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Review

Active Casein Coatings and Films for Perishable Foods: Structural Properties and Shelf-Life Extension

Muhammad Rehan Khan [1,*], Stefania Volpe [2], Marika Valentino [1], Nicoletta Antonella Miele [1], Silvana Cavella [1] and Elena Torrieri [1]

[1] Department of Agricultural Science, University of Naples Federico II, Via Università 133, 80055 Portici (NA), Italy; marika.valentino@unina.it (M.V.); nicolettaantonella.miele@unina.it (N.A.M.); cavella@unina.it (S.C.); elena.torrieri@unina.it (E.T.)

[2] Centre of Food Innovation and Development in the Food Industry, University of Naples Federico II, Via Università 100, 80055 Portici (NA), Italy; stefania.volpe2@unina.it

[*] Correspondence: muhammadrehan.khan@unina.it

Abstract: There is an urgent need to increase the food supplies to fulfil the demands of future generations as the population of the world is expected to grow beyond 10 billion by 2050. An essential component for ensuring global food security is to reduce food losses during the post-harvest stage. Active edible coatings and films are a promising sustainable preservation technology for shelf-life extension of food products by hindering decay kinetics of minimally processed fruits and vegetables (F&V), by restricting the mass transfer of moisture, aroma, or gases and carrying an active compound, such as an antioxidant or antimicrobial. Active protein-based coatings and films have the potential to extend the shelf-life of food products by decreasing their respiration rates, as they exhibit an excellent gas barrier and good mechanical properties as compared to other biopolymeric packaging. Among protein-based biopolymers, casein and its derivatives as packaging films have been extensively studied due to their low cost, complete biodegradability, and availability. Currently, there is no review study focusing on caseinate-based active coating and film, thus, this review aims to give insights on the composition, rheology, structure, and properties of caseinate-based formulations by critically discussing the results presented in the literature. A methodological approach was followed to obtain relevant literature to discuss the influence of additives on the shelf-life of F&V. Furthermore, changes in secondary structure of casein were observed after incorporation of bioactive compounds (i.e., phenolic acids). Likewise, there is a need to explore chemical interactions among bioactive compounds and biopolymer material by using in silico and laboratory trials as food additives have shown to influence the physicochemical properties of film and shelf-life of food products.

Keywords: active coatings; films; proteins; shelf-life; caseinate; structural properties; fruits and vegetables

1. Introduction

One of the major global challenges right now is how to ensure food security and to reduce food loss for rapidly increasing global population while ensuring attainment of sustainable development goals [1]. There is an urgent need to increase the food supplies to fulfil the demands of future generations as the population of the world is expected to grow beyond 10 billion by 2050. According to the United Nations Environment Program Report 2021, almost 17% (about 931 million tons) of the food products (especially F&V) were lost in 2019 due to improper handling, microbial contamination, and inadequate packaging [2,3]. Minimally processed fresh F&V suffer from loss of quality due to accelerated decay during shelf-life because of oxidation reactions, microbial growth, and environmental stress. Furthermore, plastic-based packaging of petrochemical origin has been widely utilized in the food industry due to its many advantages; however, they pose a public health threat due to their non-biodegradable nature [4,5]. In the past decade, the researchers have shifted their attention from non-biodegradable packaging to biopolymeric packaging [4]. Among

biopolymers, proteins have especially been an area of focus for developing biodegradable and edible coatings and film. Protein-based coatings and films are quite advantageous as packaging materials because they are considered food additives and because they have the potential to extend the shelf-life of food products by decreasing their respiration rates and exhibiting better mechanical properties as compared to other biopolymeric packaging [6].

Casein is a type of a protein-based biopolymer obtained from milk [7]. Sodium caseinate is a compound obtained through acid precipitation of casein, and is an interesting biomaterial that can be used for food packaging [8]. Casein-based films are realized by means of casting or extrusion, while coatings are synthesized by mechanisms similar to solution casting and are applied generally to F&V either by dipping or spraying method.

Active packaging is a type of packaging in which active compounds are intentionally added to improve the packaging performance and to extend the shelf-life of the food products. In the past decade, the research was more focused on the use of naturally existing active compounds (i.e., polyphenols) in food packaging rather than artificial ones (i.e., benzoic acid, citric acid, sorbic acid, and sodium nitrite, etc.) because of their potential adverse effects and regulatory constraints [9]. Several active food additives of natural (essential oils, plant extracts, and probiotics) and synthetic nature (i.e., nanomaterials) have been incorporated into active casein-based coatings/films, aiming to extend the shelf-life of fresh produce; however, the studies on caseinate coatings are quite limited as compared to casein-based films.

A review study on potential F&V application of active casein-based edible film and coating is currently not available; thus, this review aims to highlight the research done so far on active casein coatings and films. Casein structure and properties have been discussed and how they are influenced by different food additives. Furthermore, shelf-life aspects have been explored to highlight gap areas in research to appropriately design casein-based coatings and films so they can be used for preserving the quality and extending the shelf-life of minimally processed F&V.

2. Protein Based Coatings and Films

Proteins are one of the naturally occurring biopolymers of organic nature made up of α-amino acids to form primary structure by means of peptide bonds. The secondary structure of proteins is characterized by a polypeptide backbone that is important for the folding of the proteins. The tertiary structure involves the intermolecular interactions of side chains of the proteins into globular configuration. Additionally, some proteins develop a quaternary structure, which enables them to form loose reversible molecular aggregates. Thus, protein structure is important to determine the ability of the protein to formulate edible film/coatings by interacting with themselves and other additives [10]. Coatings can be directly applied onto the food products as a coat (which is quite advantageous) as compared to films (which can be placed around or between foods) [11]. Generally, protein-based coatings/films are synthesized by using water, ethanol, or water–ethanol combinations as solvents [12]. Protein-based coatings/films incorporated with additives (i.e., antioxidants and antimicrobials) have shown excellent results by displaying good mechanical, gas barrier properties and other desirable functional characteristics. The coatings ability to modify the environment around F&V to extend their shelf-life is a phenomenon that is well documented in the literature [13–16]. Among naturally occurring proteins (i.e., gelatin, whey, soy and pea protein), casein and its derivatives have been extensively explored in the past decade because of their complete biodegradability, availability, and low cost [17].

