Mohammed Wasim Siddiqui, *Series Editor-in-Chief*

Postharvest Biology and Technology Book Series

Novel Packaging Systems for Fruits and Vegetables

Kirtiraj K. Gaikwad | Suman Singh
Editors

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NOVEL PACKAGING SYSTEMS FOR FRUITS AND VEGETABLES

Postharvest Biology and Technology Series

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Edited by

Kirtiraj K. Gaikwad, PhD

Suman Singh, PhD

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As we know, preserving the quality of fresh produce has long been a challenging task. In the past, several approaches were in use for the postharvest management of fresh produce, but due to continuous advancement in technology, the increased health consciousness of consumers, and environmental concerns, these approaches have been modified and enhanced to address these issues and concerns.

The Postharvest Biology and Technology series features edited books that address several aspects related to postharvest technology of fresh produce. The series presents existing and novel management systems that are in use today or that have great potential to maintain the postharvest quality of fresh produce in terms of microbiological safety, nutrition, and sensory quality.

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ABBREVIATIONS

AA	ascorbic acid
AP	active packaging
BC	bacterial cellulose
BCG	Boston Consulting Group
BCT	box compressive strength
BHA	butylated anisole
BHT	butylated hydroxytoluene
BOPP	biaxially-oriented polypropylene
CAP	controlled atmosphere packaging
Cat	catalase
CFB	corrugated fiber board
CFR	code of federal regulations
CH	chitosan
CIN	cinnamaldehyde
CMAP	controlled modified atmospheric packaging
CMC	carboxymethyl cellulose
CO	carbon monoxide
DBD	dielectric barrier discharge
DE	degree of esterification
DHAA	dehydroascorbic acid
DNA	deoxyribonucleic acid
EAB	elongation at break
EC	edible coatings
EF	edible films
EFSA	European Food Safety Authority
EO	essential oils
FAP	food additive petition
FAO	Food and Agriculture Organization
FCM	food contact materials
FCS	food contact substance
FC&V	fresh-cut fruits and vegetables
FDA	food loss and waste
FFS	film-forming solution

FI	freshness indicators
GA	gallic acid
GMP	glycomacropeptide
GOx	glucose oxidase
GRAS	Generally Recognized As Safe
HDPE	high-density polyethylene
HEC	hydroxyethyl cellulose
HMC	hydroxymethyl cellulose
HNT	halloysite nanotubes
ILAC	International Laboratory Accreditation Cooperative
IP	intelligent packaging
IUPAC	International Union of Pure and Applied Chemistry
KGM	konjac glucomannan
LAB	lactic acid bacteria
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
LSE	litchi shell extract
MAP	modified atmosphere packaging
MC	methyl cellulose
Micro-EDM	micro-electric discharge method
MMT	materials montmorillonite
MOF	metallic organic frame work
MRP	mangosteen rind powder
MT	metric tonnes
MW	molecular structure
MWCNT	multiwalled carbon nanotubes
NPs	nanoparticles
ORAC	capacity for radical oxygen absorption
OTG	on the go
OTR	oxygen transmission rate
PAM	pressure-assisted micro-syringe printing
PBAT	polybutylene adipate terephthalate
PBS	polybutylene succinate
PdNP	palladium nanoparticles
PE	polyethylene
PET	polyethylene terephthalate
PG	propyl gallate
PHAs	polyhydroxyalkanoates

PHB	poly(3-hydroxybutyrate)
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	polylactic acid
PP	polypropylene
PPO	polyphenol oxidase
PRS	pattern reorganization system with algorithms
PS	polystyrene
PVA	polyvinyl alcohol
PVC	polyvinylchloride
PVDC	polyvinylidene chloride
QR	quick response
RFID	radio-frequency identification
RO	residual oxygen
ROS	reactive oxygen species
RSS	reduced space symbology
RTC	ready-to-cook
RTE	ready-to-eat food
SC	sodium carbonate
SOPs	standard operating procedures
SO_2/MA	sulfur dioxide/modified atmosphere
SP	special packaging
SPC	soy protein concentrate
SPI	soy protein isolate
TPS	thermoplastic starch
TS	tensile strength
TSS	total soluble solids
TTI	time-temperature indicators
UGVs	unmanned ground vehicles
WHO	World Health Organization
WP	whey proteins
WPC	whey protein concentrates
WPI	whey protein isolates
WVP	water vapor permeability
ZnONP	zinc oxide nanoparticles

