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Physical – Chemical, Mechanical and Antimicrobial Properties of Bio-Nanocomposite Films and Edible Coatings

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ABSTRACT

Bio-nanocomposite films and edible coatings constitute of metal nanoparticles incorporated in biopolymers on the shelf life and quality of food were studied. It has been seen that the application of bio-nanocomposite films and edible coatings to fruits and vegetables may lead to decreasing the color changes, respiration rate, weight loss and extended shelf life, delaying ripening and being environmentally friendly. Physical-chemical properties such as moisture barrier, oxygen scavengers, and antimicrobial properties have been reviewed. In addition, the physicochemical characterization which covers surface and structure characterization, as well as contact angle, thickness, transparency, colour characterization and thermal stability were included. Moreover, it has been seen that novel bio-nanocomposite films and edible coatings are able to enhance the texture, improve the product appearance, and prolong the shelf-life by creating semi-permeable barriers to gases and moisture, such as carbon dioxide and oxygen.

Keywords- Bio-nanocomposite films, Edible films, Coatings, Nanoparticles, Moisture barrier, Oxygen scavengers, Antimicrobial properties, Physical-chemical characterization.

I. INTRODUCTION

Most of the conventional packaging is petroleum-derived plastics such as polypropylene, polyethylene, and polystyrene, which after product consumption becomes a major concern due to environmental damage provoked by their difficult degradation. However, serious environmental problems are caused due to the nonbiodegradability of these materials, thus increasing the interest of researchers in biodegradable packaging production using natural polymers extracted from renewable sources for application in food packaging [1] [2].

In this sense, many researchers have shown interest in coatings and edible films which represent an environmentally friendly alternative for food packaging. Edible packaging is known as a potential alternative to protecting food quality and improving shelf life by delaying microbial spoilage and providing moisture and gas barrier properties. Developments in edible packaging and technology have shown promising results in enhancing the shelf life of food products. In 2016, the edible packaging market was valued at $697 million and by 2023 is expected to hit $1097 million growing at a compound annual growth rate (CGAR) of 6.81% from 2017 to 2023 at global level. In global edible packaging markets specific industries including MonoSol LLC, Tate & Lyle Plc, WikiCell Designs Inc., JRF Technology LLC, Safetraces, Inc., BluWrap, Skipping Rocks Lab, Tipa Corp., Watson Inc., and Devro plc have played a key role [3].

New packaging materials are an emerging field in the food industry. Poor mechanical, thermal, chemical, and physical properties of biopolymers, and also their inherent permeability to gases and vapor have increased this interest. Biopolymeric materials (matrix) require fillers, which can react/interact with available matrix in order to provide new formulations with improved properties. Many studies have shown the potential use of metal nanoparticles in biopolymeric packaging and edible coatings for improving their properties. According to European law, biopolymers and bioplastics must be biodegradable, especially in terms of composting, so they can act as soil softeners and fertilizers. There is a difference between smart food packaging and active food packaging. Smart food packaging monitors the condition of packaged foods to provide information about their quality and nutrients, before consumption, while in active food packaging, there are some mechanisms to control microbial growth, moisture, and oxidation [4].

Antimicrobial nanoparticles (NPs) form an integral part of edible coatings and films (ECF) which serves as matrixes and then they are used on the fruits and vegetables to prolong shelf life and enhance storage quality. The antimicrobial activity of ECF with NPs might be mainly due to the electrostatic interaction between the cationic polymer or free metal ions and the charged cell membrane, the photocatalytic reaction of NPs, the detachment of free metal ion, and partly due to the antimicrobial activity of edible materials. Physical-chemical, mechanical and releasing properties might be influenced by the concentration of NPs. Various ECF with NPs might be used as the ideal materials for the food preservation potential on the quality of fruits and vegetables [5].

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To date, chitosan (CS) is among the most common materials in the formulation of these biodegradable packaging together with polysaccharides, proteins, and lipids [6]. Chitosan (CS), starch and β-cyclo-dextrin (β-CD) are carbohydrate-based polymers s used as ECF matrixes [7] [8] [9]. The future of packaging materials lies in the research and development of novel bio-nanocomposite made from polymeric materials and inorganic nanoparticles (NPs) for food preservation.

Polysaccharides are characterized by poor gas and water barrier properties, usually acting as sacrificing agents for moisture loss [10]. Proteins are known for their ability to form film, similar to that of polysaccharides with excellent mechanical and barrier properties, although they make poor water vapor barriers. The optimization of composition is one of the most important steps to be considered in the edible film formulation, to maintain or improve the quality of food packed. A nanocomposite is characterized by one or more discontinuous phases distributed in one continuous phase. The continuous phase is called the matrix, whereas the discontinuous phase is called the reinforcement or reinforcing material. In the discontinuous phases, one of the phases with components has at least one dimension that is approximately 10^{-9} m. Nano-scaled materials, biopolymers, and cross-linkers act as legitimate members in bionanocomposite fabrications. Among numerous composite hydrogel systems, carbon nanotubes-based nanocomposite hydrogels have gained significant attention due to their high mechanical strength, effective surface area, and high electrical conductivity [11].

Titanium dioxide (TiO_2) as inorganic nanoparticles which has photocatalytic activity when is exposed to visible and/or UV light irradiation, and responsible for activating its antimicrobial properties and is used as an antimicrobial agent to coat different materials [12]. Meanwhile, silver nanoparticles (AgNPs) thanks to its electrocatalytic activity could provide the excellent antimicrobial property for its extensive application by incorporating into edible polymers as an active food packaging [13] [14]. As permeation barrier in conjunction with antimicrobial activity can act ZnO [15].

II. PHYSICAL-CHEMICAL, MECHANICAL AND ANTIBACTERIAL PROPERTIES OF EDIBLE FILMS

The properties of a composite material depend on its constituent materials such as natural biopolymers or synthetic biodegradable polymers and inorganic or organic nanomaterials or nano-scale minerals. Currently, several nano-materials are used in food packaging as efficient additives; however, because of the differences in their chemical structure and features, each nanomaterial presents different properties in the matrix, which leads to different functional packaging applications [16].