3. Casein-Based Packaging

3.1. Structure

Casein (Figure 1) is a proline rich rheomorphic, major open structured milk protein comprising of four protein fractions: α s1-casein (38%), α s2-casein (10%), β-casein (36%), and kappa-casein (13%) [18] with estimated production of 0.43–0.46 million tons [19].

The unique properties of these protein fractions can influence the film forming ability of the casein [20]. Caseins have the ability to form edible films/coatings easily from aqueous solutions without additional processing due to a large number of electrostatic, hydrophobic, and intermolecular hydrogen bonds. Moreover, caseins' random-coil nature causes a strong interchain cohesion which further contributes towards this ability [21]. The unique properties of casein, i.e., high thermal stability, biodegradability, capability to form micelle, capability for emulsification, and ability to bind with small ions and molecules makes it a highly desirable biomaterial for the preparation of edible coatings [22]. The high thermal stability of casein can be attributed to relatively low secondary or tertiary structure due to absence of disulphide bridges, and interruption of α-helix and β-strands by the proline peptides in the casein structure [23]. The surface of casein micelle is covered with kappa-casein fractions (which are hydrophilic in nature) and stabilizes the micelle through steric repulsion and electrostatic intermicellar interactions, while both alpha caseins act as linking agents because of their phosphate center (with α s2-casein being most hydrophilic among all casein) [24]. On the other hand, β-casein is amphiphilic in nature due to the presence of highly charged N-terminal and a major hydrophobic C-terminal (due to which casein can be used to encapsulate hydrophobic bioactive compounds) [25]. Furthermore, caseinate is a type of compound, which because of its unique property (i.e., degradation in 30 days in an isotonic saline solution, solubility, and rapid dispersion in aqueous mixtures), it can be considered as an interesting biomaterial for the development of active packaging systems [26].
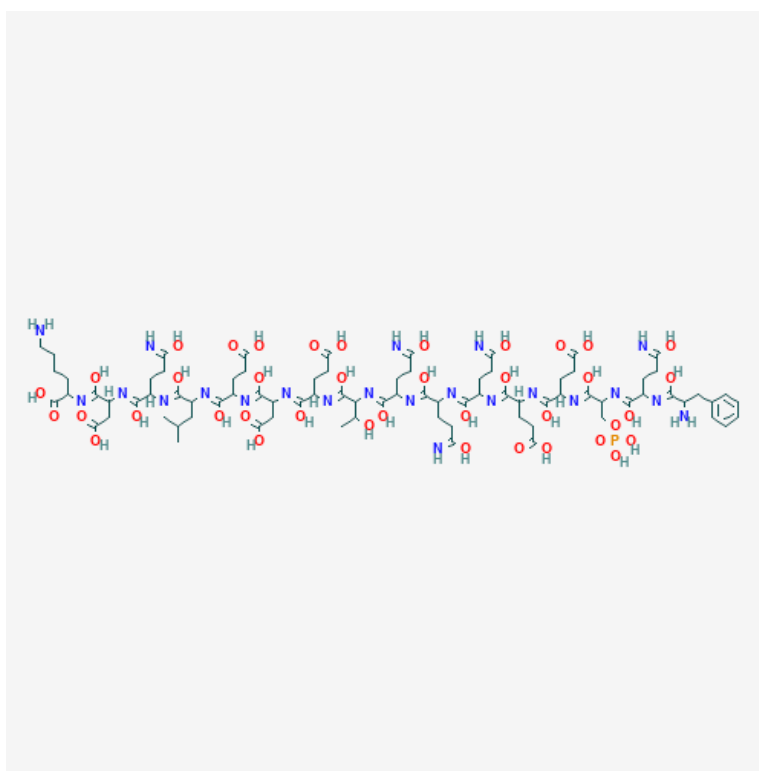
Figure 1. 2D structure of casein (https://pubchem.ncbi.nlm.nih.gov/ (accessed on 27 July 2021)).

Casein-based blends with other biopolymers are generally prepared to improve physicochemical properties of the film (for instance mechanical properties) and are known as composite complexes. Composite polymer complexes are formed due to electrostatic forces between polymers because of opposite charges. When pH of the protein-based polymers (especially casein) is below their isoelectric point, proteins (having positive charge) can interact with phosphate, carboxylic acid, and sulfate groups of anionic polysaccharides. This leads to the formation of soluble and insoluble complexes which are influenced by

ionic strength and pH (since both of these factors influence the intensity of electrostatic forces) [27]. For instance, at low pH (i.e., 3–4) chitosan (a polycationic polysaccharide) have similar charge as sodium caseinate, so they can easily dissociate into each other and form polymeric complexes, at a pH of 5.3, different concentrations and ratio chitosan/sodium caseinate can interact and affect the structure as well as the physical properties of the obtained blended films [28]. Indeed, in an acidic environment and above the isoelectric point of casein, the NH_2 ammino group of chitosan can be protonated to NH_3^+ and forming electrostatic interactions with the COO^- group of the casein. On the other hand, at pH above isoelectric point of casein, casein and Arabic gum (a polyanionic polysaccharide) can form soluble complexes [29]. Similarly, amino group (protonated) of casein has been reported to form amide bond with carboxylate group of sodium alginate due to electrostatic attractions (due to absence of characteristic peak of carboxylate group), consequently forming protein/polysaccharide complex with excellent structural integrity for delivery of bioactive compounds [30]. This information will be useful for the development of solutions/dispersions which ultimately can be used for packaging purposes.

### 3.2. Film Forming Solution/Dispersion Properties

Coating application on minimally processed F&V involves controlling the viscosity of the film forming solution. The viscosity, as well as the density and the surface tension, affects the thickness of both the deposited liquid and dry film of coating; the latter being one of the factors that defines the internal atmosphere modification. However, the dry coating load depends on the viscosity and the solid concentration of the film forming solution [31]. Thus, the thickness of liquid film coating could be estimated as a function of solution viscosity and draining time, an approach recently applied for sodium caseinate film forming solutions with good results [32].

