0.78^{D}_{b}$

[1] For each column, similar capital letters (superscript) were not significantly different at $p \leq 0.05$ among days. For each treatment, similar small letters (subscript) in rows were not significantly different at $p \leq 0.05$. [2] For cantaloupe, there was no significant difference between uncoated and coated groups.

It is apparent from the table that the resistance effect of intact strawberry epicarp against water transfer was superior to other groups. However, coating application decreased the surface resistance of strawberry against water transfer significantly ($p < 0.05$). Additionally, the effect of storage time was also significant at the $p = 0.05$ level.

3.6. Water Vapor Permeability of Edible Films and Expected Weight Loss During Storage

The measured values of WVTR were 2131 ± 299 g/(m^2·d), which equals a Q_{100} of 1635 ± 372 g·100 µm/(m^2·d) at (average films thickness was 78 µm), and a permeability of 103 ± 24 g·100 µm/(m^2·d·hPa) (at a humidity of 100% RH→50% RH, at 23 °C, which equals 28 hPa→14 hPa). The single measured values can be found in the Supplementary Materials online. These values are comparable to those achieved by other researchers, who produced cast films [48,55,56].

The approximate expected weight loss of cantaloupe and strawberry samples based on the measured water vapor permeability of alginate films was calculated and is illustrated in Figure 6. It is

important to note that the calculation was based on the measured coating thickness of alginate films on the samples (0.187 ± 0.076 mm and 0.235 ± 0.077 mm for cantaloupe and strawberries); the storage conditions, as in Section 3.2 (10 °C, 90% RH in the atmosphere, 0.99 a_w in the fruit, equals a partial pressure difference of 1 hPa), and storage time (up to 15 days).

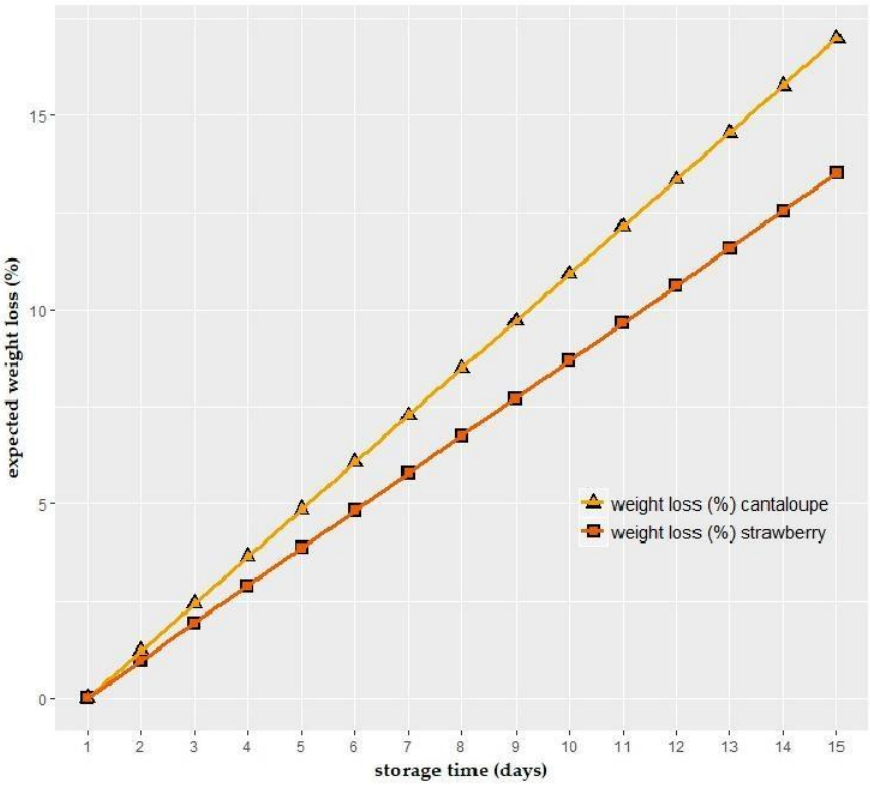

Figure 6. Expected weight loss (%) of cantaloupe and strawberry samples based on the measured water vapor permeability of alginate films produced in Petri dishes.

4. Discussion

4.1. Coating Uniformity and Thickness

Continuity and a uniform film thickness are important assumptions and prerequisites for the reliability and comparison of the measured values during the determination of thickness-dependent characteristics, such as the barrier properties of edible coatings [57,58]. By possessing very hydrophilic or hydrophobic surfaces, both samples encounter different types of challenges in forming uniform coating. The hydrophilic characteristic of the cut surfaces of fruits such as fresh-cut apple or cantaloupe does not allow for good adhesion of the coating material on the surface through a simple dipping method [59]. Due to the dilution of the coating by the surface moisture, the affinity of the coating material to the cut surfaces of horticultures is limited, which can lead to an uneven, discontinuous coverage of the targeted surface [45,57]. On the other hand, leafy vegetables and fruits such as strawberries have rough surfaces with micro- and nanostructures made of unwettable wax crystals and exhibit strong hydrophobicity [60].

Initial dipping into the calcium lactate solution improved the coating method and led to uniform layer formation on both very hydrophilic and hydrophobic fruit surfaces. It enables the present work and future studies on alginate-based coating to evaluate the transport rate of molecular components more accurately.

The average thicknesses of applied alginate coatings are 0.187 ± 0.076 mm and 0.235 ± 0.077 mm for cantaloupe and strawberries, respectively. Pavlath and Orts [61] and Skurtys et al. [59] specified the thickness of the edible coating layer usually inferior to 0.3 mm and 0.25 mm, respectively, and stated that a coating with higher thicknesses is designated as a "sheet" [59]. According to that, the crosslinked gel formed on the surface of the produce was still within acceptable thickness limits.

In the present study, the alginate-based coating formed a relatively thicker gel on the fresh-cut cantaloupe surface (≈187 μm) compared to the thickness values reported in the literature. Tapia et al. [22] measured the alginate-based coating thickness as 136.81 ± 14.05 μm on papaya; Rojas-Graü et al. [62] obtained 132.45 ± 20.48 μm on fresh-cut apples. On the other hand, Sipahi et al. [63] found 180 ± 2.0 μm for 1 g/100 g alginate and 412 ± 0.9 μm for 2 g/100 g sodium alginate incorporated coatings on fresh-cut watermelon surface. Similarly, Narsaiah et al. [64] found that the thickness of the alginate films increased with increasing alginate concentration incorporated into the coating formulation (i.e., 122.11 μm, 188.75 μm, and 300.46 μm for 1%, 1.5%, and 2% alginate concentrations, respectively). Therefore, the formation of a thicker gel can be ascribed to the difference of the alginate-based formulations (i.e., presence and amount of ingredients) that can lead to different solution viscosities or the difference in coating methods.

4.2. Relative Weight Loss during Storage at 10 °C, 90% RH

Free water stimulates microbial deterioration, the physical splitting of commodities, browning, callusing, rooting, and the sprouting of horticultural products [2]. The moisture loss process is a function of time and temperature [36].

In the case of cantaloupe, the values were not well comparable to those that could be theoretically expected, as in Figure 6. However, the final value of strawberries after 12 days of storage was close to the value expected based on the water vapor permeability measurements (~13.5% weight loss after 15 days of storage). Whereas the weight loss could be expected to correlate linearly with storage time based on pure permeability assumptions, in reality, many other factors play an important role, which is described in the following sections.

Statistical comparison revealed that from day 0 to day 8 there was no significant differences between cantaloupe samples in the same treatment group ($p > 0.05$). However, in the following days, the amount of water loss increased significantly and rapidly. This drastic increase in water loss can be explained by the decay of fresh produce, which originates from mechanical injuries, microorganisms, fast respiration rates, etc., and increases with longer storage periods. The increased deterioration also affects the structure of the produce and leads to accelerated water loss.

The water loss phenomenon of the wounded tissue was explained by Wills et al. [2] as follows: Wounding causes high concentration of solute release from the tissue. The high osmotic property of the solutes attracts water vapor and leads to droplet formation. Under high RH conditions (e.g., in package), the volume of the formed droplets continues to grow and continues to extract osmotica from the plant tissue.