Bionanocomposite coating films are composite materials that consist of natural or synthetic biodegradable polymers and nano-scale materials. Bionanocomposites are known as a novel class of advanced materials. In bionanocomposites, the polymer matrix, which includes natural or synthetic polymers or biomolecules, is considered the biological origin, whereas nano-scale materials are regarded as value-added materials. Composite materials exhibit stronger physical, chemical and mechanical properties than their constituent materials [17]. The properties and applications of a bionanocomposite coating film depends on the characteristic of the nano-scale materials. Furthermore, the properties of a bionanocomposite coating films depend on the characteristics of the biopolymers, the stoichiometric ratio of the constituent materials, and the cross-linking among the constituent materials as well as on the biopolymer macromolecular matrix.

Nano-sized materials have a greater surface area compared to similar masses of large-scale materials, as the surface area per mass of a material increases, a higher and better interaction could occur with the surrounding materials resulting in affective reactivity; a cube of 1 cm on one side has a surface area of 6 cm^2; however, if this cube can be divided into smaller cubes of 1 nm size on each side, that would increase dramatically the surface area to 6m^2. The substantial interfacial area between the nano fillers and the biopolymer, as a consequence of the high surface area of the nanosized filler, causes a modification in the molecular relaxation and mobility as well as an improvement in the barrier, thermal, and mechanical properties of bio-nanocomposites [18]. In Fig.1 are summarized the composition of bio-nanocomposite films and its properties.

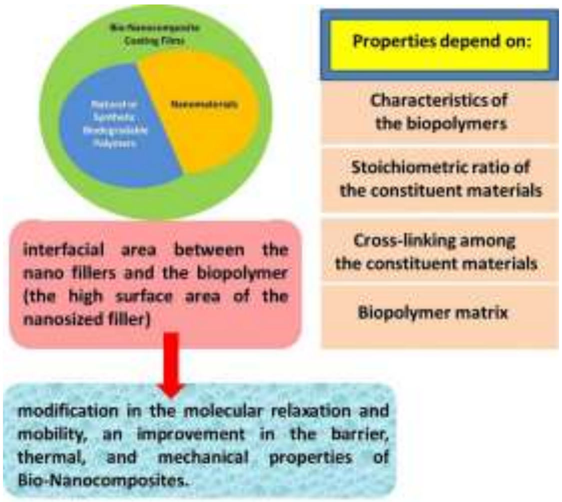

Figure 1: Composition of bio-nanocomposite films and its properties

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II.I. Physical-Chemical Properties:

It was found by many researchers that various sizes of nanoparticles had influence on the mechanical and physical properties, filtering ultraviolet (UV) light, as well as their antimicrobial activity [13]. In addition, nanomaterials can improve sensory quality of foods by imparting novel texture, colour, appearance, processability and stability during shelf life [19].

In Figure 2 schematic mechanical and physical properties of nanomaterials are presented.

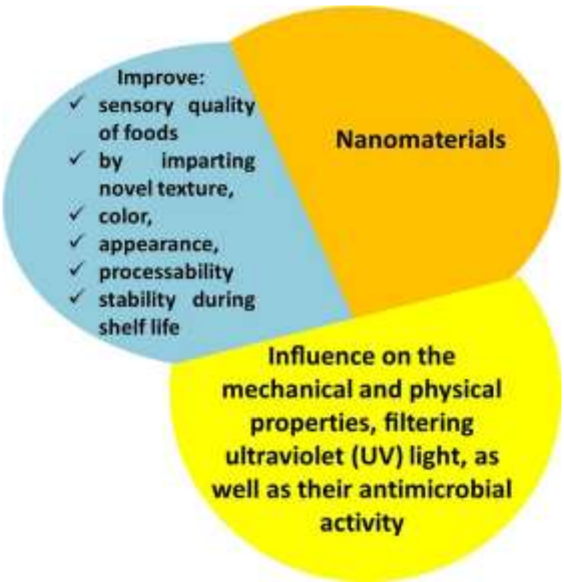

Figure 2: Schematic representation of the mechanical and physical properties of nanomaterials.

II.I.I. Moisture Barrier:

The path of water vapor (WV) from the neighboring air into food products or the loss of moisture from the foodstuff to the adjacent atmosphere meaningfully influences the stability and quality of the packaged food throughout the storage period. The barrier properties of the film contribute to giving a better indication of the applications of food packaging films, whereas the coating films are used to prevent dehydration of fruits [20].

The coating films containing beeswax have lower moisture contents than the chitosan coating films. These results were reported by Elena Velickova et al. [21]. Unlike other lipids, beeswax has noticeable resistance to moisture transport.

The bio-nanocomposite films/coatings contribute to further reducing weight loss by acting as an obstacle to moisture loss. Moreover, edible coatings enhance the texture, improve the product appearance, and prolong the shelf-life by creating semi-permeable barriers to gases and moisture, such as carbon dioxide and oxygen [22] [23].

A bio-nanocomposite coating with sodium alginate and nano-ZnO were developed by Emamifar & Bavaisi [24] and applied on strawberry. According to their results, nano-ZnO significantly increased the moisture barrier of films; therefore, reduced the weight loss of strawberry. Uncoated fruits displayed higher weight loss than coated fruits at the end of the storage (20 days). Chi et al. [25] claimed that the Ti and Ag NPs improved the water barrier property of PLA films. Moreover, the investigation of PLA films incorporated with essential oils and nano-TiO_2/nano-Ag on mangoes (15 days stored at room temperature) showed that the weight loss of mangoes packed by nano packaging film was the lowest among all packages. Zhang et al. [26] reported that the PLA films embedded with Ag NPs showed an outstanding moisture barrier property. Moreover, they stated that the mass loss of strawberry fruits packed by PLA-Ag was lower than that of the control film (without NPs).

II.I.II. Oxygen Scavengers:

The presence of residual headspace oxygen on packaged foods can negatively influence the quality and shelf-life by allowing the growth of aerobic microorganisms or oxidation of the product, which results in sensorial, color, or nutritional changes [27]. Oxygen scavengers are by far considered to be the most commercially important subcategory of active packaging because they are able to maintain food product quality through decreasing food metabolism, reduce oxidative reactions, inhibite enzymatic browning and oxidation of labile pigments, controll enzymatic discoloration, and inhibite the growth of aerobic microorganisms [28].