Flow behavior of caseinate solutions can be divided into two categories, depending on their solid content. At concentrations <9%, the solutions were essentially Newtonian, meanwhile at concentrations >9%, they were slightly shear thickening, with a viscosity that increased as the sodium caseinate concentration increased too [33]. Caseinate solutions with a suitable viscosity for coating applications could not be obtained, even at high concentrations, therefore it is blended with other biopolymers. Although, when proteins and polysaccharides are mixed, they may remain close to each other in a single-phase or separate into two phases, depending on the intensity of associative and segregative forces between the two biopolymers [34]. The combination of caseinate with another polymer, such as high methoxyl pectin, determined a transition from Newtonian to shear thinning flow behavior, but the physical stability of the system depended on both biopolymer ratio and pH [35]. A shear thinning behavior was also observed for blends of caseinate and chitosan [36]. Guar gum and sodium caseinate showed limited compatibility and had a demixing tendency at higher concentrations in an aqueous medium, suggesting segregative interactions, which resulted in a protein-rich and a polysaccharide rich phase [37]. When a monophasic system was formed the solutions showed a shear thinning behavior, with a viscosity that increased at increasing the guar gum concentration. Recently, the compatibility of sodium caseinate and Persian gum, an anionic arabinogalactan with a structure and emulsifying effectiveness similar to that of gum Arabic but much cheaper, was verified and it had poor results [34] but was improved by the inclusion of sucrose [38].

Sodium caseinate could be used to prepare not only solution-based films/coatings, but also emulsion-based films/coating. In caseinate stabilized emulsions, the effect of biopolymers and surfactants on stability was recently reviewed [39], underlining that the effect of these components depends on pH, thermal treatment, concentration, and ionic strength. However, in both systems, it generally required the inclusion of a plasticizer, such as glycerol, for the impact on the mechanical properties, and this inclusion tended to decrease the viscosity of the system [33].

3.3. Composition and Preparation

Caseinate films are realized either by casting or extrusion processes. Generally, solvent casting is quite an advantageous methodology for developing film at lab scale, since no expensive equipment is required for it and in this process, caseinate powder (5%–8%) and plasticizers (10%–35% of total solid content) are dispersed in deionized/distilled water at room temperature for 2–4 h. Finally, solution is degassed to remove air bubbles and casted onto Petri plates and placed in the oven to obtain films. On the other hand, extrusion is not a widely reported process for making casein-based films on a lab scale (although it can be used for bulk production of packaging films on commercial scale and a good alternative to casting). This process generally utilizes a twin-screw extruder in which caseinate is introduced in the first zone by using a gravimetric feeder and plasticizer is added through a piston in the second zone with a temperature range between 40–100 °C, depending upon material requirement. The molten mixture is then forced through a die and the thickness of the resultant film is controlled by the speed of nip rollers [40–46]. Edible coatings are formulated using the similar processes and mechanisms linked with casting of the films. Coating is obtained when a dilute protein solution is applied to the food product surface, and solvent evaporates [47,48]. Generally, to obtain caseinate-based coatings, sodium caseinate powder (5%–8%) is dispersed in deionized water continuously for 2–4 h at room temperature. Glycerol is commonly utilized as a plasticizer at a concentration ranging between 10%–30% based on the protein content [32,44,49–52]. Finally, the solution is homogenized (usually in case of active coatings) by using a rotor stator homogenizer (Figure 2). To produce active coatings, a wide range of active additives (i.e., essential oils, probiotics, and polyphenols) have been added into caseinate-based coatings. Table 1 summarizes the different compositions of caseinate-based coatings prepared and discussed in the literature over the last two decades. Dipping was the most used method to coat the food products from caseinate-based coatings; generally, F&V are dipped into the dispersions for 1–3 min and are allowed to dry. This is best suited for irregular-shaped food products, i.e., F&V [50]. However, final formed coatings are less uniform as compared to spraying. Multiple dipping procedures might be required for full coverage of the food product; additionally, due to the hydrophilic nature of certain food products—e.g., fresh cut F&V—excellent adhesion is hard to achieve, thus a layer-by-layer technique might be required in which F&V are dipped in a polyelectrolyte solution with opposite charges to enhance adhesion with actual coating (Figure 3) [10,11].
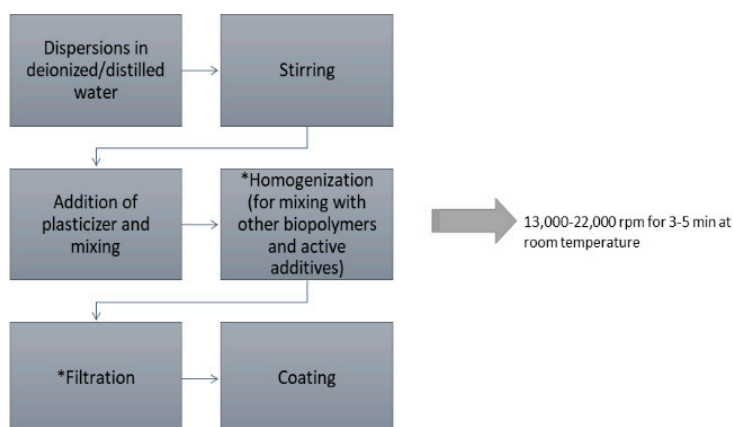
- *Represents additional steps required for obtaining active/composite coating solutions/dispersions
- After probiotic incorporation, dispersions only shaken not homogenized

Figure 2. Process of coating development.

Table 1. Composition, formulation and application method of caseinate coatings.