FOREWORD

Fruits and vegetables contain protein, fatty acids, vitamins, minerals, dietary fibers, and antioxidants. A diet rich in vegetables and fruits can prevent or reduce several serious health issues such as heart attacks, some types of cancer, digestive issues, and blood sugar. With the constantly evolving international trade, fresh fruits and vegetables are increasingly becoming one of the most important categories in global supermarkets.

Due to its restrictive shelf life, fresh produce typically requires expedited movement from farm to retail. While the use of optimal postharvest treatments helps maintain quality of the produce—packaging methods, processes, and technology can enhance shelf life and quality of the fresh produce through its distribution. An optimal rate of respiration, transpiration, ethylene production, and other metabolic processes are essential factors in choosing suitable packaging for fresh produce. With the target of maintaining or enhancing their shelf life, novel packaging techniques such as active packaging, intelligent packaging, and bioactive packaging involves an intentional interaction between the produce, packaging, and the internal/external environment.

This book on packaging technologies for quality preservation of fresh fruits and vegetables brings together a unique insight into the various novel packaging systems, packaging materials, and design elements. Some of the most innovative information on various aspects of packaging to effectively preserve the quality of fruits and vegetables can be found in this book. It is hoped that students currently enrolled in graduate and postgraduate programs and teaching professionals in packaging technology, food science and technology, and horticultural science will find this book useful. Benefits will also accrue to academic scientific research community members and the horticulture and packaging industries.

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PREFACE

Due to high demand for fresh fruits and vegetables, the market for packaging materials has experienced notable growth over the last 10 years, as per the US Department of Agriculture. This growth is expected to continue in the coming years. The growth is the result of immense knowledge on packaging technology learned through research and development work and material science and processing technology advances. For the past 10 years, there have been several patents, published research articles, and research projects undertaken by the food and packaging industries, academics, and scientists. The influence of sustainability agendas, carbon footprinting, and a keen interest in biodegradable and natural materials have further driven, and will continue to boost, the growth and interest in packaging materials. In addition, polymeric packaging material and novel technologies are adding value to the agricultural and food processing industries. With such a background, this book on Novel Packaging Systems for Fruits and Vegetables was structured. This book brings together packaging materials and novel techniques from different scientific disciplines from the academic and research institutes and the food industry (fruits and vegetables processing industries).

Novel packaging techniques considerably increase the shelf life of fresh produce. For example, freshness and quality indicators can be impregnated into the packaging to check the quality and safety of packaged fresh produce in smart packaging.

This book is composed of 12 chapters contributed by packaging technology experts. The book starts with important biopolymeric films for fresh produce packaging and a historical and common overview, followed by two chapters on the mechanical and physical and permeability properties and recent developments in investigative techniques of biopolymers as well as their applications in modified atmosphere packaging used in fresh produce packaging. These two chapters also comprise a detailed description of polymers' fabrication and engineering properties utilizing biomaterials. The next four chapters discuss detailed applications of natural/organic active agents, including oxygen scavenger, ethylene scavenger, antioxidants, antimicrobial agents, etc., for the fabrication of active packaging for maintaining the quality of fresh produce during storage and transportation. The next chapter deals with active (antimicrobial, antioxidant) edible films and coating used to preserve the quality of fresh produce. The following three chapters in the book deal with protective packaging, package designing aspects, and safety and security packaging for agricultural produce in the supply chain.

This book discusses the commercially available packaging technologies for fresh produce. Each author has constructed their chapter comprehensively so that each chapter could stand on its own. This book was constructed to aid a beginner in packaging technology in addition to those already engaged in the area, with the intention that the topics covered in the edited book will prompt future novel ideas and processes.

Our honest and immense gratitude goes to all authors for their contributions in writing the book chapters and to all the professor/scientists/authors who have worked hard to keep the interest and continued advancement of packaging technology. A special thanks goes to Dr. Mohammed Wasim Siddiqui, editor-in-chief of the Postharvest Biology and Technology book series, and Apple Academic Press, Inc. for their motivation, patience, and wholehearted support for the development of this book.