Iron-based oxygen scavengers are the most widely used agents for the preservation of packaged foods [29] which principle of operation is based on the oxidation of iron in the presence of water [30].

Di Maio et al. [31] investigated a three-layer oxygen scavenging film with polylactic acid (PLA) containing iron-based agents for the packaging of freshly cut apples. After 15 days of storage, the freshly cut samples compared well with a control sample. Films based on oxidizable transition metals (Cu, Zn, Mg, Mg, Al, Pd and Ti) are also known. Photocatalytic oxygen scavenging films have also been developed by the incorporation of nanocrystalline titania particles [32]. Mahieu et al. [33] developed an extruded oxygen scavenging thermoplastic starch film with ascorbic acid and iron powder and studied its oxygen scavenging capabilities, water sorption capacity, and mechanical properties at different relative humidity. By increasing the relative humidity, the film was activated and showed an excellent oxygen scavenging function. Yildirim et al. [34] studied Pd, another metallic oxygen scavenging compound. The active agent was deposited into films in layers using the vacuum method to remove residual oxygen in food packages after modified atmosphere packaging (MAP). The oxygen scavenging rate of the coated film depended strongly on the thickness of the palladium deposit. The authors found that PET, aluminum oxide-coated PET, oriented polypropylene (PP), and PLA are the most suitable substrates for palladium-based oxygen scavengers. In addition, the application of an intermediate SiOx layer between the substrate and the palladium layer substantially increased the oxygen scavenging rate for all packaging films. Hutter et al. [35] showed that an implementation of this OS film in packaging prevented discoloration of oxygen-sensitive food such as cooked cured ham.

Numerous antioxidant compounds (e.g., quinones, catechol, hydroxylamines, and ketoximes) can also be used as oxygen scavengers [36].

Enzymatic scavengers are another approach to regulate the oxygen concentration in the food package. In enzyme-based oxygen scavenger systems, a substrate reacts with the enzyme to remove oxygen. In the presence of moisture, glucose is oxidized to gluconic acid and hydrogen peroxide by glucose oxidase [37].

Johansson and co-workers [38] [39] developed starch oxygen scavenging coatings and films based on laccase and lignosulfonates. The prepared materials was useful for the active packaging of high-moisture foods. Furthermore, stiffness and water resistance of starch-based films were increased by the laccase-catalyzed oxidation of lignosulfonates. Recently, Gaikward and coworkers [40] developed an oxygen scavenging film based on a modified LDPE film with a pyrogallol coating. The prepared film showed an effective oxygen scavenging capacity and was moisture activated. Farneth et al. [41] have developed a printable oxygen scavenging formulation using a calcium ascorbate-laccase (CaAsc/Lac)-based system coupled with a binder [42].

II.II. Antimicrobial Properties:

One of the main contamination reasons for fruit and vegetable is the lack of proper packaging. As the demand for fresh vegetables and fruits is rising, there is an urgent need to extend the shelf life of the products to preserve their quality and minimize losses. An antimicrobial active packaging system loaded with antimicrobial agents can be applied to minimize the spoilage of fruits and vegetables and to control their microbial growth. NPs with high aspect ratios are particularly interesting because of their high specific surface area, antimicrobial properties and reinforcement effects in the matrix.

Over the past few decades, silver nanoparticles (AgNPs) have been investigated extensively due to their superior physical, chemical, and biological characteristics, and their superiority stems mainly from the size, shape, composition, crystallinity, and structure of AgNPs compared to their bulk forms. AgNPs have made a substantial impact across diverse biomedical applications as antimicrobial agents, biomedical device coatings, drug delivery carriers, imaging probes, and diagnostic and optoelectronic platforms. Bratovcic, 2020 [43] carried out the green way of the synthesis of silver nanoparticles and showed that by increasing the concentration of orange peel extract, the formation of silver nanoparticles is increased.

Nanosilver particles have a broad antibacterial effect on a range of Gram-negative and Gram-positive bacteria and antibiotic-resistant bacteria strains. Nanosilver is an effective antifungal agent against a broad spectrum of common fungi. NSPs can inhibit the growth of Candida albicans, Candida glabrata, Candida parapsilosis, Candida krusei, and Trichophyton mentagrophytes effectively [44].

Emamifar and Bavaisi [24] claimed that the lowest growth of microorganisms was observed in strawberries coated with 1.5% sodium alginate and 1.25 g/L nano-ZnO. The addition of nano-ZnO into the coating formulation improves its antimicrobial properties and prolongs the preservation of fresh fruits for up to 20 days. Li et al. [45] investigated the effect of nano packaging films included ZnO NPs and PLA matrix, on the quality of fresh-cut apple at 4°C during the 14 days of storage. The results revealed remarkable inhibition on the microbial growth and suggested that the nanocomposite films could be used to enhance the shelf-life of fresh-cut produce. Xing et al. [46] studied the impacts of the chitosan/nano-TiO_2 composite coating on mangoes. They found that this coating could prevent microbial growth and preserve mangoes' natural nutrient composition while playing a pivotal role in maintaining the fruit quality at 13°C. Barikloo & Ahmadi [47] examined the effect of nanocomposite packaging on strawberries' characteristics during storage and found that the clay nanocomposite packaging can improve the microbial stability and the shelf life of strawberries.

In Figure 3 is given an example of nano-enabled packaging of food which represent a form of packaging technique that controls temperature, moisture, pH, and freshness of the fabric within the packet, and contains information for consumers, and controls the environment to increase the period of time of the product.

Figure 3: Examples of novel active and intelligent nano- enabled packaging of food.