Composition		Plasticizer Used	Formulation Conditions	Application Method	Reference
Type	Active Additives				
Sodium caseinate (4%–14%)	Gallic acid (0.005%) and rosemary essential oil (1.5%)	Glycerol (0.4%–1.4%)	Sodium caseinate powder dissolved in deionized water with stirring for 4 h at room temperature and glycerol was added to form coating. For active coating preparation sodium caseinate was dissolved in HCl tris buffer at room temperature for 4 h by stirring. After adding glycerol, active additives were added, and solution was homogenized at 15,500 rpm for 4 min.	Dipping	[32]
Sodium caseinate + potato starch (2%)	*L. plantarum* (5 × 10^7 CFU/ml)	Glycerol (-)	The coatings were prepared by dispersing 2% biopolymers in deionized water at room temperature for 2 h, oleic acid was added, at a ratio of biopolymer: oleic acid (1:0.1), homogenized at 13,600 rpm and sterilized. After cooling, *L. plantarum* was added into dispersions.	Spraying	[49]
Sodium caseinate (1%) + arabic gum (5%)	Cinnamon and lemon grass oils (1%–2%)	Sorbitan monooleate (1%)	After arabic gum was dissolved in deionized water for 90 min at low heat by stirring, plasticizer was added. The pH was adjusted to 5.6 by using 1 N NaOH. Similarly, sodium caseinate was dissolved in deionized water. This formulation was added into the formulation of arabic gum and stirred. Finally, essential oils were added and the mixtures were homogenized to obtain coatings.	Dipping	[53]
Sodium caseinate (11.1%) + bees wax (5%–15% of protein content) + stearic and palmitic acid blend (5%–15% of protein content)	-	Glycerol (3.3%)	Dipping solutions were prepared by dissolving sodium caseinate in distilled water. After adding the plasticizer, beeswax and stearic + palmitic blend was added. Finally, the solutions were homogenized at 22,000 rpm for 5 min to get coating.	Dipping	[54]
Sodium caseinate (10%)	-	Glycerol/PEG	The system was prepared by adding sodium caseinate gradually into distilled water. Finally, glycerol/PEG was added.	-	[55]

Table 1. *Cont.*

| Composition		Plasticizer Used	Formulation Conditions	Application Method	Reference
Type	Active Additives				
Sodium caseinate	-	Sorbitol and glycerol	Coatings were prepared separately from sodium caseinate + glycerol and sodium caseinate + sorbitol.	Spraying	[56]
Sodium caseinate (0%–1%) and sodium carboxy methyl cellulose (0.1%–1.5%)	-	Glycerol (0%–2%)	Sodium caseinate and sodium carboxy methyl cellulose were dissolved in distilled water, after that glycerol was added. The solutions were homogenized for 3 min at 21,500 rpm.	Dipping	[57]
Sodium caseinate (8%–13%) + sodium azide (0.02%)	-	Glycerol (10%–30% w/w of total solids)	Sodium caseinate and sodium azide were dispersed in distilled water for 30 min at 60 °C while stirring. Glycerol was added into the dispersion and the mixture was again stirred for 30 min at room temperature.	-	[33]
Sodium caseinate (2%)	-	Glycerol (28% w/w of total solids)	Sodium caseinate was dispersed in deionized water with magnetic stirring at ambient temperature. After glycerol was added, the coatings solution was obtained after filtration.	Dipping	[58]
Calcium caseinate (5%) + carboxy methyl cellulose (0.25%) + CaCl$_2$ (0.125%)	-	Glycerol (2.5%)	The components were mixed in distilled water to get homogenized mixture, heated for 30 min at 80 °C and cooled.	Dipping	[59]
Sodium caseinate (5%)	Oleoresins	Glycerol (25% of total solids)	Sodium caseinate was added gradually into distilled water and stirred continually for 3 h to get coating.	Dipping	[60]
Sodium caseinate (2%) + chitosan (1%)	1% citric acid, ascorbic acid and calcium chloride as anti-browning agents	Glycerol (10% of total solids)	1% and 2% chitosan and caseinate solutions were prepared respectively. Blend solution was prepared with 1:1 ratio of caseinate and chitosan.	Dipping	[36]
Sodium caseinate (4%) + chitosan (2%)	1% citric acid, ascorbic acid and calcium chloride as anti-browning agents	Glycerol (10% of total solids)	2% and 4% chitosan and caseinate solutions were prepared respectively. Blend solution was prepared with 1:1 ratio of caseinate and chitosan.	Dipping	[61]

Whereas (-) = not reported.
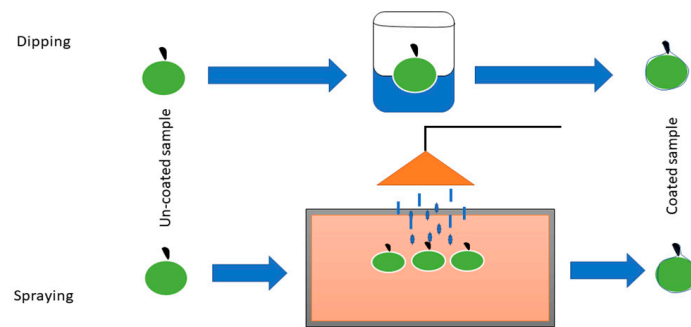
Figure 3. Different coating techniques applied in literature for casein-based coatings.

4. Methodology

This review was aimed to evaluate studies that focused on the active caseinate formulations for minimally processed F&V. Specific objectives were to discuss the following aspects: (i) the influence of active compounds on the structural properties of the film and (ii) the effectiveness of the active coating and film based on caseinate on the shelf-life extension of F&V. Systematic literature review search was conducted on the databases, i.e., ScienceDirect and Google Scholar to identify relevant literature published over past two decades (from January 2001 to December 2020) [62,63]. The keywords to identify relevant articles (research articles and short communications) included: "casein" or "sodium caseinate" or "films and coatings" or "structural properties" or "shelf-life" and "active additives" which yielded 2160 articles. The inclusion criteria included: (1) studies on simple and active caseinate dispersions/suspensions/coatings and films with, (2) applications on fresh and minimally processed food products, (3) and/or studies elucidating the influence of active additives (i.e., essential oil, probiotics, phenolics, plant extracts, and nanomaterials) on structural properties of the protein itself, packaging film, and product shelf-life. The exclusion criteria included: (1) studies published before January 2001 and (2) studies related to other biopolymeric formulations (films/coatings) with/without applications on foods. The literature search identified studies that were used to highlight and critically discuss the influence of casein films/coatings on the shelf-life of the food products (Figure 4). The bibliography of key studies was also searched for any relevant article; furthermore, a manual search was also done to evaluate any missing reference that is of importance for the literature review analysis of shelf-life studies of casein-based formulations.
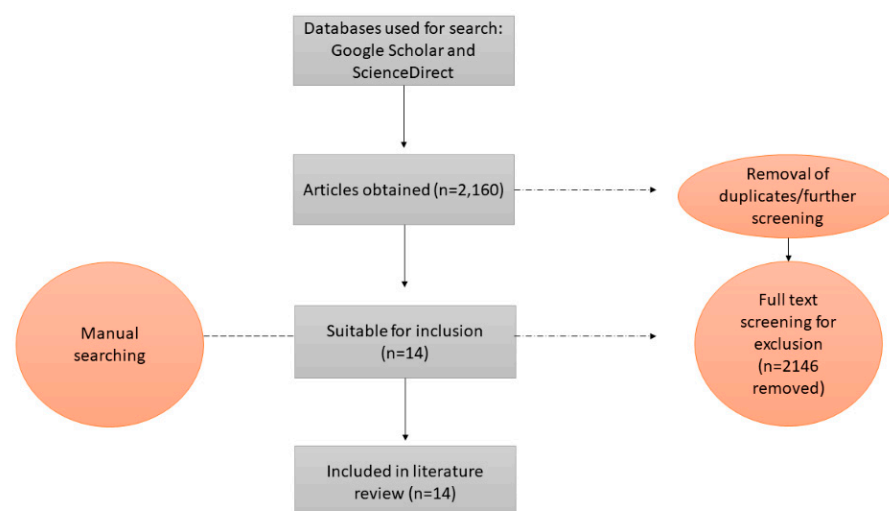