CHAPTER 1

BIOPOLYMERS AS PACKAGING MATERIALS FOR FRESH PRODUCE APPLICATIONS: PREPARATION AND PROPERTIES

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ABSTRACT

Food packaging plays a crucial role in storing, protecting, preserving, handling, and transporting a food product. Synthetic plastics are nonbiodegradable and their usage over the century has created serious damage to ecosystem. There is urgent need of substituting them with an eco-friendly alternative. In this context, biopolymers are the novel materials that can be explored for their potential in packaging sector. They can be classified into three classes: extracted from biomass, polymers derived from bio-based monomers, and the polymers produced by microorganisms. This chapter discusses different types of biopolymers for packaging of fresh produce, their key properties, and different methods employed to produce films and coatings from these biopolymers. These biopolymers can be an effective tool to prevent postharvest losses of fruits and vegetables.

Novel Packaging Systems for Fruits and Vegetables. Kirtiraj K. Gaikwad & Suman Singh (Eds.)

1.1 INTRODUCTION

Oil-derived plastics have been an integral part of mankind as they are cheap, easily producible, flexible, lightweight and possess superior properties. These plastics are derived from nonrenewable sources and account for 45% of the packaging sector with a global production of 360 metric tonnes (MT) in 2018. One of the limitations of these petrochemical plastics is that they are nonbiodegradable in nature and consequently leads to the generation of enormous amount of waste. Packaging sector is one of the dominant sources of plastic waste in the world. In 2015, approximately 407 MT of plastics were manufactured and three quarters of it ended up as waste. It is evaluated that out of the 6300 MT plastic waste produced, only 9% goes for recycling, while the rest of it gets accumulated as a waste in the landfill sites or seabed (Ritchie and Roser, 2020). Thus, to mitigate the negative ecological impact of plastics, there is an urgent need to shift from nonbiodegradable plastic packaging to natural biodegradable polymer-based packaging materials.

Biopolymers are natural, biodegradable and can be a promising alternative to the synthetic plastics. They are generally produced from food sources like polysaccharides, proteins, lipids or synthesized by natural or genetically modified microorganisms. They are developed with the primary goal of reducing plastic waste to promote sustainability and circular economy. In 2019, the world's production of biopolymer-based packaging was 2.11 MT with a market value of USD 4.65 billion, and it is estimated to increase up to 2.43 MT by the end of 2025 with a CAGR of 17.04% (Shaikh et al,, 2021). The use of biopolymer packaging materials offers many advantages over the conventional ones such as nontoxicity, excellent recyclability, easy processability, and good film formability properties. However, these biopolymers lack some of the properties like poor barrier and mechanical properties, along with high cost of the packaging material. These limitations have hindered the large-scale commercialization of the biopolymer packaging films. Although these issues have been addressed through the incorporation of plasticizers, fillers etc., still much attention is required to explore their full potential as packaging materials.

Fresh fruits and vegetables are consumed on a huge scale globally owing to their high nutritional profile (mineral, vitamins, antioxidants). The perishable nature of fresh produce makes them prone to postharvest deterioration and invasion by microorganisms. This results in shorter shelf life and huge loss. In addition to this, any mechanical injury in the supply chain may trigger biochemical changes accelerating senescence in fruits and vegetables. Biopolymer packaging is a cheap, effective post-harvest technique that can be applied to improve the storability characteristics of fresh produce. This chapter provides an outline of different types of biopolymers which can be utilized to develop packaging materials for fruits and vegetable packaging. Different methods like casting, extrusion, coating, and electrospinning which can be utilized for the production of these packaging materials are discussed in detail. Diverse applications of the biodegradable packaging for elevating the safety, freshness, and shelf-life of different climacteric and non-climacteric fruits and vegetables are also reviewed.