Although alginate is a hydrophilic polymer and does not target the control of water vapor migration due to its hydrophilic nature, results showed that water loss in cantaloupe samples was significantly decreased. These phenomena can be explained by two mechanisms: (i) Fresh-cut melon is a porous product with 0.133 ± 0.006 real porosity (%) values [65]. The bulk movement of gas transfer (including water vapor, oxygen, and carbon dioxide) is controlled by small pores called stomate [2]. The pores might be plugged by coating, and in this way, the tissue structure on the surface might be modified [2]. (ii) The continuous alginate film might be considered a means of sacrificing moisture agent; i.e., moisture evaporates from the film instead of the fresh-cut surface of the cantaloupe [66–69].

In contrast to the cantaloupe application, water loss in strawberry samples was increased with coating application. The pronounced negative impact can be explained by the surface characteristics of the strawberry fruits. Leaves of higher plants and fruits are covered by cuticle, namely, an extracellular membrane that is composed of polymeric cutin matrix and soluble cuticular waxes [70,71].

Surface waxes, which can be divided in epicuticular (on the surface of cutin matrix) and intra-cuticular (embedded within the polymer framework) waxes, constitute the protective outer covering and establish a barrier against water loss [39,70–72]. The water-based coating might impair the aforementioned surface structure and also result in a decrease of WVR values.

4.3. Water Desorption as a Means of Mass Loss During Relative Humidity Decrease

At the very beginning of the experiment (<20 h), coated strawberries showed a drastic decrease in mass loss followed by a relatively linear decrease, while uncoated samples had a linear decrease throughout the entire process. This might show the drying process of the coating and followed by the water loss of the product, which was similar linearity with the uncoated samples. This effect could not be observed in coated cantaloupe samples, possibly due to the very fast water transport inside the sample, i.e., from the product to the coating gel, which kept the coating hydrated.

The permeation rate is equal to the driving force (i.e., pressure difference, Δp) divided by the resistance (surface of the product with or without coating) [11]. Although the coating application increased the resistance of the surface, this effect might be very small compared to the big pressure differences between the relatively bigger chamber volume and very small surface area of the piece (Δp between $p_{\text{surrounding}}$ and $p_{\text{fruit surface}}$). Therefore, coating did not influence the water loss results of each small piece used in the present experiment. On the other hand, coating decreased the water loss (%) amount of coated fresh-cut cantaloupe pieces packaged in small aPET trays in the previous section (Section 3.3). Unlike the experimental conditions in the vapor sorption analyzer, many coated pieces were packed in small packages with little air space. Due to the small driving force between little air space in the packages and increased resistance formed on many coated pieces, the coating influenced the water loss results.

It is a very interesting observation that the RH of the surrounding atmosphere (in other words partial pressure difference; $a_{w\ food} - RH_{surrounding}$) did not influence the water loss amount of the samples within 80%→60% RH. This incident also indicates that the limiting factor to water loss may be the water transport, which takes place inside of the fruit.

In conclusion, the current experimental setup of the test might be revised in order to answer emerging scientific questions.

4.4. Water Activity (a_w)

The migration of moisture is controlled mainly by the water activity (in other words, partial pressure), not by the water content, while the hydration of the components tends to achieve a balance in their water activity, not in their water content [73–75]. It is a well-known fact that most of the water in fresh or wet food exerts a vapor pressure that is very close to that of pure water [76]. Water activity values of fresh foods are 1.00–0.95, which makes them susceptible to spoilage from some yeasts, Gram-negative rods, and bacterial spores [77]. The water activity values of cantaloupe were determined as 0.95–0.993 [65,78–80]. Water activity of fresh strawberries were determined previously in the literature as 0.98–0.99 [34,35,81]. In the present study, the initial a_w values of the products were consistent with these previous findings (Figure 5).

The sorption isotherm (i.e., shows the relationship between the water content and water activity of a sample) of a food product with high water content had a J-shaped curve (Type III isotherm pattern) and at high water activity levels, where water is bounded due to the macro-capillary forces, and water content increases very rapidly with water activity [32,82–85]. The sorption isotherm of high water content products indicates that even a drastic decrease in water content does not cause a significant decrease in water activity. Hence, it was expected that water activity results would not be affected markedly during the storage in 90% RH.

The samples stored in perforated packages showed a drastic increase. The low water vapor transmission rate of the aPET trays combined with the out-coming water of the edible coating and the transpiration of the strawberries might cause a saturation of the package atmosphere and cause

condensation inside the package with a very high a_W value of the strawberries (>0.99). Fishman et al. [86] reported that perforations (2 mm, 4 holes) on the package affected the oxygen concentrations to a much greater extent than the RH% of the inside atmosphere. Using the same calculation method, Müller and Gibis [87] demonstrated a calculation example for water loss in zucchini through the pinholes. According to the presented method, the water vapor flux through the nine pinholes could be calculated as ≈0.09 g/day. Therefore, even though the number of perforation holes was increased to $n = 9$, we can argue that they did not aid in decreasing the relative humidity inside the packages and led to elevated a_w values.

4.5. Water Vapor Resistance (WVR) of Edible Coating

The underlying reason for the attenuated resistance of coated strawberries against water transfer would be the alteration of the skin structure by the coating. As described above in weight loss studies, coating might harm the naturally occurring protective waxes on the strawberry surface.

On the other hand, the WVR results of coated and uncoated cantaloupe samples required more detailed evaluation. Once again, coated cantaloupe samples had a significantly lower amount of water loss compared to uncoated samples, and thus, they confirmed the results found previously in Section 3.2. Notwithstanding decreased water loss results, no significant differences were found between the calculated WVR values of coated and uncoated cantaloupe samples ($p > 0.01$).

In the present study, the WVR of coated cantaloupe and strawberry samples was determined as 6.77 ± 0.33 s/cm and 6.28 ± 0.76, respectively. Similarly, Poverenov et al. [45] determined the WVR of uncoated melon pieces as 7 s/cm and alginate-coated melon pieces as 9 s/cm. Rojas-Graü et al. [62] reported that sunflower oil added to an alginate coating increased the WVR of apples significantly, since uncoated apples had 15.70 s/cm, while coated samples had 19.2 s/cm. However, the experiment was conducted in chambers equilibrated at 33% RH and at 25 °C. In the present study, the low WVR of alginate-coated fresh-cut cantaloupes could be attributed to the high permeability values of a polysaccharide film at high RH conditions. Vargas et al. [88] and Perdones et al. [89] stated that the high RH (90%) of the storage atmosphere led to highly plasticized film formation, and therefore, its barrier characteristics were greatly reduced with increasing water vapor permeability. In addition, Vargas et al. [90] stated that the coating application of chitosan with a simple dipping method did not have any significant effect on the WVR of the samples; coated and uncoated samples had 1.87 s/cm and 1.72 s/cm WVR, respectively, after 9 days of storage.

4.6. Water Vapor Permeability of Edible Films and Expected Weight Loss During Storage

The reducing rates of water loss by the packaging material depends on the permeability of the package to water vapor transfer [2]. Investigating the transfer of water vapor through the stand-alone film, without the food product, can provide a researcher a chance to observe the effect in relatively ideal conditions and not on a complex multi-component system such as fruit.

According to Figure 6, which shows the approximate expected weight loss of cantaloupe and strawberry samples based on the measured water vapor permeability of alginate films, the weight loss of cantaloupe will be higher than strawberry samples. This computation is valid for $t \leq 10$ days storage.

5. Conclusions

In the present study, the alginate-based coating layer was applied to fruits to protect them from the surrounding medium. The water vapor barrier performance of the alginate-based coating was presented on two different coated food products and as stand-alone films. In this way, the findings provide additional information about the water barrier characteristics of alginate-based coating.

Additional immersion in a calcium lactate solution at the beginning of the coating process promotes gel formation on the fruit surface and the uniformity of the coating. The new coating process allows researchers to improve the adhesion of their designed alginate-based coatings and may be considered a promising aspect of increasing the effects of edible coatings on quality parameters.