Figure 4. Process of literature selection for systematic review.

5. Results and Discussion

5.1. Influence of Different Additives on the Structure and Properties of Coatings and Films

Coatings and films can serve as carriers of additives that perform a specific function besides general coating function (i.e., barrier properties, etc.). For minimally processed F&V, different additives (i.e., antimicrobials and antioxidants) can be incorporated into coating solutions to retard growth of bacteria, yeasts, and molds during storage [64]. Thus, active films and coatings (due to the presence of active compounds) can reduce loss of nutritional quality due to oxidation and decrease growth of microbes beyond control respiratory rate and maturation in F&V [65]. Several active food additives of natural (probiotics, essential oil, plant extract, and phenolics) and synthetic (nanoparticles) nature have been reported to incorporate in caseinate-based formulations to improve its properties (i.e., physicochemical) and extend the shelf-life of F&V, since the presence of active compounds in the polymer matrix can affect the structure of the resultant film positively by enhancing its mechanical and barrier properties and enhance the expression of certain functional groups displaying antimicrobial/antioxidant properties, ultimately leading to improved shelf-life of the product. Thus, it is essential to highlight the influence of active compounds on the material structure and product shelf-life.

5.1.1. Essential Oils

Incorporation of essential oils into the biopolymeric formulations enhances their antimicrobial and antioxidant properties [66]. It has been reported in the literature that certain compounds in the essential oils (i.e., lemon grass and cinnamon) contain polar O-H and C=O, while some contain non-polar lipophilic groups. These lipophilic moieties are responsible for the antimicrobial activity of the bioactive compounds present in the essential oils [67]. Mishra and Murmu [53] prepared caseinate and Arabic gum coatings with cinnamon and lemon grass essential oil (1%–2%). The authors reported that coating formulations formed a semi-preamble film on the guava samples. This could be due to the formation of covalent and hydrogen bonds among casein, gum and active compounds present in the essential oils, which resulted in an increase in β-sheet structure and relative decrease in random coil, α-helix, β-helix structure of casein, as a result improved barrier properties were observed due to low availability of free volume for the transport of gas and water vapors (Figure 5) [68]. Ranjbaryan, Pourfathi, and Almasi [43] reported that hydrophobic nature of oil led to a decrease in water vapor permeability of the caseinate films from 10.24×10^{-9} to 9.47×10^{-9} g m^{-1} h^{-1} Pa^{-1}. Structural differences due to oil type are influenced by different behavior of oil droplets upon drying and complex interactions taking place among the protein (i.e., casein), the lipid (i.e., oil), and the solvent [69]. For example, ginger oil formed aggregates in casein film matrix upon drying leading to roughness in the film structure, and on the other hand, cinnamon oil upon drying produced a homogenous structure [69]. Additionally, microstructural and mechanical properties of casein film can be also affected by the oil incorporation. For instance, essential oils make the casein film matrix more uniform, smooth, and less porous as compared to neat films (by increasing the amorphous regions of film structure and also due to the fact that oil covers the irregularities of casein matrix) [43,45,70,71]. Generally, when emulsified oil droplets are added into biopolymeric film, it becomes less stiff (decreased tensile strength and Young's modulus) and more flexible (increased elongation at break) due to availability of the free volume through protein structure relaxation (which is formed as a result of discontinuation that directly effects the stretching ability of the film) [72]. It was reported that incorporation of *Matricaria recutita* essential oil into casein-based film reduced the tensile strength of casein film (2.5 MPa) as compared to neat film (10.9 MPa) due to structural discontinuation due to free volume increase provoked by the essential oil [73]. A possible solution is the incorporation of the essential oil as nanoliposomes. In fact, the nanoliposome incorporation led to reduced oil evaporation during the drying step of the film which resulted in much thicker and coarser structure of protein matrix as compared to the neat films, thus improving its barrier properties [74].
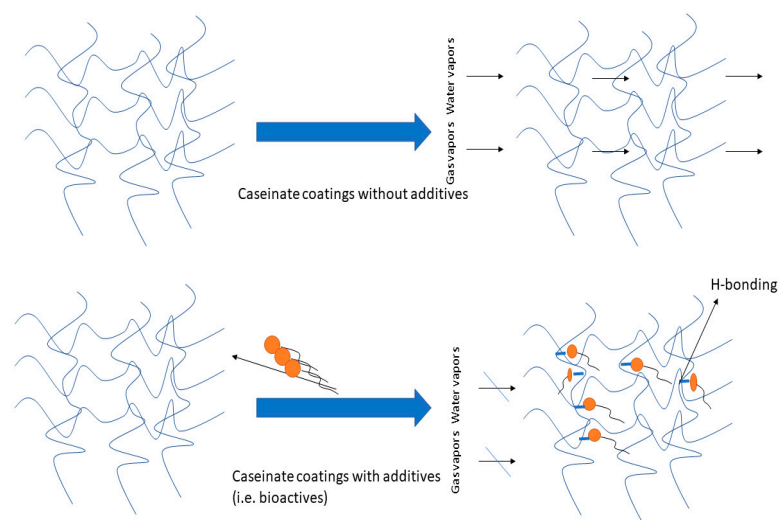
Figure 5. Influence of additives on physicochemical properties of active casein coatings.