1.2 BIOPOLYMERS FOR PACKAGING OF FRESH PRODUCE

Polymers that are biodegradable and derived from natural renewable sources can be classified as biopolymers. Biopolymers used for the preservation of different horticultural commodities are mainly divided into three categories: biopolymers extracted from natural sources (polysaccharides and proteins), biopolymers synthesized via chemical methods (polylactic acid, polyvinyl alcohol, polycaprolactones), and biopolymers produced by microorganisms (polyhydroxyalkanoates (PHAs) or bacterial cellulose), as illustrated in Figure 1.1. The detailed description of these biopolymers is given below.

1.2.1 NATURALLY DERIVED BIOPOLYMERS

1.2.1.1 PLANT SOURCE-BASED BIOPOLYMERS

1.2.1.1.1 Cellulose and Its Derivatives

Cellulose is the naturally occurring biopolymer found in ample amount. It is a polysaccharide comprising unbranched chain of D-glucopyranosyl units linked with β-1,4 bonds and forms an important constituent of plants cell wall. Due to high crystallinity, cellulose is insoluble in almost all the solvents. As a result, it is not possible to cast or extrude pure cellulose into films. Hence, it is modified into cellulose derivatives which are utilized for the films development with better structural properties. These include methyl and acetate derivatives like carboxymethyl cellulose

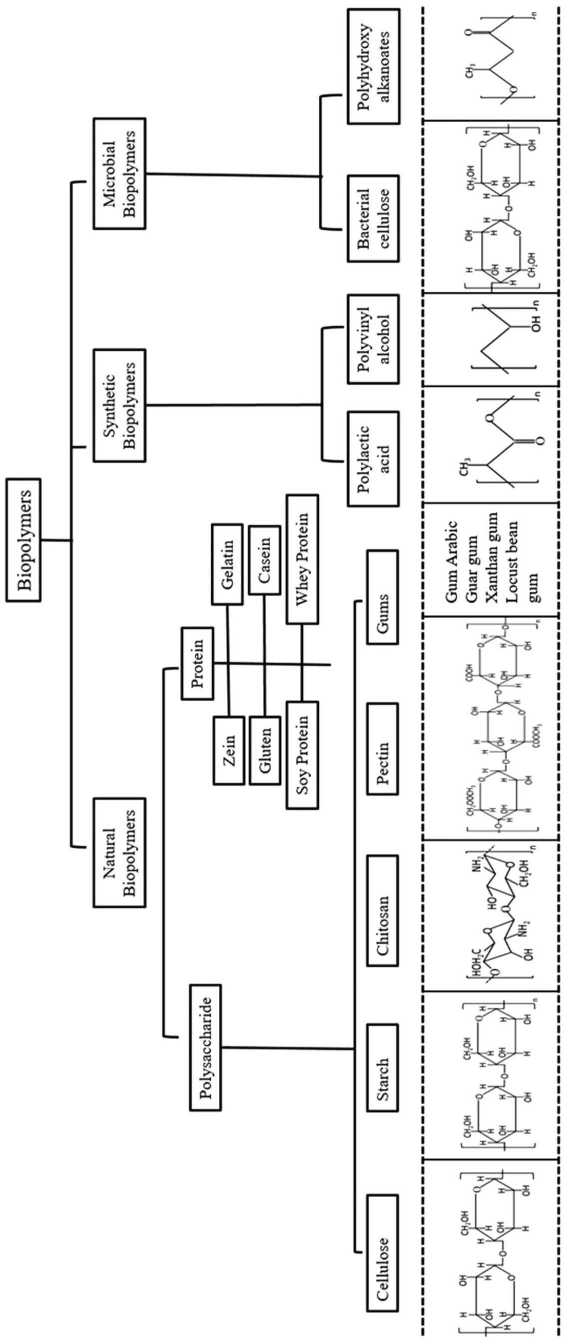

FIGURE 1.1 Classification of biopolymers.

(CMC), hydroxymethyl cellulose (HMC), methyl cellulose (MC), and cellulose acetate. These compounds are water soluble and used to develop cellulose-based films and coatings (Cazón et al., 2017). The incorporation of glutaraldehyde has shown a positive impact on decreasing the water vapor permeability of methylcellulose films. Similarly, water resistance capacity of CMC films can be enhanced by chemical cross-linkers and photo-cross-linkers for food packaging applications (Deng et al., 2022). Cellulose acetate is derived through the acetylation process of cellulose. These films are more popularly used than the films from other cellulose derivatives due to their good barrier properties. It forms clear films which can be used to pack fresh produce. The composite films produced by blending cellulose with chitosan display very good functional properties as they yield homogeneous film solution due to similar structures. The degradation of cellulose in soil is complex as it is conjugated with hemicellulose and lignin, but pure cellulose degrades quickly.