Coating treatment efficiently reduced water loss in fresh-cut cantaloupe pieces. However, it promoted water loss in the strawberry samples. The alginate-based coating process together with an additional calcium dipping step shows a promising effect on hydrophilic cut surfaces, especially on porous food samples, but the effect on waxy surfaces can be investigated in more detail. Moreover, different experimental setups for the vapor sorption analyzer can be employed to help this examination and to aid researchers in understanding the occurred phenomena better. In further studies, the vacuum impregnation method can be used instead of a simple dipping method to increase the penetration of the film forming solution into the porous product and increase the WVR of the surface.

As argued in discussions, results indicate that the limiting factor of water loss may be the transport of water inside the fruits. Future studies can fruitfully explore this issue further and investigate the association between these transport mechanisms.

Supplementary Materials: The following are available online at http://www.mdpi.com/2304-8158/8/6/203/s1, Table S1: Water vapor transmission rate values.

Author Contributions: Conceptualization: T.S.P., M.S., and K.M.; investigation: T.S.P., M.L., and I.R.; methodology: T.S.P. and M.L.; supervision: M.S. and K.M.; writing—original draft: T.S.P. and M.L.; writing—review and editing: T.S.P.; M.L.; I.R.; M.S.; and K.M.

Funding: This work was supported by the German Research Foundation (DFG) and the Technical University of Munich (TUM) in the framework of the Open Access Publishing Program.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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Chapter VIII.

Concluding Discussion

The overall research target of the thesis was to provide an edible coating method/materials that granted improved quality to fresh-cut or whole fruits. Cantaloupe and strawberry were selected as model fruit samples due to their high popularity in the fruit market, their important postharvest losses, and their different surface properties (i.e., cantaloupe is strongly hydrophilic while strawberry is strongly hydrophobic, caused by the outermost wax layer).

The overall aim was achieved by dividing the research into technical and scientific sub-goals, which helped to develop a coating method that provides:

- Coherent and sufficiently homogeneous coating layer formation
- Good wettability on the substrate surface, even if it is strongly hydrophilic or hydrophobic
- Coating formulation regarding surface characteristics of substrates
- Barrier properties against liquid water and water vapor transport and improved understanding of water transport through coated food samples
- Relatively neutral sensorial properties

Food-Related Properties

The preliminary trials were conducted to summarize the scientific questions arising in the edible coating process and also to explore options with possible antimicrobial effects to decrease the fast deterioration of the samples.

Shelf life extension of fresh-cut cantaloupe samples was evaluated with a coating application of 1.25% alginate, 2% glycerol, 0.125% sunflower oil, 0.1% tween 40 (polyoxyethylenesorbitan monopalmitate), and 0.6% span 80 (sorbitan monooleate). Calcium lactate was used as a crosslinking agent due to the importance of taste attributes; calcium chloride imparts a bitter taste to the food. Antimicrobial agents, hop extract, and potassium sorbate were added to different coating stages of the alginate-based edible coating.

Microbial deterioration

The high initial microbial population of the samples can be explained by the insufficient decontamination of the cantaloupe rind with drinkable tap water. As suggested by surface decontamination research, efficient surface sanitation can be performed using H_2O_2 (hydrogen peroxide) to improve the microbiological quality and shelf-life of fresh-cut cantaloupe.

Two different antimicrobial agents (the equal amounts of hop extract and potassium sorbate, 625 μg/g solution) were incorporated into different stages of the coating process to achieve an advanced microbial inactivation. The highest microbial reduction was achieved when the antimicrobial agent was incorporated into both coating and crosslinking steps. The diminished antimicrobial effects of hop addition to the alginate solution only or to the calcium lactate solution only, could be explained by the dissolution of the alginate layer (including the antimicrobial agent in the alginate layer) in the calcium solution during gel formation. When antimicrobials are added to both steps, the amount and effect will be cumulative. Hop extract incorporated coating led to a microbial log reduction of 1 and approximately 1.5 days shelf life increase. Furthermore, hop did not significantly reduce the number of yeast cells in the samples, while potassium sorbate was effective against the yeast population. The amount of hop extract was limited by its bitter flavor and determined with preference tests. For future studies, the bacterial reduction ability of hop can be promoted with the reduction of the pH of the coating and crosslinking solutions.

Weight loss

The most notable positive effect was observed in weight loss results. The coating application decreased the water accumulation at the bottom of the packages significantly. On the other hand, the type of and/or an additional step of antimicrobial agent did not cause any significant difference. The reduction of water leakage was interesting, particularly as, being a polysaccharide-based coating, the alginate-based formulation was not expected to be an effective water vapor barrier. Kester and Fennema [175] wrote that although moisture transport in foods happened mainly because of water vapor difference, other factors such as capillary forces, gravity, and differences in the transport area of the water phase could also have effect. The barrier properties of the coating-substrate combination against liquid water and water vapor have been re-evaluated in Chapter VII in detail.

Color alterations

Generally, the films formed on the product should not adversely alter the food color. In preliminary trials, the coating increased the yellowness of the coated surface due to the

color given by sodium alginate. Although it can be considered as a desirable characteristic for cantaloupe, the color alterations should be investigated in more detail when different colored fruits and vegetables are targeted. Both luminosity and yellowness decreased with increasing storage time. The highest color differences ($\Delta E_{Lab,}$ refers to the numerical comparison of the samples' color to Day 1) were observed in antimicrobial added samples, which can be explained with the dark color of hop and oxidative browning of potassium sorbate over time.

Sensorial properties

Similar to the color features, the film formed on the product should not adversely alter the flavor of the food (both aroma and taste). However, in addition to color, the coating had a negative impact on sensorial properties. Because of its strong bitter taste, particularly fresh-cut cantaloupes coated with hop added alginate coating had very low overall quality scores. As an antimicrobial agent, hop extract was a very challenging ingredient due to adding a specific (mostly unfavorable) flavor to the foodstuff. Therefore, determining an optimum amount in terms of achieving good antimicrobial properties with high sensorial scores was an unrealistic aim.

The poor adhesion properties and peeling of the coating layer were the major cause of low sensorial scores given to the coated samples. Therefore, attempts were made to achieve better adhesion properties and wettability of the substrate's surface in the subsequent studies.

During the preliminary studies, various questions about the coating and process itself arose from the results in relation to the research objectives: These questions could be summarized briefly as:

(i) what were the effects of coating parameters and techniques on the quality attributes?

(ii) how could the surface characteristics of irregular surface products be accurately measured?

(iii) which ingredients and quantities should be selected for coating formulation?

(iv) how could a relatively uniform, well-adhering coating be designed for different surface characteristics?

(v) how could the juice accumulation at the bottom of the package of fresh-cut cantaloupe be avoided?

It is necessary to emphasize that the questions raised were also linked to each other.

It was found that the developed questions mentioned above constituted a knowledge gap in edible coating studies. These deficits and provided solutions were well aligned with the objectives of the thesis and established the next parts of the study; i.e., coating process-related properties:

Coating process

The type of coating process (dipping, vacuum impregnation, spraying, etc.) and the independent parameters used (such as time, pressure, etc.) have a decisive role in the formation of good quality coatings. Dipping (and likewise vacuum impregnation) is a more convenient method for the coating of cantaloupe pieces because of the cubic shape of the samples. The main objective of the experiments presented in Chapter IV was to find out which coating parameters should be used in the following studies and to determine the effects of those parameters on the coating amount and optical - textural properties of the samples. In this way, more technical information concerning the conventional coating (dipping) and a novel coating method (vacuum impregnation) and their comparison would also be produced. The adequate draining times of alginate and crosslinking solutions were determined as the first step because of the complexity of evaluating the interaction of all variables. After this, different dipping times in coating and crosslinking solutions and their interactions were analyzed.

Weight gain (%) results of various draining times (10 s - 5 min, 7 levels), following 120 s alginate, and calcium lactate dipping showed that 60 s draining time was not significantly different than longer draining periods both for coating and crosslinking steps. Interaction of various dipping times (30 s - 240 s, 4 levels) into alginate and calcium solutions showed that dipping times and their interaction did not significantly affect the weight gain results. 2 min dipping into the solutions caused similar weight gain results compared to 4 min dipping. This effect can be explained by the dissolution of alginate in calcium solution during longer dipping times. Taken together, 2 min dipping and 1 min draining times were selected for both alginate and calcium solutions as dipping parameters.