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III. EDIBLE FILMS CHARACTERIZATION

III.I. FT-IR Characterization of Edible Films:

Bio-nanocomposite films containing different proportions of ginger essential oil (GEO), chitosan (Ch), and montmorillonite (MMT) were prepared and characterized, and the antibacterial effect of bio-nanocomposite films on chilled beef was evaluated [48]. FT-IR is a commonly used technique for identifying chemical components and their internal molecular functional group infractions as valid. Fourier transform infrared analysis showed a series of intense interactions among the components of the bio-nanocomposite films. The characteristic absorption peaks were observed at 3325 cm^{-1} (axial stretch-OH), 3273 cm^{-1} (asymmetrically stretched -NH group), 2882–2934 cm^{-1} (C-H bond of methyl), 1638 cm^{-1} (amide group), at 1403–1550 cm^{-1} (amide group), bone vibrations at 1342 cm^{-1} (involving amide C-N bond stretching), 1342–1403 cm^{-1} (-CH_2 folded), 874–1143 cm^{-1} (bone vibration involved in C-O bond stretching), and at 1134 cm^{-1} (C-O-C bond asymmetrical stretching) [49] [50].

Compared with the original chitosan film, adding GEO MMT showed a minor difference in the spectra, which may be due to the small and small content of MMT and GEO. The characteristic peaks of chitosan were found in all the samples. However, some changes in the intensity of absorption peaks were also observed to the overlapping chemical bonds of absorption peaks, thus, indicating a strong interaction that was consistent with Souza et al. [51].

The thickness of the film was increased by incorporation of the GEO, reduced the tensile strength of the film, and increased the percentage of breaking elongation and the water vapour permeability. The migration of phenols in the films began to increase exponentially and reached equilibrium at about 48 h. The bio-nanocomposite films (Ch +0.5% GEO group, and Ch + MMT + 0.5% GEO group) effectively delayed the rise of hue angle, pH, and moisture values of chilled beef upon time and slowed down the lipid oxidation and the growth of surface microorganisms on chilled beef. Thus, the prepared bionanocomposites can be used as promising materials to replace commercial and non-degradable plastic films.

III.II. The surface structure of Edible Films:

SEM micrographs of cassava and whey starch films presented a smooth surface without surface cracks and with the presence of small clusters. The microstructure of the films became more irregular with the increasing cassava starch concentration. This behaviour can be attributed to the interactions between starch and whey. Whey proteins can adhere to the surfaces of starch granules, resulting in a clumping effect [52].

III.III. Contact Angle of Edible Films:

Edible films and coatings gained renewed interest in the food packaging sector with polysaccharide and protein blending being explored as a promising strategy to improve properties of edible films.

Contact angle results serves to predict the prospective interactions of the packaging materials with food.

Sultan et al. 2021 [53] prepared chitosan–beeswax films to preserve Le Conte pears postharvest. The surface of the film is partially hydrophobic which indicate the contact angle of the chitosan film (79.8°) due to the occurrence of hydroxyl groups in the chitosan/glycerol blend. The contact angle value was increased to 109.7° by adding the beeswax and pollen grains, which displays the enhancement of the hydrophobic character of the prepared film. Due to the surface hydrophobicity of the film, the spreading of water droplets was limited [53].

Composite edible films in different proportions of pectin (P), alginate (A) and whey Protein concentrate (WP) were formulated with a simplex centroid mixture design and evaluated for physical-chemical characteristics to understand the effects of individual components on the final film performance. A whey protein component in general lowered the viscosity of the initial solutions compared to that of alginate or pectin solutions. Subsequently, a whey protein component lowered the mechanical strength, as well as the affinity for water, as evidenced from an increasing contact angle. The effect of pectin was reflected in the yellowness index, whereas alginate and whey protein affected the opacity of film. Whey protein favoured higher opacity, lower gas barrier values and dense structures, resulting from the polysaccharide-protein aggregates. All films displayed however good thermal stability, with degradation onset temperatures higher than 170°C [54]. The increase in whey protein contributed to lowering the viscosity but significantly favoured hydrophobicity of the films, causing a reduction of the water absorption that can act as plasticizer. The best performances in term of thermal, mechanical and gas barrier behaviour were observed for lower P and WP concentration and higher A amount, or when the same P/A/WP content was used even though with similar thermal degradation patterns. The presence of WP was observed to play a beneficial role in decreasing the wettability of the edible film, making them suitable for food wrapping applications. Considering the synergistic effects, the tertiary blends of P/A/WP have scope to be further optimized to provide blends with improved barrier and mechanical properties. The investigated films could be taken into consideration as potential natural packaging materials for improve the shelf life of bakery food.

III.IV. Thickness of Edible Films:

Maruddin et al., 2020 [55] showed that plasticizers could improve the flexibility, elasticity and friability of edible films. The characteristics of edible

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film made from caseinate sodium were influenced by the use of plasticizer types such as glycerol, sorbitol and polyethylene glycol (PEG). The differences in material source and molecular weight of plasticizers type various result in the interaction of hydrogen bonds between water-protein-plasticizer molecules and further cause differences in the physical characteristics of edible films. The edible film characteristics observed were colour L* (brightness), elongation and thickness. Data were analyzed with complete random design and repeated for three times. The use of plasticizer type affected the edible colour value (L*) around 85.62-87.43 (close to white). However, the type of plasticizer did not affect the elongation and thickness of the edible film. The range of elongation and thickness of the edible film with the use of a type of plasticizer was around 15.96-16.22% and an average of about 0.15 mm. The colour value of L* (brightness) of edible film using sorbitol plasticizers type was higher than that using glycerol and PEG. The characteristics of edible films using sorbitol plasticizers were better, compared to those using glycerol and PEG.

III.V. Transparency and Colour Characterization of Edible Films:

Edible films based on a chitosan–zein mixture with three different essential oils (EOs) such as anise, orange, and cinnamon were developed by Escamilla-García et al. 2017 [56]. The addition of an EO into an edible films significantly affected ($p < 0.05$) the a* (redness/greenness) and b* (yellowness/blueness) values of the film surface.

When EFs were incorporated with OR and CN, the a* values showed 27% and 6% more negative values, indicating a redness tendency, whereas the EF with AN added showed the highest a* value among the treatments (greenness tendency). All EFs incorporating EOs increased their b* values, indicating a yellowness tendency. Polysaccharide films are usually colourless, essential oils show a slightly yellow appearance, and the incorporation of EOs into polysaccharide-based EFs have been reported to affect colour and transparency [57] [58].