1.2.1.1.2 Starch

It is an abundantly available renewable biopolymer found in nature and can be found in many sources like wheat, rice, corn, millets, tapioca, cassava, yam, potato, and many more. It is a polysaccharide comprising glucose monomers and main source of energy for plants. It is composed of two subunits: 20–25% amylose (D-glucose linked by α-1,4 glycosidic bonds) along with 75–80% amylopectin (α-1,4- and α-1,6-D-glucopyranoside). Starches are not solubilized in cold water due to the presence of strong hydrogen bonding. Upon heating, these interactions get weakened leading to starch solubilization (gelatinization). Gelatinization process converts starch into thermoplastic starch (TPS) which is important for the production of starch-based films. This starch suspension is casted onto a Teflon substrate and dried to form the film. During drying, recrystallization occurs leading to the formation of new bonds between polymer chains (retrogradation) (Adeyeye et al., 2019).

Films and coatings made from starch without any additives are brittle, fragile and lack tensile strength. Hence, plasticizers like sorbitol, polyethylene glycol, and glycerol are added to increase the films flexibility. Films made from starch offer several advantages such as biodegradability, nontoxicity, odorless, tasteless, and good oxygen barrier properties (Sameen et al., 2021). However, due to hydrophilic nature of starch, they possess poor water barrier capacity. These technical issues can be overcome by employing certain physical, chemical, enzymatic, and thermal post treatments that helps to modify the starch structure and alter film characteristics. In one study high amylose starch was first modified using the extrusion process by exposing it to high temperature and pressure conditions and then formed into thin films using the casting method. The developed films displayed improved barrier properties and helped to preserve the quality attributes of mango (Calderón-Castro et al., 2018). The characteristics of starch films are related to many factors such as plasticizer concentration, starch source, amylose/amylopectin ratio, and method of processing. Depending upon the type and amount of plasticizer used, or the method like injection molding, compression molding or extrusion or casting can have a significant effect on the functional and structural properties of the films (Hejna et al., 2019).

Over the past few decades, bioactive components like antioxidants and antimicrobial agents are being added to the starch-based films to develop active packaging solutions for different fruits and vegetables. In relation to the biodegradation rate of starch, it is being reported that major part of starch starts to degrade within 3 days due to the cleavage of glycosidic bonds by the action of glycoside hydrolases. Thus, biodegradable starch films could be a potential packaging material to prevent postharvest losses in fruits and vegetables.

1.2.1.1.3 Gums

Gums or hydrocolloids are also polysaccharides. They can be derived from various sources like seed endosperm (guar gum), plant exudates (tragacanth gum), bacteria (xanthan gum), algae (agar), and trees (gum arabic) (Tahir et al., 2019). Gums-based edible coatings provide some benefits such as delaying ripening, extending shelf life, decreasing respiration rate, and maintaining postharvest quality of fruits and vegetables. The gums are very hydrophilic as the number of hydroxyl groups present in their structure is large. This leads to the formation of strong inter- and intramolecular hydrogen bonds which is a requisite for film formation. Polysaccharide gum coatings act as a semipermeable barrier and help to control the exchange of gases and moisture between the product and its external environment. Films produced from locust bean gum and tara gum show higher value of tensile strength and %EB (elongation at break) than the films made from guar gum (Liu et al., 2020). Gums-based films/coatings offer many advantages over the synthetic ones like sustainability, eco-friendly, biodegradability, biosafety, and they are approved as GRAS by FAO. Main disadvantages of gums-based edible films are high solubility and low strength. However, optimizing film formulations such as type of gum, amount of the gum used, plasticizers, cross-linkers, and mixing gums with other biopolymers can produce films with desirable mechanical, physical, and thermal properties (Zibaei et al., 2021). These materials can be considered prospective replacers of synthetic plastic polymers for packaging of fresh produce.