To better understand the role of essential oils (and the bioactive compounds present in the oils) on structural and rheological properties of casein-based coatings, molecular docking (a bioinformatic tool) can be used as a starting point for learning about the chemical interactions between the polymeric chains and the bioactive compounds. Since, molecular docking studies can be used to identify possible binding sites of polyphenols with protein fractions using Autodock Vina and possible interactions can be visualized (i.e., which type of amino acids are involved in bond formation with phenols, bond type, binding affinity, and hydrophobicity, etc.) [75].

5.1.2. Probiotics

Probiotics are food supplements having a defined number of microbes in sufficient quantity that are used to reach the gut in a viable state inducing health benefits after ingestion. Furthermore, microencapsulation of probiotics in active packaging is a promising strategy to deliver these food additives effectively to improve the quality of the package and the product [76]. Probiotics have also been used in one study as active materials for the preparation of active casein coatings; however, the focus of the study was to develop anti-fungal coatings to reduce fungal spoilage and their influence on grape quality parameters [49]. Generally, when culture of probiotics (i.e., *Lactobacillus casei*, *Lactbacillus acidophilus* and *Lactobacillus sakei*) is incorporated into casein film there is no significant difference observed in permeability values of the films because of the small mass of bacterial culture as compared to total polymeric matrix mass [77,78]. Similarly, it was reported that no significant change was observed in mechanical properties (tensile strength = 1.96–2.57 MPa and elongation at break = 130%–201%) of casein films incorporated with lactic acid bacteria and the control because of an insignificant mass of bacterial cells added [77,79]. Alternatively, one study reported a decrease in mechanical properties of sodium caseinate/carboxy methyl cellulose films when probiotics (at concentration of 9 log CFU mL^{-1}) were added, due to decrease in cohesive forces in the matrix through the introduction of microbial culture, indicating no interaction between polymeric chains and probiotic cells [80]. Lactic acid bacteria incorporation into active coatings/films on F&V could be quite advantageous because they are generally recognized as safe (GRAS), obtained from natural sources and act as biocontrol agents; however, standardization procedures are highly required to obtain coating formulation that is applicable on fresh and minimally processed F&V to extend their shelf-life and delay the onset of decay kinetics by showing water resistance.

5.1.3. Phenolic Compounds

Interaction of different bioactive compounds (phenolic acids and glycosides) with casein fractions have also been reported in literature with the main changes observed in

the secondary structure of casein. For instance, ferulic acid was docked against β-casein in a study in which authors observed that ferulic acid brought significant changes in casein structure as the amide-I and II fingerprint regions in FTIR spectra displayed intensity reduction due to disturbance in protein's secondary structure, more specifically, a reduction in α-helical structure due to interactions of the protein and phenolic acid causing a reorganization of the functional groups (i.e., of C−N and C=O). Furthermore, ferulic acid interacts with polar uncharged, non-polar, and negatively charged amino acids (i.e., glutamine, glutamic acid, and phenylalanine) to form hydrogen bonds [81]. In another study, eriocitrin was used to study its interactions with β-casein, and as previously reported, secondary structure of β-casein changed after the addition of the glycosidic compound; the peak position of amide-I band shifted from 1641 to 1644 cm^{-1} after the addition of eriocitrin in casein structure. The main forces involved in the interactions were hydrophobic, hydrogen bonding and van der Waals force [82]. Furthermore, when carvacrol (10%) was added into caseinate films, strong wide bands for O-H stretching vibration (3100–3600 cm^{-1}) and multiband pattern (2800–3100 cm^{-1}) was observed overlapping with N-H and O-H stretching vibration of casein, suggesting more hydrophobicity of films as compared to neat films [46]. β-casein have been utilized in several studies as a carrier of bioactive compounds because of its hydrophobic moiety, thus it can be further explored for its applications as a packaging material in food industry.

5.1.4. Plant Extracts

Besides the above-mentioned additives, plant extracts have also been utilized to prepare casein-based packaging. Generally, plant extracts like seaweeds with increase in concentration (i.e., from 25 to 50%) can increase the protein film hydrophilicity due to the presence of higher number of hydroxyl groups by increase in polar component of surface free energy [83]. However, when extracts like (*Zingiber officinale*) were incorporated in casein films, a decrease in water vapor permeability (from 3 to 2 g Pa^{-1} s^{-1} m^{-1}) was observed with increase in concentration of the extract (0–500 ppm) due to the hydrophobic character of extract. Furthermore, interactions of phenolic compounds in the extract with the matrix reduced the chain mobility leading to increase in elongation at break (from 39 to 76%) [84]. However, this trend varies from extract to extract and mainly depends upon its concentration, nature and composition [85].

5.1.5. Nanoparticles

Several nanoparticles (NPs), i.e., organic and inorganic NPs reported in literature were utilized to improve the properties of casein-based films [86–89]. Generally, inorganic hydrophobic NPs, i.e., CuO, TiO_2, and ZnO, can form hydrogen bonds with the polymeric chains of protein biopolymers in such a way that it creates a convoluted pathway for the transfer of oxygen and water vapor thus, decreasing their transport across the protein/nanomaterial matrix (Figure 3) [86–89]. Similarly, these NPs with high surface area and stiffness can interact with polymeric chain to increase the tensile strength and Young's modulus of the material. However, this is true up to a certain limit; after that, jamming of NPs occurs, which could lead to a reduction of physicochemical properties of the films. Generally, neat caseinate-based films appear without pores and cracks with excellent structural integrity; however, after the addition of NPs the film matrix appear granular (which affects its permeability negatively) [90,91]. Furthermore, inorganic NPs have also been reported to possess good antimicrobial activity, especially against food borne pathogens [92]. These NPs can attack different cellular organelles of the bacterial cell to induce cell death. For instance, ZnO could release Zn^{+2} ions which could penetrate bacterial cell wall and interact with cytoplasmic content or ZnO NPs can generate hydrogen peroxide, which induces oxidative stress and damages membrane wall [93]. Regardless of their many advantages, NPs pose certain drawbacks, e.g., leeching and migration of NPs into food products and potential toxicity [77]. Thus, both in vivo and in vitro safety trials need to be conducted to get enough quantitative data before the NPs (especially

inorganic) can be approved by Food and Drug Authority (FDA) for their incorporation into biopolymer film for F&V.