The EFs presented a refractive index between 1.35 and 1.55, and thus are classified as transparent. The physical properties of EFs with an added EO were improved, and films that incorporated the anise EO showed significantly lower water vapour permeability (1.2 ± 0.1 g mm h^{-1} m^{-2} kPa^{-1}) and high hardness (104.3 ± 3.22 MPa). EFs with an added EO were able to inhibit the growth of *Penicillium sp*. and *Rhizopus sp.* to a larger extent than without an EO. Films' structural changes were the result of chemical interactions among amino acid side chains from zein, glucosamine from chitosan, and cinnamaldehyde, anethole, or limonene from the EOs as detected by a Raman analysis. The incorporation of an EO in the EFs' formulation could represent an alternative use as coatings to enhance the shelf life of food products.

III.VI. Thermal Stability of Edible Films:

Andrade Martins and co-workers were produced films with different proportions of whey (63.75–67.50%) and cassava starch (7.50–11.25%). The films showed reduced solubility with increasing concentrations of cassava starch, and those with the highest proportions of whey were more stable to thermal decomposition. The increase in concentration of cassava starch altered the microstructure of the films, making them more irregular and with an accumulation of matter. The production of biodegradable polymer blend films is an important step in the development of films for use in packaging, with the formulation of 67.50/7.50% whey/cassava starch being the best film for continued future work [59].

III.VII. Structural Characterization of Edible Films:

Edible coatings are non-toxic packaging materials that can regulate metabolic processes, improve the appearance of stored fruits, delay deterioration, and preserve product quality by extending the shelf life of fruits as well as ensure their brightness as an attractive factor for consumers [60] [61]. Currently, biodegradable edible coating alternatives for postharvest fruit preservation are attracting attention from researchers. The chitosan–beeswax films showed good self-healing aptitudes ranging from 86.7 to 96.3 and the tendency to increase the stiffness of the film. The film treated with pollen grains showed an enhanced water contact angle compared with the chitosan film. The elongation % at break was reduced from 35.81 to 14.09. Fruit quality parameters were evaluated in cold storage for 105 days during shelf life after a simulated marketing period of 7 days. All coated fruits successfully showed decrease in weight loss, decay and rate of softening. Therefore, chitosan–beeswax/pollen grains can be considered safe and effective coating for the fruit preservation [53]. The incorporation of long chain hydrocarbon beeswax into self-healing chitosan-based composite films creates a considerably less flexible coating film. The reduction in film elasticity may be a result of the lower absorbed water content in the self-healing chitosan composites containing beeswax [62].

IV. NOVEL SYNTHETIZED BIO-NANOCOMPOSITES FOR FOOD PACKAGING AND ITS CHARACTERIZATION

Chen & Chi, 2021[63] have developed novel active films based on pullulan and carboxylated cellulose nanocrystal (C-CNC) incorporated with tea polyphenol (TP) by solution casting method. The effect of TP addition on the mechanical, barrier, microstructural, optical, functional properties of the resultant pullulan/C-CNC/TP (PC-TP) bionanocomposite films was systematically evaluated. An appropriate TP adding was well distributed within the PC-TP bionanocomposite matrix seen by scanning electron microscopy (SEM). New hydrogen bond was formed among the pullulan, C-CNC, TP revealed by Fourier transform infrared spectroscopy (FTIR). Addition of 3%, *w*/w TP on a dry basis of the weight of pullulan and C-CNC led to stronger intermolecular interactions and more compact microstructure, and thus enhanced the thermal stability, water barrier properties, and tensile strength of the resultant bionanocomposite films. Nevertheless, overloading of TP in the bionanocomposite films might produce some aggregations and thus have negative effects on their performance. In addition, the incorporation of TP significantly improved the UV-barrier properties, antioxidant activity and antimicrobial activity of PC-TP bionanocomposite films, while induced a decrease in the transmittance. These results revealed that PC-TP bionanocomposite films with TP at appropriate levels had potential to be used as active food packaging.

A novel chitosan/negatively charged graphitic carbon nitride self-activation bionanocomposite films was prepared by one-step electrostatic self-assembly [64]. First, the antibacterial efficiency of this film could reach to 99.8 ± 0.26% against *E. coli* and 99.9 ± 0.04% against *S. aureus* through self-activated under visible light. Second, this film can effectively extend the shelf life of tangerines to 24 days. Finally, this film was safe and nontoxic and negatively charged graphitic carbon nitride with low-cost can improve the mechanical, thermal and hydrophobic properties of neat chitosan films. This procedure present a new pathway for the preparation of low-cost packaging films with excellent visible light responsive property and sustainable antibacterial activity.

The influence of plasticizer (glycerol (GLY)/sorbitol (SOR)) and antimicrobial (potassium sorbate (KS)/grapefruit seed extract (GFSE)) agents on crystallinity, water barrier, mechanical, thermal and anti-fungal properties of prepared with corn starch (CS)-chitosan (CH) nanoclay (Na-MMT) bionanocomposite films has been studied by Jha, 2020 [65]. Results showed that CS/CH/nanoclay/SOR/GFSE films exhibit a higher crystallinity than any other bionanocomposite films. Films plasticized with SOR showed the highest tensile strength, lowest film solubility, lowest water vapour permeability and thermal stability. The main interactions among the components in a bionanocomposite film are due to hydrogen bonding. Bionanocomposite films containing GFSE showed a maximum zone of inhibition against *Aspergillus niger*. Synthetic plastic films exhibited fungal growth on 6th day whereas CS/CH/nanoclay/SOR/GFSE films did not show the same up to 20 days when bread samples were packed at 25°C and 59% RH.

The first report of the photo-producible and photo-degradable bionanocomposite as a food packaging material has been done by Goudarzi and Shahabi-Ghahfarrokhi in 2018 [66]. Their results showed that ultraviolet A (UV-A) irradiation increased the hydrophobicity of starch films. With increasing UV-A exposure time, tensile strength and Young's modulus of the specimens were decreased. On the other hand, elongation at break of the films was increased with increasing UV-A irradiation. The glass transition temperature and melting point of the films were increased by increasing UV-A exposure time. Nevertheless, the results showed that photo-degradation properties of photo-produced starch/TiO_2 nanocomposite were significantly higher than virgin starch and virgin starch/TiO_2 films. According to obtain results and bibliography a schema was developed to describe the mechanism of photo-production and photo-degradation of starch/TiO_2 by UV-A ray. It can be concluded, the modification of starch-based biopolymer by UV-A and nano-TiO_2, is an easy and accessible process to improve the packaging properties and photo-degradability of biopolymer-based films.