1.2.1.1.4 Pectin

Pectin is a polysaccharide present in the cell wall and middle lamellae of ripe fruits. It comprises linear chain of D-galacturonic acid units connected to each other by α-1,4 glycosidic bonds. Depending upon the degree of esterification (DE), it is of two types: high methoxyl pectin where DE is greater than 50% and low methoxyl pectin in which DE is less than 50%. It can be extracted from a variety of biomass like peels, rind, and skins of different fruits and vegetable. The gelling behavior of the pectin can be utilized to develop pectin-based coatings or films for packaging of perishable fruits and vegetables (Mellinas et al., 2020). Production of neat pectin films through melt technology is not feasible due to low thermal stability of pectin and hence, the solvent casting method is the commonly used method to formulate pectin-based films. It has been demonstrated by many studies that edible coatings made from pectin pose excellent barrier to oxygen and oil, help to lock in aroma, and display good mechanical properties. Nevertheless, high hydrophilicity and low mechanical strength of pectin-based films compared to polypropylene (PP) and high-density polyethylene (HDPE) limits its industrial applications.

1.2.1.1.5 Plant Proteins

Owing to their abundant availability, outstanding film-forming capability, excellent barrier properties, and biodegradability, plant-protein-based films have received much attention in comparison to its counterparts (polysaccharides and lipids). The main plant proteins are sourced from cereals (wheat, rice, corn, barley), pseudo-cereal (amaranth, quinoa, chia), oilseeds (sesame, hemp, sunflower, cotton), legumes (soy, pea, mung bean, lentils), and green leaf (algae, beet, alfalfa) which have the tendency to form adhesive film. Soy protein, derived from soybeans, is widely utilized in packaging applications in two forms: soy protein concentrate (SPC) and soy protein isolate (SPI). Good resistance against oxygen and oil makes soy protein isolate a promising material to fabricate films and coatings for a variety of F&V. The choice of method used for producing films based on SPC and SPI depends on two factors: concentration of protein and pH of biopolymer solution. When the protein concentration is low (~5%), the solvent casting method is used and if the concentration is about 80%, the extrusion method is employed (Assad et al., 2020). Wheat gluten is also an appealing biopolymer used for preparing packaging films with remarkable oxygen barrier properties. During film preparation, glutenin gets cross-linked to gliadin via thiol-disulphide exchange reaction leading to the development of three-dimensional gluten network. This contributes to the excellent barrier properties against atmospheric gases of wheat gluten-based films (Chen et al., 2022). The tensile strength (TS) and elongation at break (%EB) of films from soft wheat gluten are higher than the hard wheat gluten films.

Another popular and widely explored protein is zein, found in corn. It is hydrophobic in nature and has remarkable film formability. High thermal stability and viscoelastic behavior above T_g aids to process zein-based films in the presence of a suitable plasticizer through the extrusion technique which is a widely used method for obtaining plastic polymers on a commercial scale. It is a hydrophobic material and has an excellent film-forming ability. Therefore, zein has been extensively used to produce biodegradable packaging films and coatings to protect fresh produce from spoilage. Various studies have demonstrated that zein films possess lower gas permeability and better strength than other biopolymer films (Martins et al., 2021).