Alginate based coating application used in this study formed a non-uniform coating, which did not allow an accurate measurement of the coating thickness using a stereomicrograph. Therefore, weight gain was used as an indicator of the thickness of the coating. Due to the application of only one coating formulation (the microstructure of the applied coatings was the same), the relationship between the weight gain and the coating thickness was assumed linear. The studies presented in Chapter VII focused on the non-uniform coating formation, and a uniform coating was obtained with an additional immersion step into a crosslinking solution.

The porosity fraction of melon (ε) was determined as 13.3±0.6% in the literature [65,176]. The high porosity of cantaloupe makes it a good candidate for the vacuum impregnation process; on the other hand, the vacuum impregnation was not applied to strawberry fruits. Three independent variables were selected: atmospheric restoration time (2-15-30 min), the time length of the vacuum period (4-10-15 min), and vacuum pressure (50-100-150 mbar absolute pressure). Due to the high viscosity of alginate

coating, longer atmospheric restoration time was added into the experimental design to achieve higher impregnation. The highest weight gain results were reached with 15 min atmospheric restoration time. It has also been found that the period of vacuum application was significantly effective on the weight gain amounts. On the other hand, no significant difference was found between vacuum pressures applied.

Interestingly, the results of dipping and vacuum impregnation methods showed that prolonged immersion in the coating solution, higher vacuum pressures, or extended atmospheric restoration time did not necessarily increase the amount of the coating film on the food. In other words, moderate process parameters such as dipping time (120 s), atmospheric restoration time (15 min), and vacuum application time (10 min) achieved the highest weight gain results during coating applications.

The vacuum impregnation method significantly changed all the color parameters excluding h* (L* values decreased, while a*, b* and therefore C* increased), while the dipping method did not affect the color of the coated products. The perception of color difference in dipping application was not noticeable (<1), while the vacuum application caused noticeable color differences ($2<\Delta E<5$) compared to control group samples. The lower the vacuum pressure and vacuum period, the greater the difference between treated and untreated cantaloupes. The change in optical properties of the vacuum treated samples can be explained by the removal of the air from the pores and gas-liquid exchange in the sample [177,178].

Both processes increased the firmness of the cantaloupe samples significantly. However, the vacuum application caused firmer textures compared to dipping. It can be stated that the vacuum impregnation method may be an effective method for coating applications; however, alterations in quality parameters, as well as the consumer responses to them should be evaluated carefully for each product.

The coating parameters for the dipping method determined in this chapter were used both for cantaloupe and strawberry samples in the following experiments throughout the thesis.

Surface characteristics

Fresh-cut produce has diverse surface characteristics. Hydrophilic and hydrophobic surfaces encounter different types of adhesion problems, which directly affect the efficiency of the coating. Accurate measurements of surface free energy and surface tension of the food and coating solution are very critical in terms of characterizing the surface and application of the uniform coating layer.

The special geometries of irregular food surfaces such as their round/wavy, curly shape, pitted structure with seeds or hairs attached to the achenes complicate the visibility of the contact points of the probe liquids on the samples' surfaces when the contact angle measurements are performed using conventional Drop Shape Analyzers (DSA). However, the correct measurement of the contact angle possesses a pivotal role in SFE, wettability, and as well as coating formulation design studies. Studies in Chapter V are

targeted to improve the visibility of contact points of probe liquids on rough and irregular food surfaces using ImageJ software with the DropSnake plugin and, in this way, determine the contact angles more accurately.

Validation of the ImageJ program with DropSnake plugin was conducted by measuring the contact angles of three different test liquids (water, ethylene glycol, diodomethane) on four different smooth polymer films (i.e., PTFE-500 μm, BOPP-20 μm, PET-160 μm, PET-12 μm) both with DSA and ImageJ. Comparison of the contact angles (θ) pointed out that although the results of the two methods showed the same increasing-decreasing pattern ($\theta_{water} > \theta_{e.glycol} \geq \theta_{d.methane}$), there were differences in the medians and the distributions of the values found with different methods. The surface free energy and its components were calculated with Owens and Wendt's two-parameters model both for the DSA and the ImageJ programs. The linear relationship between the polar, dispersive components and SFE of plastic films found with DSA and ImageJ indicated that ImageJ can be used as an alternative to DSA.

Fresh produce with rough and irregular surfaces such as strawberry and endive salad were used for the case studies. It is essential to underline that endive salad is not a model sample for the whole thesis, but a supplementary sample for the verification of the method (Publication-III). In addition, fresh-cut cantaloupe was not used as a model fruit because its surface is covered with a water layer. The probe liquids used in this thesis could not produce a droplet (in other words, contact angle) on the surface of the sliced cantaloupe pieces but formed droplets on intact strawberry and endive salad samples. Powerful and portable light sources, a high-zoom camera with a macro lens and extension tubes were the key to capturing clear photos, in which both right and left angles of the droplets could be seen. The ImageJ program with DropSnake plugin defines the contact angles for non-axissymmetric drops from digital photographs with high resolution.

It is important to note that the convex shape of strawberry led to less than 10° surface slope. The effect caused by the gravitational force was calculated and found to be very small and negligible. The contact angle results of the strawberry epicarp scatter drastically, which indicated that the strawberry surface is highly heterogenous, not only geometrically but also in terms of surface characteristics, most probably due to the outer waxy layer. It had a low energy surface (21 mN/m) with strong hydrophobicity (high dispersive forces (20 mN/m) and very low polar forces (1 mN/m)).

The results showed that the ImageJ program with the so-called snake-based approach (active contours = snakes) is an important tool for the contact angle measurement of irregular and rough food surfaces. The concept presented in this paper can be used as a guideline for the accurate measurement of contact angles on any rough and irregular surfaces, surface free energy calculations and the design of coating materials with improved surface wettability. The CA measurement and the SFE calculation concept presented in Publication-III (Chapter V) can be transferred to various scientific areas which need to determine the characteristics of rough and irregular surfaces. The research also highlighted the usefulness of the ImageJ program in food studies and outlined the points to improve it further.

The low surface free energy of the strawberry epicarp showed us that effective surface-active agents should be added to coating formulations to achieve higher wettability and sufficient adhesiveness. Therefore, a coherent, homogenous coating layer could be formed on the fruits.

Formulating the coating

The properties and effectiveness of the components in the coating solution determine the quality of the coated food product. In general, intact fruits and vegetables have low energy surfaces (e.g., strawberry and endive salad surfaces in Publication III), which points out that a reduction of the surface tension of coating solutions is crucial for achieving good wettability on the surface. Studies in Chapter VI aimed to find the effects of each potential ingredient (i.e., surfactants, vegetable oils, plasticizers, etc.) on the critical features of the coating solution and therefore determining a formulation gradually.

To achieve that goal, firstly, various concentrations of gelling agent (sodium alginate 0–3.5%, w/w), plasticizers (glycerol and sorbitol (0–20%, w/w), surfactants (tween 40, tween 80, span 60, span 80, lecithin (0–5%, w/w), and vegetable oils (sunflower oil, olive oil, rapeseed oil (0–5%, w/w) were used. The amount of sodium alginate added into the solvent is mainly determined by the viscosity of the coating that the coating formulator prefers to work with. The viscosities of the coating solutions increased exponentially with increasing alginate concentrations. The highest concentration of sodium alginate (3.5%, w/w) used in the study took a very long time to dissolve (t>6 hours at 70°C) and led to very high gel viscosity (μ=1614 ± 40 mPa.s). The alginate concentration did not have a significant effect on surface tension, suggesting that biomaterial did not have any adsorption activity in the liquid-vapor interface. 1.25% sodium alginate concentration was selected for the following steps due to requiring a decent amount of gelling agent, yet not forming a highly viscous liquid. As stated in the Levich approach, the film thickness formed on the surface increases proportionally with increasing viscosity [179,180].