5.2. Shelf-Life Aspects of FV

F&V have a relatively short postharvest life and are prone to physiological and biochemical decays [94]. To preserve the quality of F&V, several methods have been exploited depending on the aim of preservation for instance, extending shelf-life, preventing browning reactions, deterioration, microbial growth, oxidation reactions, and nutritional loss [95]. Ideally, the active coating should create a modified atmosphere around F&V by restricting the exchange of carbon dioxide and oxygen, while acting as a barrier that can retard the loss of water vapors and desirable flavor volatiles. Consequently, this modified atmosphere can reduce ethylene production and respiration rate and retard ethylene action [42,43]. Moreover, edible coatings also improve the appearance of horticultural produces by giving shine, hiding scars, suppressing decay and physiological disorder developments [94,96]. This modified atmosphere, however, should not create conditions favorable for the growth of anerobic microbes, for fermentation, and undesirable changes in flavors. Practically speaking, this phenomenon is difficult to accomplish. It has been reported in the literature that coating performance and properties are influenced by relative humidity and temperature (high temperature and relative humidity can increase respiration rates) [97]. Additionally, barrier property predictions of the biopolymeric coatings are influenced by the continuity of the coating applied on the F&V. However, this is difficult to achieve especially in case of fresh cut F&V, in which there is incomplete coverage of applied coatings due to leakage of cellular contents on the surface of F&V (furthermore, the nature of F&V and coatings, i.e., hydrophilic or hydrophobic, also plays an essential role in determining the coverage of coating on fruit surface; however, limited information is available on this domain, which restricts the application of coating on fresh and minimally processed F&V). On the other hand, drying such coatings might result in moisture loss from F&V tissue, discarding the purpose of coating such food products [98]. It is suggested that casein-based coatings can provide additional water to the coated food product (i.e., F&V), before the water is lost from coated product during transportation and storage, which in turn can delay moisture loss from coated product and maintains the sensory quality of the produce [97]. Additionally, Uslu et al. [54] reported that water loss of cherries was successfully reduced during storage at 4 °C up to 63 days by applying an edible coating based on sodium caseinate and milk protein concentrate. Generally, edible caseinate coatings stick smoothly to the surface of fruits, delay oxidative stress, and display high consumer acceptance after ripening [53]; however, this also depends on the type of additive one wants to incorporate into the coating solution.

However, in the literature it is reported that caseinate is not able to extend the shelf-life of F&V. In fact, a recent study reported that the application of edible coatings of sodium caseinate (2%) does not affect the quality parameters of fresh cut nectarine storage at 3 ± 1 °C for 7 days and, thus, it does not promote a longer shelf-life compared with non-coated nectarine sections [58]. This result was validated by Correa-Betanzo et al. [56] on berry cactus. Fruits that were treated with a sodium caseinate based edible coating plasticized with sorbitol and glycerol, were packed in clam shell boxes and stored at 5 ± 1 °C for 15 days and their phytochemical contents were evaluated. Edible coating of sodium caseinate did not have any effects on the antioxidant capacity of the fruits. A valid approach could be represented to blend casein with other biopolymers, which can positively affect the properties of coatings and in turn prolong the shelf-life of F&V. Volpe et al. [36] found that chitosan/sodium caseinate blend coating was able to reduce the respiration rate of minimally processed apples, as well as to preserve the color of the product. In a further study, the same authors showed that chitosan/sodium caseinate blend led to a reduction in respiration rate equivalent to the reduction obtained with 5% of oxygen. Moreover, the coating preserved the antioxidant properties of minimally processed apples and extended the shelf-life at 5 °C from 7 to 11 days of storage [61]. Sodium caseinate was also combined

with chitosan and applied as either coatings produced by food immersion in the film-forming solutions or just as packages (by wrapping the food using a film) on carrots. The chitosan/caseinate blend improved the bactericidal properties of samples with respect to those of the neat chitosan film [99]. In another study it was found that sodium caseinate appeared to be the most significant factor influencing the weight loss, firmness, total color difference, total soluble solids content, and titratable acidity of coated Berangan banana during storage, when used in combination with carboxymethyl cellulose and glycerol [57]. Edible coatings could contain various active ingredients such as flavorings, colorings, and sweeteners enhancing the nutritional and sensory attributes of fruits and vegetables [94]. Likewise, the coatings could also encapsulate aroma compounds, antioxidants, pigments, and ions that slow down browning reactions of fresh and fresh-cut F&V [95]. As reported by Valentino et al. [32], sodium caseinate can be a good substrate for dispersion active compounds. In this study, the antioxidant compound of gallic acid 0.50 μg mL^{-1} and rosemary essential oil (1.5%) was added in the solution of sodium caseinate (4%). As a general trend, the antioxidant activities increased by the addition of gallic acid and rosemary essential oil. The lowest inhibition (1%) was detected for caseinate, which assume a value of 5.9 $\pm$ 1.5% after 2.5 h and 13 $\pm$ 0.3% after 4 h. When gallic acid was added to the caseinate solution, I% reached a value of 79.3 $\pm$ 0.4% after 2.5 h, and then remained constant.