1.2.1.2 ANIMAL SOURCE-BASED BIOPOLYMERS

1.2.1.2.1 Chitosan

Chitin is an acetylated polysaccharide comprising N-acetyl-d-glucosamine monomers bonded by β-1,4 glycosidic linkages. It is a naturally occurring biopolymer, present in exoskeletons of insects or crustaceans shells. Chitosan is a polysaccharide which is obtained by carrying out the deacetylation process of chitin. The linear structure of chitosan comprises N-acetyl-glucosamine and D-glucosamine. The former is an acetylated unit while the latter is a deacetylated unit. It is insoluble in water but soluble in acids like acetic acid. It is very well known for its good film-forming capability. Chitosan-based films and coatings are selectively permeable to the atmospheric gases like oxygen and carbon dioxide (O_2 and CO_2). Moreover, they also possess excellent mechanical properties (Y. Liu et al., 2020). But they have high permeability to water vapor, which limits their applications for packaging of minimally processed fruits and vegetables. Different approaches can be undertaken to tackle this issue. Some of them include cross linking, incorporation of fillers, blending with other biopolymers, and enzyme treatment. Blending of chitosan with other biopolymers such as gelatin, cellulose, gums, pectin, and many more has been explored extensively to improve the physical, mechanical, barrier, and thermal properties of films and coatings made from chitosan (Haghighi et al., 2020). Recently, in a study chitosan was blended with the starch derived from white turmeric rhizome and films were fabricated by the solvent casting technique. The prepared films not only exhibited excellent antioxidant and antimicrobial characteristics, but also water resistance capacity and mechanical properties were improved significantly (Hiremani et al., 2021). Furthermore, degree of acetylation and molecular weight of chitosan are two important factors which help to determine the different properties of chitosan film-forming solution, particularly mechanical properties (González-Espinosa et al., 2019).

The antimicrobial activity of chitosan against a broad spectrum of microbes is widely known and explored for various applications in food. The remarkable antimicrobial activity could be due to a number of mechanisms. One such mechanism involves the disruption of cellular membrane of microorganisms due to interaction between negatively charged microbes and positive amine groups of chitosan. This results in leakage of bacterial constituents to outside and eventually leads to the death of microbes. Another possible reason for the antimicrobial property could be related to the low molecular weight of chitosan which enables it to enter microbial cell and disrupt the synthesis of DNA (Nair et al., 2020). Chitosan films/coatings are biocompatible, biodegradable, eco-friendly, and nontoxic.

1.2.1.2.2 Gelatin

Gelatin is an odorless, tasteless, and water-soluble protein. Collagen is a fibrous protein found in abundant amount in the connective tissues, skin, hides, and bones of the animals and acid/alkali hydrolysis of collagen yield gelatin. The sources from which gelatin can be derived include mammalian sources (pig, bovine), poultry sources (fish), and marine sources (chicken, duck). Depending upon the method used for gelatin extraction, it is of two types: Type A gelatin extracted from acid-treated collagen of pig skin, isoelectric point at pH 8-9, and Type B gelatin obtained from alkali-treated collagen of beef skin or cattle hides with isoelectric point at pH 4-5. Gelatin is a mixture of three polypeptide chains—α, β, and γ chains (Ahmad et al., 2017). It is used in food industries in many applications like thickening agent, gelling agent, stabilizer etc.

With the increase in demand of bio-based polymers for food packaging, gelatin has also been explored as a promising biopolymer for fabricating films and coatings because of low cost, excellent film-forming ability, and abundant availability as byproduct of agro-food industry. Generally, films made from gelatin display good oxygen barrier properties against oxygen at low or intermediate relative humidity along with excellent mechanical properties. The triple helical structure of the gelatin provides physical strength to the films, while the presence of different amino acids like proline and glycine helps to block UV radiation to pass through the packaging films. This aids in safeguarding packaged fruit and vegetables from oxidative damage. Several studies have reported the tensile strength for mammalian gelatin-based film within the range of 2.40–63.25 MPa. This is comparable to conventional plastics like high-density polyethylene (HDPE) and low-density polyethylene (LDPE) having tensile strength of 17.3–44.8 MPa and 8.2–31.4 MPa, respectively (Said et al., 2021). Despite these advantages, there are certain limitations in the application of gelatin-based films. Standalone gelatin films are highly sensitive to moisture and provide very poor protection from the humid environment. They tend to swell and disintegrate in contact with moisture (Andreuccetti et al., 2017). Hence, it becomes crucial to modify gelatin using different methods to address these constraints. Functional properties of gelatin films/coatings can be altered by the use of additives such as plant extracts (Riahi et al., 2021), cross-linkers, plasticizers (Suderman et al., 2018) or strengthening biopolymers (Soo and Sarbon, 2018).