V. CONCLUSION

It has been shown that nanotechnology is starting to become one of the most useful tools to overcome the current challenges related to food packaging materials. It has been proved that nanocomposite serves to enhance the quality and safety of food packaging materials by improving their barrier, mechanical, thermal, optical, crystallinity, physical, and morphological properties through loading a low concentration of various nanoparticles, such as nano-clay, zinc, copper, silver, gold, selenium, and titanium, metal oxides. The present article reviews the role and influence of metal NPs in the modification of different properties of bio-nanocomposite films as a novel food packaging material with regard to their physical, mechanical and antimicrobial performance. However, more studies are needed on the migration of nanoparticles in food products and their possible effect on the safety of packaging and the environment. It has been seen that recently developed bionanocomposite films could potentially be useful for active packaging in extend the shelf life; maintain its quality and safety of food products thus substituting synthetic plastic packaging materials.

REFERENCES

[1] Filho, J.G.D.O., De Deus, I.P.B., Valadares, A.C.F., Fernandes, C.C., Estevam, E.B.B. and Egea, M.B. (2020) Chitosan Film with Citrus limonia Essential Oil: Physical and Morphological Properties and Antibacterial Activity. *Colloids Interfaces*, 4, 18. https://doi.org/10.3390/colloids4020018
[2] Mahcene, Z., Khelil, A., Hasni, S., Akman, P.K., Bozkurt, F., Birech, K., Goudjil, M.B. and Tornuk, F. (2020) Development and characterization of sodium alginate based active edible films incorporated with

essential oils of some medicinal plants. *International Journal of Biological Macromolecules*, 145, 124–132. https://doi.org/10.1016/j.ijbiomac.2019.12.093

[3] Suhag R., Kumar N., Trajkovska Petkoska A. and Upadhyay A. (2020) Film formation and deposition methods of edible coating on food products: A review. *Food Research International*, 136, 109582. https://doi.org/10.1016/j.foodres.2020.109582

[4] Ahari, H. and Soufiani, S.P. (2021) Smart and Active Food Packaging: Insights in Novel Food Packaging. *Frontiers in Microbiology*, 12, 657233. https://doi.org/10.3389/fmicb.2021.657233.

[5] Nile, S.H., Baskar, V., Selvaraj, D., Nile A., Xiao J., and Kai G. (2020) Nanotechnologies in Food Science: Applications, Recent Trends, and Future Perspectives. *Nano-Micro Letters*, 12, 45. https://doi.org/10.1007/s40820-020-0383-9.

[6] Díaz-Montes, E. and Castro-Muñoz, R. (2021) Trends in Chitosan as a Primary Biopolymer for Functional Films and Coatings Manufacture for Food and Natural Products. *Polymers*, 13(5):767. https://doi.org/10.3390/polym13050767.

[7] Shahabi-Ghahfarrokhi, I., Khodaiyan, F., Mousavi, M. and Yousefi, H. (2015) Green bionanocomposite based on kefiran and cellulose nanocrystals produced from beer industrial residues. *International Journal of Biological Macromolecules*, 77, 85–91. doi: 10.1016/j.ijbiomac.2015.02.055.

[8] Xing, Y., Xu, Q., Li, X., Chen, C., Ma, L., Li, S., Che, Z. and Lin, H. (2016) Chitosan-based coating with antimicrobial agents: Preparation, property, mechanism, and application effectiveness on fruits and vegetables. *International Journal of Polymer Science*, 2016, 4851730. https://doi.org/10.1155/2016/4851730.

[9] Goudarzi, V., Shahabi-Ghahfarrokhi, I. and Babaei-Ghazvini, A. (2017) Preparation of ecofriendly UV-protective food packaging material by starch/TiO_2 bio-nanocomposite: Characterization. *International Journal of Biological Macromolecules*, 95, 306–313. https://doi.org/10.1016/j.ijbiomac.2016.11.065.

[10] Kester, J.J. and Fennema, O.R. (1986) Edible Films and Coatings—A Review. *Food Technology*, 40, 47–59.

[11] Bratovcic A. (2020) Nanocomposite Hydrogels Reinforced by Carbon Nanotubes. *International Journal of Engineering Research and Applications*, 10 (5) (Series-IV), 30-41. doi: 10.9790/9622-1005043041.

[12] Yemmireddy, V.K. and Hung, Y.-C. (2015) Effect of binder on the physical stability and bactericidal property of titanium dioxide (TiO_2) nanocoatings on food contact surfaces. *Food Control*, 57, 82–88. 10.1016/j.foodcont.2015.04.009.

[13] Li, H., Li, F., Wang, L., Sheng, J., Xin, Z., Zhao, L., Xiao, H., Zheng, Y. and Hu, Q. (2009) Effect of nano-packing on preservation quality of Chinese jujube (Ziziphus jujuba Mill. var. inermis (Bunge) Rehd). *Food Chemistry*, 114, 547–552. https://doi.org/10.1016/j.foodchem.2008.09.085

[14] Davoodbasha, M., Kim, S.-C., Lee, S.-Y. and Kim, J.-W. (2016) The facile synthesis of chitosan-based silver nano-biocomposites via a solution plasma process and their potential antimicrobial efficacy. *Archives of Biochemistry and Biophysics*, 605, 49–58. doi: 10.1016/j.abb.2016.01.013

[15] Shahabi-Ghahfarrokhi, I., Khodaiyan, F., Mousavi, M. and Yousefi, H. (2015) Preparation of UV-protective kefiran/nano-ZnO nanocomposites: Physical and mechanical properties. *International Journal of Biological Macromolecules*, 72, 41–46. https://doi.org/10.1016/j.ijbiomac.2014.07.047.

[16] Bahrami, A., R. Delshadi, E. Assadpour, S. M. Jafari, and L. Williams. (2020) Antimicrobial-loaded nanocarriers for food packaging applications. *Advances in Colloid and Interface Science*, 278, 102140. doi: 10.1016/j.cis.2020.102140.