Generally, incorporation of essential oils up to a certain extent into casein-based coating materials enhance shelf-life of food products by improving sensory attributes and reducing microbial contamination. For example, when cinnamon and lemon grass oils were used at a lower concentration (i.e., 1 to 2% combined and separately), the guava samples displayed good color attributes (i.e., L* value ranged between 63–72). However, when both oils were used at highest concentration together (i.e., 2%), poor color attributes were observed (i.e., L* value was 39) along with increased polyphenol oxidase activity which led to brown peel color and poor color scores [53]. Similarly, the edible coating-based on sodium caseinate (1%), Arabic gum (5%), and essential oil of cinnamon and lemon (1%–2%) grass on guava had shown effect on firmness and polyphenol peroxidase activity (PPO). Samples with coating showed the lowest browning score, highest overall acceptability score, lower activity of PPO and POD enzymes, higher DPPH radical scavenging activity, higher retention of phenol and flavonoid content, slower rate of rise of reducing sugar and total sugar in guava. Likewise, when edible coatings made from 1% sodium caseinate and 2.5% of tulsi extract were used to pack guava samples, they displayed no mold growth and peel color and pulp firmness comparable to that of ripened guava [68] (Table 2). On the other hand, casein coatings when incorporated with beeswax reduced the respiration rates of bell pepper fruits (<4 mL CO$_2$ kg^{-1} hr^{-1}) as compared to simple casein coatings (>5.5 mL CO$_2$ kg^{-1} hr^{-1}) [100]. Thus, protein-polysaccharide based active coatings will probably function best (i.e., to reduce respiration rates) when storage conditions (i.e., high relative humidity and low temperature) are not met. Furthermore, authors observed that literature related to shelf-life studies of casein-based coatings and films is scarce, with focus on sensory parameters with few studies on microbial quality thus, this sector can be further explored by adding active additives in casein-based formulations to obtain more quantitative data on shelf-life.

Additionally, authors conducted review of literature on patented research on casein-based formulations for minimally processed F&V. A lot of research has been patented on protein and polysaccharide-based coatings and films, i.e., an aqueous coating formulation was patented comprising of carboxy methyl cellulose and fructose esters of fatty acid to extend the shelf-life of pears and apples [101]. However, patented research on casein-based formulations for F&V is almost non-existent, since studies on caseinate-based coatings/films are undergoing and a lot of work is required that needs to be done to achieve advancements in this field.

Table 2. Application of different casein-based packaging formulations.

Packaging Composition	Food Product	Impact on Shelf-Life	Reference
Sodium caseinate (4%–14%) + gallic acid (0.005%) and rosemary essential oil (1.5%)	Fennel	-	[32]
Sodium caseinate + potato starch (2%) + *L. plantarum* (5×10^7 CFU/ml)	Grapes	Higher weight loss (~3%) and maturity index (67) for grape samples packed in casein coating (incorporated with probiotics) as compared to control.	[49]
Sodium caseinate (1%) + arabic gum (5%) + cinnamon and lemon grass oils (1%–2%)	Guava	Highest pulp firmness values (10.01) for samples coated with (2% concentration of both lemon grass and cinnamon essential oils). However, highest polyphenol peroxidase activity (~7 units/100 mg protein) was also observed due to toxic effects.	[53]
Sodium caseinate (11.1%) + bees wax (5%–15% of protein content) + stearic and palmitic acid blend (5%–15% of protein content)	Bing cherries	Improved firmness (4.2−4.5) and appearance (4.2−4.6) as compared to control.	[54]
Sodium caseinate	Berry cactus	Total polyphenol content of berries was not affected by casein coatings.	[56]
Sodium caseinate (0%–1%) + sodium carboxy methyl cellulose (0.1%–1.5%)	Berangan banana	Increased biopolymer concentration led to decrease in weight loss of banana samples.	[57]
Sodium caseinate (2%)	Fresh-Cut nectarine	Lower weight loss (3.09%) of nectarine samples wrapped in caseinate packaging as compared to control.	[58]
Calcium caseinate (5%) + carboxy methyl cellulose (0.25%) + $CaCl_2$ (0.125%)	Potatoes and apples	Coating effectively delayed browning by acting as oxygen scavengers.	[59]
Sodium caseinate (5%) + oleoresins	Butternut squash	-	[60]
Sodium caseinate 2% + chitosan 1% + 1% citric acid, ascorbic acid and calcium chloride	Apples	Hardness remained relatively stable (20−22 N) for blended coatings throughout the storage period.	[36]
Sodium caseinate (4%) + chitosan (2%) + 1% citric acid, ascorbic acid and calcium chloride	Apples	Better hardness values (>95 N) as compared to control (<80 N) at the end of storage.	[61]
Sodium caseinate (2.5%) and chitosan (2%) + sodium caseinate (2.5%)	Cheese, carrot and salami	A slight inhibitory influence of film forming solution (10−12 mm) and films (4.2 cm^2) (of casein and chitosan) was observed on cheese and salami microflora. However, inhibitory effect on carrot was observed when packed in composite packaging film (which may be due to direct contact of film).	[99]

Whereas (-) = not reported.

6. Conclusions and Perspectives

Active coatings and films are a promising sustainable preservation technology for shelf-life extension of minimally processed foods through restricting the mass transfer of moisture, aroma or gases, and carrying active additives, i.e., antioxidants or antimicrobials. Among protein-based biopolymers, casein was found effective because of its ability to carry small molecules and ions (with β-casein as most functional fraction of casein due to its hydrophobic domain). This review was focused to elucidate the interactions of active additives with casein, which in turn has a role in controlling the structural properties of coatings and films, furthermore, changes in secondary structure of casein were observed after incorporation of bioactive compounds (i.e., phenolic acids). Among all the additives incorporated into casein-based coating formulations, essential oils (i.e., cinnamon and lemongrass oils) have shown promising results in maintaining the sensory and nutritional quality of fresh produce (since NPs and probiotics have certain limitations) at 1%–2% concentration. On the other hand, because of the empirical nature of casein-based formulations it was not easy to extrapolate quantitative data and correlate conditions and cases besides those investigated. Furthermore, exploitation of the relationship between the nature of coating and F&V is necessary to highlight its importance for adequate coverage on F&V surface. Cross-linking of casein with bioactives can provide a solution to its short-comings against extreme environmental conditions (hydrophilic medium, acidity, and high temperatures). Thus, there is a need to explore chemical interactions among bioactive compounds and casein by using computational and in vitro trials as food additives have shown to influence the physicochemical properties of film. Furthermore, by learning about interaction mechanism we can compute the release of kinetic parameters of bioactive compounds from packaging material, which could lead to the development of a casein packaging with better design that can extend the shelf-life of minimally processed produce.

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