1.2.1.2.3 Casein

Milk primarily consists of two proteins: casein (~80–85%) and whey proteins (~15–20%). Casein is the most important protein and comprises four subfractions: αS1-, αS2-, β-, and κ-caseins. Casein proteins are valuable source for the production of biopolymeric films and coatings with excellent gas barrier attributes, suitable thermal stability, nontoxicity, and protection against flavor loss (Mihalca et al., 2021). Casein-based films can be developed from caseinate solutions by solubilizing them in a suitable solvent, casting onto a nonreactive substrate and then drying it adequately under room conditions. The ability of sodium caseinates to form composite films can be attributed to its unsystematic bobbin structure which helps to form intermolecular interactions between the chains, resulting in a coherent polymer matrix. Calcium caseinate films have higher tensile strength and thermal stability than those made from sodium caseinate as calcium ions lead to cross-linking between the polypeptide chains giving a tougher film structure (Karaca et al., 2019).

However, the major drawbacks of milk protein-based packaging systems like brittleness, poor resistance to moisture, and low elasticity, etc. limit their industrial applications and hence should be addressed to replace synthetic polymers with biodegradable ones. These limitations of films prepared from caseinates can be modified by incorporating chemical/enzymatic cross-linkers, plasticizers, bioactive compounds, and nanofillers into the film matrix. Wu et al. (2020) explored the potential of dielectric barrier discharge (DBD) cold plasma as a modification technique to improve packaging performance of casein-based film. Mechanical (61% increment in tensile strength) and barrier properties (61% decrement in WVP (water vapor permeability)) of the formed films were notably improved due to casein aggregation. Similarly, addition of tannic acid (polyphenolic compound) as a cross linking agent in casein films helped to improve the thermal stability along with different physico-chemical properties of films (Picchio et al., 2018). Recently, several research studies have developed different approaches to create functional films of casein using additives like nanoparticles, antimicrobial agents, and antioxidants. Films obtained by blending polyvinyl alcohol with casein hydrolysates were utilized as a protective carrier of biocontrol agents (lactic acid bacteria) (Settier-Ramírez et al., 2021) which can be used for potential active packaging applications. A casein-based nanocomposite coating incorporated with

ZnO nanoparticles was formulated through double polymerization. The films not only demonstrated antibacterial properties but also the water barrier property increased markedly (Ma et al., 2019).

1.2.1.2.4 Whey Protein

Whey is a by-product of dairy industry obtained during manufacturing of cheese. Whey proteins (WP) account for approximately 15% of the total proteins present in milk and comprise five major globular proteins: 50% β-lactoglobulin, 20% α-lactalbumin, 15% glymacropepetide (GMP), 8% bovine serum albumin, and 10% immunoglobulin.

Whey protein is an important bio-based polymer that can be used to produce edible and biodegradable packaging films for fresh fruits and vegetables. Whey-based films can be produced from two forms of whey protein namely whey protein concentrates (WPC) and isolates (WPI). WPC are obtained by the ultrafiltration process of whey, and it comprises 40–80% protein with very less amount of fats and cholesterol. On the other side, further processing of WPC through ion exchange chromatography yields WPI having 90% protein content with zero lactose (Carter et al., 2021). Thermal denaturation is the commonly used technique to develop coherent films of whey protein. The film-making process of whey protein-based films can be separated into different steps. Firstly, at pH 6 and temperature >40°C, β–lactoglobulin converts from dimeric to monomeric form. Furthermore, when the temperature reaches above 60°C unfolding of β–lactoglobulin molecule occurs, exposing the functional and hydrophobic groups of whey protein. The exposed groups form new interactions like intermolecular disulfide bonding, or hydrogen bonding, van der Waals interaction, and hydrophobic bonding. This leads to irreversible denaturation of WP resulting in the formation of a 3D network. Hence, the films formed have uniform structure (Schmid and Müller, 2019).

Whey proteins-based films and coatings are transparent, biodegradable, flexible, odorless, colorless, and have great barrier and mechanical properties compared to the films made from polysaccharides and other proteins (Tsai and Weng, 2019). Compared to the films made from other proteins, films made from WPC and WPI possess better oxygen permeability, high WVP, and low tensile strength (Kandasamy et al., 2021). They also exhibit excellent oil, oxygen, and aroma barrier properties (KS Silva 2018). Films/coatings based on whey protein have also been utilized as carriers of active