[17] Haniffa M. A. C. M., Ching Y. C., Abdullah L. C., Poh S. C. and Chuah C. H. (2016) Review of Bionanocomposite Coating Films and Their Applications. *Polymers*, 8, 246. doi:10.3390/polym8070246.

[18] Rhim, J. W., L. F. Wang, and S. I. Hong. (2013). Preparation and characterization of agar/silver nanoparticles composite films with antimicrobial activity. *Food Hydrocolloids*, 33, (2), 327–35. doi: 10.1016/j.foodhyd.2013.04.002.

[19] Bratovcic A. (2020) Nanomaterials in Food Processing and Packaging, its Toxicity and Food Labeling. *Acta Scientific Nutritional Health*, 4, (9), 07-13. https://www.actascientific.com/ASNH/pdf/ASNH-04-0745.pdf

[20] El-Sayed S. M., El-Sayed H. S., Ibrahim O. A. and Youssef A. M. (2020) Rational design of chitosan/guar gum/zinc oxide bionanocomposites based on Roselle calyx extract for Ras cheese coating. *Carbohydrate Polymers*, 239, 116234. doi: 10.1016/j.carbpol.2020.116234.

[21] Velickova E., Winkelhausen E., Kuzmanova S., Alves V. D. and Moldão-Martins M. (2013) Impact of chitosan-beeswax edible coatings on the quality of fresh strawberries (Fragaria ananassa cv Camarosa) under commercial storage conditions, *LWT–Food Science Technology*, 52(2), 80–92. https://doi.org/10.1016/j.lwt.2013.02.004.

[22] Duran, M., Aday, M.S., Zorba, N.N.D., Temizkan, R., Büyükcan, M.B. and Caner, C. (2016) Potential of antimicrobial active packaging 'containing natamycin, nisin, pomegranate and grape seed extract in chitosan coating'to extend shelf life of fresh strawberry. *Food and Bioproducts Processing*, 98, 354–63. https://doi.org/10.1016/j.fbp.2016.01.007.

[23] Jafarzadeh, S., Alias, A.K., Ariffin, F. and Mahmud, S. (2018) Physico-mechanical and microstructural properties of semolina flour films as influenced by different sorbitol/glycerol concentrations. *International Journal of Food Properties*, 21, 1, 983–995. https://doi.org/10.1080/10942912.2018.1474056.

ISSN: 2349-8889
Volume-8, Issue-5 (September 2021)
https://doi.org/10.31033/ijrasb.8.5.22

[24] Emamifar, A. and Bavaisi, S. (2020) Nanocomposite coating based on sodium alginate and nano ZnO for extending the storage life of fresh strawberries (Fragaria×ananassa Duch.). *Journal of Food Measurement and Characterization*, 14, 1012–1024. https://doi.org/10.1007/s11694-01900350-x.

[25] Chi, H, Song, S., Luo, M., Zhang, C., Li, W., Li, L. and Qin Y. (2019) Effect of PLA nanocomposite films containing bergamot essential oil, TiO_2 nanoparticles, and Ag nanoparticles on shelf life of mangoes. *Scientia Horticulturae*, 249, 192–198. https://doi.org/10.1016/j.scienta.2019.01.059.

[26] Zhang, C., Li, W., Zhu, B., Chen, H., Chi, H., Li, L. Qin, Y. and Xue, J. (2018) The quality evaluation of postharvest strawberries stored in nano-Ag packages at refrigeration temperature. *Polymers (Basel)*, 10, 8, 894. doi: 10.3390/polym10080894.

[27] Yildirim, S., Röcker, B., Pettersen, M.K., Nilsen-Nygaard, J., Ayhan, Z., Rutkaite, R., Radusin, T., Suminska, P., Marcos, B. and Coma, V. (2018) Active packaging applications for food. *Comprehensive Reviews in Food Science and Food Safety*, 7, 165–199. https://doi.org/10.1111/1541-4337.12322

[28] Rooney, M.L. (1995) Active packaging in polymer films, in: M.L. Rooney (Ed.), *Active Packaging*, Blackie Academic and Professional, London, England, 74–110.

[29] Gibis, D. and Rieblinger, K. (2011) Oxygen scavenging films for food application, *Procedia Food Science*, 1, 229–234. https://doi.org/10.1016/j.profoo.2011.09.036.

[30] Solovyov, S.E. (2010) Oxygen scavengers, in: K.L. Yam (Ed.), The Wiley *Encyclopedia of Packaging Technology*, third ed., John Wiley & Sons Ltd., Hoboken, NJ, 841–850.

[31] Di Maio, L., Scarfato, P., Galdi, M.R. and L. Incarnato (2015) Development and oxygen scavenging performance of three-layer active PET films for food packaging, *Journal of Applied Polymer Science*, 132, (7). https://doi.org/10.1002/app.41465.

[32] Mills, A. Doyle, G., Peiro, A.M. and Durrant, J. (2006) Demonstration of a novel, flexible, photocatalytic oxygen-scavenging polymer film. *Journal of Photochemistry and Photobiology A*: *Chemistry*, 177, 2-3,, 328–331. https://doi.org/10.1016/j.jphotochem.2005.06.001.

[33] Mahieu, A., Terrié, C. and Youssef, B. (2015) Thermoplastic starch films and thermoplastic starch/polycaprolactone blends with oxygen scavenging properties: influence of water content. *Industrial Crops and Products*, 72, 192–199. https://doi.org/10.1016/j.indcrop.2014.11.037.

[34] Yildirim, S., Röcker, B., Rüegg, N. and Lohwasser, W. (2015) Development of palladium-based oxygen scavenger: optimization of substrate and palladium layer thickness. *Packaging Technology and Science*, 28, 8, 710–718. https://doi.org/10.1002/pts.2134.

[35] Hutter, S., Rüegg, N., Yildirim, S. (2016) Use of palladium based oxygen scavenger to prevent discoloration of ham, *Food Packaging and Shelf Life*, 8, 56–62. https://doi.org/10.1016/j.fpsl.2016.02.004.