Secondly, the type and amount of plasticizers were studied. Due to being not tensio-active substances, the addition of plasticizer (i.e., glycerol and sorbitol) even at elevated concentrations did not alter the surface tension results. Glycerol was selected due to having a natural taste compared to the sweet taste of sorbitol. 2% glycerol was chosen as plasticizer concentration in the designed formulation since Tapia, *et al.* [181] showed that 2% glycerol improved the water vapor resistance (WVR) of the alginate films. Subsequently, vegetable oils (olive oil, sunflower oil, rapeseed oil) were incorporated to the coating formulation (1.25% alginate + 2% glycerol) as lipid source. The reason behind lipid source addition to the formulation was promoting the WVR properties of the coating, which was evaluated in the subsequent studies (Chapter VII). Even though olive oil addition led to the lowest surface tension results, there was no drastic difference between the surface tension values of the coating solutions in which rapeseed oil or sunflower oil was added. Therefore, sunflower oil was selected as the lipid source due to certain drawbacks of olive oil, such as dark color, strong odor, flavor and expense.

Lastly, non-ionic surfactants and soy-lecithin were added to the formulation (1.25% sodium alginate + 2% glycerol) to evaluate the effects on surface tension. Porter [182] states that a decrease of surface tension by increasing the concentration of surfactants produces discontinuous graphs; i.e., surface tension falls rapidly until a point is reached where a monolayer of surfactant covers the surface and after that, the slope of the surface tension decrease is close to zero. Different surfactants give different sizes and shapes of hydrophobic and hydrophilic groups packed on the surface [182]. It was found that vegetable oils and surfactants diminished the surface tension in similarly descending curves. Rational functions in the form of $y = f(x) = (a+cx)/(1+bx)$) could be applied as fit functions. The variable "a" is approximately the same for each equation (~71) due to having the same starting point (surface tension of water, zero concentration of surfactant or oil). The "b" and "c" values were important in the distribution of surface tension values. In future studies, the functions can help us find the monolayer of the surfactant coverage point without the necessity of conducting labor intensive-time consuming experiments.

Span 80, tween 80 and tween 40 were found to be the most effective surface-active agents. Although low concentrations of tweens (<0.5%) could be sufficient to reach their saturation point, higher concentrations of span 80 (>1%) reduced the surface tension more effectively. Increasing concentration of surfactants and sunflower oil caused a decrease in polar forces; while on the contrary, dispersive forces increased. Most effective surfactants (tween 40, tween 80, and span 80) possessed higher dispersive forces compared to their polar counterparts (span 60, lecithin). Experiments investigating the interactions of selected surfactants and oil showed that there was no significant difference between solutions in which tween 40 or tween 80 were added in terms of surface tension values. Statistically, both two-way and three-way interactions between sunflower oil, tween 40, and span 80 had significant effects.

Emulsion stability of selected coatings and wettability of the hydrophobic surface

Emulsion droplet sizes were determined along with optical evaluations under the automated imaging microscope to learn more about the emulsion stability. Particle size measurements had some limitations. These were (i) dilutions of the surfactants (i.e., tween 40, tween 80, and low concentrations of lecithin) in water in the stirred sample cell, (ii) replicate measurements of span 60 and span 80 did not overlap. It was an interesting point that each and every time, span components in different concentrations formed two similar peaks in graphs (particle size vs. volume (%) graphs). The reason for this measurement challenge could be explained by the presence of larger span particles (>10 μm) in the solutions and could only be solved with better integration of the components to the emulsion. Optical examinations of agglomerations, micelle formations, and evaluation of homogeneity agreed well with particle size measurements. Once the individual effects of the components were determined, three formulations were designed:

- Formula 1: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80

- Formula 2: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 40
- Formula 3: 1.25% sodium alginate + 2% glycerol + 0.2% sunflower oil + 1% span 80 + 0.2% tween 80

Particle sizes, creaming index values and wettability parameters of all formulations were measured. Phase separation or creaming was not observed during 26 h storage. The highest wettability result (−17.8 ± 2.3 mN/m) was achieved by Formulation 1 (the definition and the calculation method of wettability are given in Section 2.4). However, considering the particle size results, tween 80-incorporated formulation (Formulation 3) with −21.1 ± 4.6 mN/m wettability could also be successfully used. Importantly, the wettability achieved in the study is remarkably high compared to the previous formulations in the literature designed for hydrophobic fruit surfaces. Ribeiro, Vicente, Teixeira and Miranda [116] also studied the strawberry epicarps and found that the wettability values of starch, carrageenan, and chitosan-based coatings were −44.61±3.05 mN/m, −45.28±0.88 mN/m and −38.89±2.83; respectively. Andrade, *et al.* [183] formulated gelatin-based coating solutions and determined the wettability of banana and eggplant as -22.44 mN/m and -32.95 mN/m, respectively.

Publication-IV provides an evaluation of the effects of various coating components on surface tension and emulsion droplet size to design and optimize an effective coating on food surfaces. The formulation is built gradually; therefore, the main effects, as well as the interactions between components, can be elucidated. Therefore, this paper aims to provide an important methodology for the edible coating/film formulators and creates a reference source for future studies of edible coating/film design.

An edible coating formulation of 1.25% sodium alginate, 2% glycerol, 0.2% sunflower oil, 1% span 80, and 0.2% tween 80, which had good wettability and emulsion stability properties, was selected and used for the subsequent water barrier studies.

Effect of the coating formulation on techno-functional properties

During the preliminary analysis, questions arose as to how a uniform coating layer on the surface could be produced, and queries were raised about decreasing water leakage from the fresh-cut fruits as a polysaccharide-based coating. As stated by Baldwin, *et al.* [184], predictions of barrier properties assume continuity of the coating especially applied on horticultural produce. A discontinuous coverage or different thicknesses on certain areas may lead to different water barrier characteristics on different parts of the surface. Also, Donhowe and Fennema [16] underlined that the permeability was particularly sensitive to the variations in coating thickness. Therefore, a special focus was given to the uniform coating formation.

The final studies of this thesis concentrated on investigating the effects of a suggested formulation (determined in Chapter VI) on achieving a uniform coating, coating thickness and water barrier characteristics. Although continuity and uniform film thickness are important prerequisites for the effective coating application to modify the barrier

properties, this issue has been scarcely investigated and checked in alginate-based coating studies. The paper presented in Chapter VII proposed a new approach to uniform alginate-based coating preparation.

As mentioned earlier, the conventional alginate coating method formed thicker gels, especially on the edges/corners and thinner structures in the middle. The gels had adhesion problems and peeled easily from the surface. Initial immersion of the fresh-cut cantaloupe pieces (hydrophilic surface) and strawberry (hydrophobic surface) into a calcium lactate solution followed by dipping in alginate and calcium solutions for crosslinking led to a gel formation that completely covered the low and high points (e.g., seed holes) and formed a smoother, sufficiently uniform gel surface. Adhesion of the alginate gel to the fruit surface was improved when there was already a thin calcium layer on the surface. The coating thicknesses were monitored using a stereomicrograph by randomly taking five measurements at different points of the cross-section of 10 samples (n=5×10). The coating thicknesses on cantaloupe and strawberry surfaces were determined as 0.187 ± 0.076 mm and 0.235 ± 0.077 mm, respectively.

Once the uniformity and adhesive properties of the coating were improved, the water barrier properties could be evaluated. As a first step, weight loss (%) experiments previously performed in Chapter III were repeated under constant operative temperature and humidity (10°C, 90% RH). A small pile of fresh-cut cantaloupe cubes was packed in APET trays with lids. The time range of the experiment was extended by incorporating $t<1$ day and $t>8$ days. The amount of water loss increased rapidly after the 8th day of storage, probably due to increased decay of the fresh produce. It is clearly indicated in the edible coating literature that hydrocolloids exhibit poor water resistance due to their hydrophilic nature, which interacts with water vapor [16,124,135]. Kester and Fennema [135] put this down to the greater solubility of the easily condensable water vapor in the hydrophilic nature of the barrier film. However, the results showed that water loss in the cantaloupe samples was significantly reduced. At this point, it was important to differentiate between two different water transfer mechanisms, i.e., (i) transport of liquid water through pores of the substrate, and (ii) transport of water vapor. Most probably, the small pores (stomate) were plugged by the coating, and in this way, liquid-water transfer could be diminished.

A similar experiment was conducted using only one piece of cantaloupe (same-sized pieces) during regular RH decrease (80%→60%) in an automated water sorption analyzer to observe the effect of RH. Surprisingly, there were no distinguishable differences between coated and uncoated cantaloupe samples (Average drying speed, $|dm/dt| = 0.33 \pm 0.01$ %·h^{-1}). The results indicated that the coating could decrease the liquid-water loss leakage of a pile of cantaloupe pieces in a package, but the effect was not observed when experiments were conducted with one single piece. Although stereomicroscope images of coated cantaloupes showed sufficiently uniform coating formation on the substrate surfaces, the porosity of the coating was not quantified. The film layer formed might have a low value of porosity and inhomogeneity, which led to an inhomogeneous contact of coating and the substrate. When the substrate pieces were piled in a package, surfaces

touched each other, and they were exposed to other factors such as gravity, mechanical pressure, capillary effect, etc. that might lead to diminished liquid-water transfer.

Water vapor transport is mainly controlled by water activity [185]. Therefore, a_w values of coated and uncoated samples packed in different packaging conditions (i.e., closed, perforated, and open aPET boxes) were determined on day 1, day 5, and day 8. The a_w of cantaloupe samples slightly decreased throughout storage. However, the type of packaging did not affect the results significantly. The results supported the theory of the predominance of liquid-water transfer in alginate coated hydrophilic surface over the water vapor transport.

The effect of coating on WVR results of samples required a more detailed evaluation. The WVR (s/cm) of the samples were found using $WVR = (a_w - \%RH/100) \cdot P_{sat} R^{-1} T^{-1} A J^{-1}$ where a_w is the water activity of fruit pieces, %RH is the relative humidity of the climatic chamber, P_{sat} is the saturated water vapor pressure (mmHg), R is the specific gas constant for water vapor ($mmHg \cdot cm^3 \cdot g^{-1} \cdot K^{-1}$), T is the temperature of climatic chamber (K), A is the surface area of the food samples (cm^2) and J is the slope of weight loss in food sample versus storage time (g/s) [186]. As found once again in weight loss experiments, uncoated cantaloupe samples had a significantly higher amount of water loss compared to coated samples (variable J in the equation). Nevertheless, no significant differences were found between the calculated WVR values of uncoated and coated cantaloupe samples. The experiment confirmed that water vapor transport models could not explain the water transfer from the alginate-coated hydrophilic substrates.

The same water barrier experiments were conducted for strawberry samples. The water loss reduction ability of an alginate-based coating to enhance the natural barrier of strawberry was evaluated. However, the weight loss of coated strawberry samples increased drastically, particularly after 10 days of storage. Mass loss results during 80% →60% RH decrease (in the moisture sorption analyzer) were compatible with the previous findings in weight loss (%) experiments. The coating led to faster mass loss (%), especially at the earlier stages of the experiment (<20 h). Average drying speed of coated and uncoated strawberries was found to be 0.11 ± 0.02 $\%\cdot h^{-1}$ and 0.08 ± 0.01 $\%\cdot h^{-1}$, respectively. a_w of the coating increased the available, unbound water amount, especially for strawberry samples packed in perforated packages. The perforations (9 holes, diameter=2mm) on the top surface of the packages led to ≈0.09 g/day water vapor flux (calculated using the study of Müller and Gibis [187]), which did not aid in decreasing the RH inside the packages and led to elevated a_w values. Similarly, the WVR of whole strawberries were superior compared to coated strawberries and coated/uncoated cantaloupes.

The most remarkable result to emerge from the water transport tests on strawberry was that the coating application, with additional calcium lactate dipping, significantly decreased the surface resistance of strawberries against water transfer. The pronounced negative impact on water barrier characteristics was probably a result of the impairment of the protective surface waxes of strawberry by the calcium lactate + coating + calcium lactate application. The results indicate that calcium lactate is not only a crosslinking agent

but also influences the product itself. Interestingly, Morris, *et al.* [188] also stated that calcium dipping was more effective in firming and decreasing weight loss of sliced strawberry pieces than whole fruit.

Studies of the water transport of coated hydrophilic (cantaloupe) and hydrophobic (strawberry) samples showed that water vapor transport through the samples had a less dominant role compared to the liquid-water transfer. Simple models could not explain the water transport of alginate-coated hydrophilic surfaces. Furthermore, calcium lactate application on hydrophobic surfaces such as the waxy outer layer of strawberry developed additional complications on the simple model. Water loss through the fruit's surface mechanisms, surface structure and the substrate's geometry should be considered to describe the working mechanism of alginate coating. The water release model is more convenient for the alginate-based solution coated hydrophilic surfaces compared with the water vapor transport model of the coated hydrophilic substrates.

Taken all together, this thesis provided a methodology for edible coating design to achieve sufficiently homogenous coating layers on fresh-cut or whole fruits with vastly different surface characteristics. It provided technical information about the effects of coating parameters, demonstrated a way to determine the surface energies of rough and irregular food samples and presented the design of a coating formulation adapted to the target substrate with improved wetting properties. Attempts were made to describe the water transport phenomena in coated fresh-cut fruits by simple transport/barrier models. Although the simple model was not optimal to specify the liquid water transfer and include the changes of the substrate's surface characteristics after coating. Nevertheless, the studies helped us to improve the understanding of the water transport properties of the coating-substrate combination.

Chapter IX.

Summary

The use of biomolecules for the preparation of biodegradable packaging materials can be considered as an emerging trend that can have an impact on the reduction of postharvest losses, the extension of shelf-life of fresh-cut produce, and food safety.

The overall goal of this thesis was to provide an edible coating method that improved the postharvest quality of stored fresh-cut or whole fruits. In connection with the primary purpose, specific sub-aims were determined and studied, as stated below.

The thesis began with a general survey that included postharvest losses, specifications of fresh and fresh-cut produce used as model systems, components of an edible coating as well as the surface free energy measurement methods and wettability. Cantaloupe and strawberry were selected as model systems due to their high popularity in the fruit market, having naturally important postharvest losses and their hydrophilic and hydrophobic surface characteristics. In a subsection, a published review article was included, which synthesized information about alginate material, crosslinking mechanism, active ingredients incorporated into formulations, application methods, research and development studies of coated food products, mass transfer and the barrier characteristics of the alginate-based coatings/films.

The initial technical sub-target was to define an edible coating method and components with water barrier properties (liquid-water and/or water vapor) and also to evaluate the antimicrobial effect of two additives (i.e., hop extract and potassium sorbate) when incorporated into the coating solution. Shelf-life studies, as well as the postharvest losses, were determined using fresh-cut cantaloupe pieces as food samples. A relatively small amount of hop extract could be added to the formulation due to its unfavorable taste. The results showed that antimicrobials should be added to both coating steps (i.e., both alginate and calcium lactate solutions) in order to achieve higher microbial inactivation. The addition of 625μg/g hop extract or potassium sorbate to both the coating and the crosslinking solution led to a log TVC reduction of 1. On the other hand, the effects of hop and potassium sorbate on the yeast count differed significantly. Hop extract was ineffective, but potassium sorbate reduced the yeast count significantly. The most drastic changes were observed in water loss tests, i.e., coatings decreased the water loss of the product significantly. The coating itself, as well as the incorporated antimicrobials, changed the color of the samples significantly. The peeling of the coating from the cut surface was the indication of a lack of adhesion ability of the coating solution on the

watery food surface and led to the decreased sensorial scores and diminished barrier properties. Those issues identified were studied in the following chapters.

The formation of a continuous edible coating layer is related to the coating amount attached to the target surface. Determining the effects of coating parameters (i.e., immersion and draining time) on the coating amount covering the surface of the cantaloupe pieces was the next technical sub-target for the subsequent experiments. Regarding the target, the desirable characteristics of the coating layer for fresh-cut cantaloupe pieces were defined as: causing no drastic color change, increasing firmness, and relatively higher weight gain results (an indication of increased coating thickness for enhanced barrier properties (for further studies)). To begin with, the effects of various time intervals (10 s-5 min) on weight gain results were evaluated. After which, the effects of 3 selected parameters on color and texture characteristics were also determined. The results showed that longer immersions did not increase the coated amount, most likely due to increased solubilization. 2 min immersion and 1 min draining were defined for the subsequent coating analysis with a conventional dipping application.

The formation of a continuous, homogenous, adhesive coating layer is connected mainly with the wettability properties of the target fruit surface by the coating solution. On the other hand, the wettability of the food surface is strongly dependent on the accurate measurement of the coating's surface tension and the surface free energy of the food surface. However, accurate measurements of the contact angle and thus the surface free energy of rough and irregularly-shaped food samples such as strawberry were particularly challenging. To solve this problem, the usability and accuracy of a contact angle measurement method, namely the ImageJ program with DropSnake plugin were evaluated in the following chapter. The system was validated using a conventional drop shape analyzer (DSA) with the help of four different plastic films and three different probe liquids. Subsequently, the surface free energy of the strongly hydrophobic surface of strawberry (γ_s=21.26 mN/m) was determined.

As stated above, to achieve a good wettability value, the second important characteristic is the surface tension of the coating solution, which should be specifically designed for the coating surface. Therefore, in the next study, the effect of the presence and amounts of the ingredients (i.e., base material, plasticizers, vegetable oils, surfactants) on the adhesion ability and stability of the coating solution was assessed. The main and interaction effects of components with various levels were evaluated. Therefore, this study provided an important methodology for coating design studies and edible coating/film formulators. Formulations were created by evaluating surface tension, emulsion droplet size, optical characteristics, creaming index, and wettability results. For fresh fruits, which are covered with a hydrophobic waxy outer layer, the surface tension of the formulated emulsions should be decreased significantly to achieve higher wettability. As a compromise between achieving the maximum reduction of surface tension and using the minimum amount of coating component, the formulation was constituted using 1.25% sodium alginate, 2% glycerol, 0.2% sunflower oil, 1% span 80 with 0.2% tween 80.

Lack of adhesion of the coating solution on the fruit surface was one of the major limitations determined. Our research aimed to find a solution for the challenging adhesion problem of alginate-based coatings both on strongly hydrophilic and strongly hydrophobic surfaces. Coating uniformity was achieved with the addition of an extra immersion step into a calcium lactate solution initially before the conventional coating steps. Visual inspection of the coating layers on the fresh-cut cantaloupe (strongly hydrophilic surface) and strawberry pieces (strongly hydrophobic surface) were performed using a stereomicroscope. With the help of the new coating strategy, the continuity and uniformity of the coating layer were obtained. The average coating thicknesses were found to be 0.187 ± 0.076 mm and 0.235 ± 0.077 mm for cantaloupe and strawberries, respectively.

Water barrier properties in terms of resistance to liquid water and water vapor were investigated in detail. Regarding the target, the results showed that alginate-based coating treatment with additional initial calcium dipping efficiently reduced liquid water transport of porous hydrophilic fresh-cut cantaloupe pieces. However, it did not decrease the water vapor resistance of the coated samples. On the other hand, it promoted water loss when applied on waxy surfaces (strawberry samples), which is most probably a harming effect of calcium lactate on the waxy protective cover. Generally, it was found that a simple water barrier model is not sufficient to explain the water transport (both liquid water and water vapor) of alginate coated hydrophilic and porous cantaloupe and highly hydrophobic strawberry surfaces. The coating process altered the surface structure of the strawberry surface. Other factors, such as a change in surface characteristics, effect of gravity, capillary forces, etc. should be considered. Nevertheless, the study helped us to have an improved understanding of the process.

This thesis provides guidance related to the edible coating design steps, the positive effects of alginate-based coating on quality characteristics of fresh-cut produce. It should encourage researchers to pay attention to the destruction of hydrophobic waxy layers on the food crops following the coating process, increase of water transport and distinguishing the difference between water losses via liquid and vapor transports. As a result, this thesis documents several key contributions made to the fields of designing a successful edible coating application.

Chapter X.

Zusammenfassung (German Summary)

Die Verwendung von Biomolekülen für die Herstellung von biologisch abbaubaren Verpackungsmaterialien kann als ein sich abzeichnender Trend betrachtet werden, der sich auf die Verringerung von Nachernteverlusten, die Verlängerung der Haltbarkeit von Frischschnittprodukten und die Lebensmittelsicherheit auswirken kann.

Das Gesamtziel dieser Arbeit war es, eine essbare Beschichtungsmethode bereitzustellen, die die Qualität nach der Ernte gelagerter Frischschnitt- oder ganzer Früchte verbessert. Im Zusammenhang mit dem Hauptzweck wurden spezifische Teilziele festgelegt und untersucht, wie unten angegeben.

Die Arbeit begann mit einer allgemeinen Übersicht, die Nachernteverluste, Spezifikationen von frischen und frisch geschnittenen Produkten, die als Modellsysteme verwendet wurden, Komponenten einer essbaren Beschichtung sowie die Methoden zur Messung der freien Oberflächenenergie und der Benetzbarkeit umfasste. Cantaloupe und Erdbeere wurden aufgrund ihrer hohen Popularität auf dem Obstmarkt als Modellsysteme ausgewählt, da sie von Natur aus bedeutende Nachernteverluste aufweisen und hydrophile und hydrophobe Oberflächeneigenschaften aufweisen. In einem Unterabschnitt wurde ein veröffentlichter Übersichtsartikel beigefügt, der Informationen über Alginatmaterial, Vernetzungsmechanismus, in Formulierungen eingearbeitete Wirkstoffe, Anwendungsmethoden, Forschungs- und Entwicklungsstudien über beschichtete Lebensmittel, Massentransfer und die Barriereeigenschaften der auf Alginat basierenden Beschichtungen/Filme zusammenfasste.

Das anfängliche technische Teilziel war die Definition einer essbaren Beschichtungsmethode und von Komponenten mit Wasserbarriereeigenschaften (flüssiges Wasser und/oder Wasserdampf) sowie die Bewertung der antimikrobiellen Wirkung von zwei Additiven (d.h. Hopfenextrakt und Kaliumsorbat) bei der Einarbeitung in die Beschichtungslösung. Haltbarkeitsstudien sowie die Verluste nach der Ernte wurden anhand von frisch geschnittenen Cantaloupe-Stücken als Lebensmittelproben ermittelt. Aufgrund des ungünstigen Geschmacks konnte der Formulierung eine relativ geringe Menge Hopfenextrakt zugesetzt werden. Die Ergebnisse zeigten, dass beiden Überzugsschritten (d.h. sowohl Alginat- als auch Calciumlactatlösungen) antimikrobielle Mittel zugesetzt werden sollten, um eine höhere mikrobielle Inaktivierung zu erreichen. Die Zugabe von 625µg/g Hopfenextrakt oder Kaliumsorbat sowohl zur Beschichtung als auch zur Vernetzungslösung führte zu einer

logarithmischen TVC-Reduktion von 1. Reduktion der Gesamtkeimzahl auf 10% des Anfangswertes. Andererseits unterschieden sich die Auswirkungen von Hopfenextrakt und Kaliumsorbat auf die Hefezahl signifikant. Hopfenextrakt war unwirksam, aber Kaliumsorbat reduzierte die Hefezahl signifikant. Die drastischsten Veränderungen wurden in Wasserverlusttests beobachtet, d.h. Beschichtungen verringerten den Wasserverlust des Produkts signifikant. Sowohl die Beschichtung selbst als auch die eingearbeiteten antimikrobiellen Mittel veränderten die Farbe der Proben signifikant. Das Ablösen der Beschichtung von der Schnittfläche war der Hinweis auf eine mangelnde Adhäsionsfähigkeit der Beschichtungslösung auf der wässrigen Lebensmitteloberfläche und führte zu den verminderten sensorischen Werten und verminderten Barriereeigenschaften. Die identifizierten Probleme wurden in den folgenden Kapiteln untersucht.

Die Bildung einer durchgehenden essbaren Überzugsschicht hängt mit der auf der Zieloberfläche aufgebrachten Beschichtungsmenge zusammen. Die Bestimmung der Auswirkungen von Beschichtungsparametern (d.h. Eintauch- und Abtropfzeit) auf die Beschichtungsmenge, die die Oberfläche der Kantalupenstücke bedeckt, war das nächste technische Teilziel für die nachfolgenden Experimente. Im Hinblick auf das Ziel wurden die wünschenswerten Eigenschaften der Beschichtung für frisch geschnittene Cantaloupe-Stücke wie folgt definiert: keine drastische Farbveränderung, zunehmende Festigkeit und relativ höhere Gewichtszunahme (ein Hinweis auf eine erhöhte Beschichtungsdicke für verbesserte Barriereeigenschaften (für weitere Studien)). Zu Beginn wurden die Auswirkungen verschiedener Zeitintervalle (10 s-5 min) auf die Ergebnisse der Gewichtszunahme bewertet. Danach wurden auch die Auswirkungen von 3 ausgewählten Parametern auf die Farb- und Textureigenschaften bestimmt. Die Ergebnisse zeigten, dass längeres Eintauchen die Beschichtungsmenge nicht erhöhte, was höchstwahrscheinlich auf eine erhöhte Solubilisierung zurückzuführen ist. Für die anschließende Beschichtungsanalyse mit einer konventionellen Tauchapplikation wurden 2 min Eintauchen und 1 min Abtropfen definiert.

Die Bildung einer kontinuierlichen, homogenen, haftenden Beschichtungsschicht hängt hauptsächlich mit den Benetzungseigenschaften der Zielfruchtoberfläche durch die Beschichtungslösung zusammen. Andererseits ist die Benetzbarkeit der Lebensmitteloberfläche stark abhängig von der genauen Messung der Oberflächenspannung der Beschichtung und der freien Oberflächenenergie der Lebensmitteloberfläche. Die genaue Messung des Kontaktwinkels und damit der freien Oberflächenenergie von rauen und unregelmäßig geformten Lebensmittelproben, wie z.B. Erdbeere, stellte jedoch eine besondere Herausforderung dar. Um dieses Problem zu lösen, wurde im folgenden Kapitel die Anwendbarkeit und Genauigkeit einer Kontaktwinkel-Messmethode, nämlich des Programms ImageJ mit dem DropSnake-Plugin, evaluiert. Das System wurde mit einem konventionellen Tropfenkonturanalysator (DSA) mit Hilfe von vier verschiedenen Kunststofffolien und drei verschiedenen Sondenflüssigkeiten validiert. Anschließend wurde die freie Oberflächenenergie der stark hydrophoben Oberfläche von Erdbeere (γs=21,26 mN/m) bestimmt.

Wie oben erwähnt, ist die zweite wichtige Eigenschaft zur Erzielung eines guten Benetzbarkeitswertes die Oberflächenspannung der Beschichtungslösung, die speziell auf die Beschichtungsoberfläche abgestimmt sein sollte. Daher wurde in der nächsten Studie der Einfluss des Vorhandenseins und der Mengen der Inhaltsstoffe (d.h. Basismaterial, Weichmacher, pflanzliche Öle, Tenside) auf das Haftvermögen und die Stabilität der Beschichtungslösung bewertet. Die Haupt- und Wechselwirkungseffekte von Komponenten mit verschiedenen Gehalten wurden bewertet. Daher stellte diese Studie eine wichtige Methodik für Studien zum Beschichtungsdesign und für Formulierer von essbaren Beschichtungen/Filmen dar. Die Formulierungen wurden durch Bewertung der Oberflächenspannung, der Emulsionströpfchengröße, der optischen Eigenschaften, des Creaming Index und der Benetzbarkeitsergebnisse erstellt. Bei frischen Früchten, die mit einer hydrophoben wachsartigen Außenschicht bedeckt sind, sollte die Oberflächenspannung der formulierten Emulsionen deutlich verringert werden, um eine höhere Benetzbarkeit zu erreichen. Als Kompromiss zwischen dem Erreichen der maximalen Verringerung der Oberflächenspannung und der Verwendung der minimalen Menge an Beschichtungskomponente wurde die Formulierung unter Verwendung von 1,25% Natriumalginat, 2% Glycerin, 0,2% Sonnenblumenöl, 1% Span 80 mit 0,2% Tween 80 zusammengestellt.

Die mangelnde Haftung der Beschichtungslösung auf der Fruchtoberfläche war eine der größten festgestellten Einschränkungen. Unsere Forschung zielte darauf ab, eine Lösung für das herausfordernde Haftungsproblem von Beschichtungen auf Alginatbasis sowohl auf stark hydrophilen als auch auf stark hydrophoben Oberflächen zu finden. Die Gleichmäßigkeit der Beschichtung wurde durch die Zugabe eines zusätzlichen Eintauchschrittes in eine Kalziumlactatlösung zunächst vor den konventionellen Beschichtungsschritten erreicht. Die visuelle Inspektion der Beschichtungsschichten auf der frisch geschnittenen Cantaloupe (stark hydrophile Oberfläche) und den Erdbeerstücken (stark hydrophobe Oberfläche) wurde unter Verwendung eines Stereomikroskops durchgeführt. Mit Hilfe der neuen Beschichtungsstrategie wurde die Kontinuität und Gleichmäßigkeit der Beschichtungsschicht erreicht. Die durchschnittlichen Beschichtungsdicken betrugen 0,187 ± 0,076 mm bzw. 0,235 ± 0,077 mm für Cantaloupe und Erdbeeren.

Die Wasserbarriereeigenschaften in Bezug auf die Beständigkeit gegen flüssiges Wasser und Wasserdampf wurden im Detail untersucht. In Bezug auf das Ziel zeigten die Ergebnisse, dass eine Beschichtungsbehandlung auf Alginatbasis mit zusätzlichem anfänglichen Eintauchen in Kalzium den Flüssigwassertransport von porösen hydrophilen, frisch geschnittenen Cantaloupe-Stücken wirksam reduziert. Sie verringerte jedoch nicht den Wasserdampfwiderstand der beschichteten Proben. Andererseits förderte es den Wasserverlust beim Auftragen auf wachsartige Oberflächen (Erdbeerproben), was höchstwahrscheinlich auf eine schädigende Wirkung von Calciumlactat auf die wachsartige Schutzhülle zurückzuführen ist. Im Allgemeinen wurde festgestellt, dass ein einfaches Wasserbarrierenmodell nicht ausreicht, um den Wassertransport (sowohl flüssiges Wasser als auch Wasserdampf) von mit Alginat

beschichteten hydrophilen und porösen Cantaloupe- und stark hydrophoben Erdbeeroberflächen zu erklären. Der Beschichtungsprozess veränderte die Oberflächenstruktur der Erdbeeroberfläche. Andere Faktoren, wie z.B. eine Veränderung der Oberflächeneigenschaften, die Wirkung der Schwerkraft, Kapillarkräfte usw. sollten berücksichtigt werden. Nichtsdestotrotz hat uns die Studie zu einem besseren Verständnis des Prozesses verholfen.

Diese Arbeit bietet eine Anleitung in Bezug auf die Konstruktionsschritte der essbaren Beschichtung, die positiven Auswirkungen der Beschichtung auf Alginatbasis auf die Qualitätsmerkmale von Frischschnittprodukten. Sie sollte die Forscher dazu anregen, der Zerstörung hydrophober Wachsschichten auf den Lebensmittelpflanzen nach dem Beschichtungsprozess, der Erhöhung des Wassertransports und der Unterscheidung des Unterschieds zwischen Wasserverlusten durch Flüssigkeits- und Dampftransport Aufmerksamkeit zu schenken. Als Ergebnis dokumentiert diese Arbeit mehrere Schlüsselbeiträge, die auf den Gebieten der Gestaltung einer erfolgreichen essbaren Beschichtungsanwendung geleistet wurden.

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v1.10 Last updated September 2015

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