[36] Cardona, E.D., Noriega, M.P. and Sierra, J.D. (2011) Oxygen scavengers impregnated in porous activated carbon matrix for food and beverage packaging applications, *Journal of Plastic Film & Sheeting*, 28, 63–78. https://doi.org/10.1177/8756087911427730.

[37] Mabeck, J.T. and Malliaras, G.G. (2006) Chemical and biological sensors based on organic thin-film transistors, Analytical and Bioanalytical Chemistry, 384, 343–353. https://doi.org/10.1007/s00216-005-3390-2.

[38] Johansson, K., Gillgren, T., Winestrand, S. Järnström, L. and Jönsson, L.J. (2014) Comparison of lignin derivatives as substrates for laccase-catalyzed scavenging of oxygen in coatings and films. *Journal of Biological Engineering*, 8, 1. https://doi.org/10.1186/1754-1611-8-1.

[39] Johansson, K., Kotkamo, S. and Rotabakk, B.T. (2014) Extruded polymer films for optimal enzyme-catalyzed oxygen scavenging. *Chemical Engineering Science*, 108, 1–8. doi: 10.1016/j.ces.2013.12.035.

[40] Gaikwad, K.K., Singh, S. and Lee, Y.S. (2017) A pyrogallol-coated modified LDPE film as an oxygen scavenging film for active packaging materials. *Progress in Organic Coatings*, 111, 186–195. https://doi.org/10.1016/j.porgcoat.2017.05.016

[41] Farneth, W.E., Hasty, N.M., Damore, M.B. and Chisholm, D.A. (2005). Method for preparing an oxygen reduced film and package. *U.S. Patent Application* 0205840 A1.

[42] Roberta, A.M. (2020) Chapter 22 - Oxygen scavenging films and coating of biopolymers for food application, Editor(s): Mariana Agostini de Moraes, Classius Ferreira da Silva, Rodrigo Silveira Vieira, *Biopolymer Membranes and Films*, Elsevier, 535-551. https://doi.org/10.1016/B978-0-12-818134-8.00022-5.

[43] Bratovcic, A. (2020) Biosynthesis of Green Silver Nanoparticles and Its UV-Vis Characterization. *IJISET - International Journal of Innovative Science, Engineering & Technology*, 7(7) 2020: 170-176. http://ijiset.com/vol7/v7s7/IJISET_V7_I7_17.pdf

[44] Bratovcic, A. (2019) Different Applications of Nanomaterials and Their Impact on the Environment. *SSRG International Journal of Material Science and Engineering (IJMSE)*, 5,(1), 1-7. doi: 10.14445/23948884/IJMSE-V5I1P101.

[45] Li, W., Li, L., Cao, Y., Lan, T., Chen, H. and Qin, Y. (2017) Effects of PLA film incorporated with ZnO nanoparticle on the quality attributes of fresh-cut apple. *Nanomaterials*. 7,8, 207. Doi: 10.3390/nano7080207.

[46] Xing, Y., Yang, H., Guo, X., Bi, X., Liu, X., Xu, Q., Wang, Q., Li, W., Li, X. Shui, Y., Chen, C. and Zheng, Y. (2020) Effect of chitosan/Nano-TiO_2 composite coatings on the postharvest quality and physicochemical characteristics of mango fruits. *Scientia Horticulturae*, 263,109135. https://doi.org/10.1016/j.scienta.2019.109135.

[47] Barikloo, H. and Ahmadi, E. (2018) Shelf life extension of strawberry by temperatures conditioning, chitosan coating, modified atmosphere, and clay and silica nanocomposite packaging. *Scientia Horticulturae*, 240:496–508. https://doi.org/10.1016/j.scienta.2018.06.012.
[48] Zhang, Y.-P.,Wang, X., Shen,Y., Thakur, K., Zhang, J.-G., Hu, F. And Wei, Z.-J. (2021) Preparation and Characterization of Bio-Nanocomposites Film of Chitosan and Montmorillonite Incorporated with Ginger Essential Oil and Its Application in Chilled Beef Preservation. *Antibiotics*, 10, 796. https://doi.org/10.3390/antibiotics10070796.
[49] Silva-Weiss, A., Bifani, V., Ihl, M., Sobral, P.J.A. and Gómez-Guillén, M.C. (2013) Structural properties of films and rheology of film forming solutions based on chitosan and chitosan-starch blend enriched with murta leaf extract. *Food Hydrocolloids*, 31,2, 458–466. https://doi.org/10.1016/j.foodhyd.2012.11.028.
[50] Woranuch, S. and Yoksan, R. (2013) Eugenol-loaded chitosan nanoparticles: II. Application in bio-based plastics for active packaging. *Carbohydrate Polymers*, 96, 586–592. https://doi.org/10.1016/j.carbpol.2012.09.099.
[51] Souza, V.G.L., Pires, J.R.A., Vieira, E., Coelhoso, I., Duarte, M. and Fernando, A. (2018) Shelf life assessment of fresh poultry meat packaged in novel bionanocomposite of chitosan/montmorillonite incorporated with ginger essential oil. *Coatings*, 8, 177. https://doi.org/10.3390/coatings8050177.
[52] Zhu, P., Wang, M., Du, X., Chen, Z., Liu, C. and Zhao, H. (2020) Morphological and physicochemical properties of rice starch dry heated with whey protein isolate. *Food Hydrocolloids*, 109, 106091. https://doi.org/10.1016/j.foodhyd.2020.106091.
[53] Sultan, M., Hafez, O.M., Saleh, M.A. and Youssef, A.M. (2021) Smart edible coating films based on chitosan and beeswax–pollen grains for the postharvest preservation of Le Conte pear. *RSC Advances*, 11, 9572-9585. Doi: 10.1039/D0RA10671B.
[54] Nallan Chakravartula, S.S., Soccio, M., Lotti, N., Balestra, F., Dalla Rosa, M. and Siracusa, V. (2019) Characterization of Composite Edible Films Based on Pectin/Alginate/Whey Protein Concentrate. *Materials*, 12,15, 2454; doi: 10.3390/ma12152454.
[55] Maruddin, F., Malaka, R., Baba, S., Amqam, H., Taufik, M. and Sabil, S. (2020) Brightness, elongation and thickness of edible film with caseinate sodium using a type of plasticizer. *IOP Conf. Series: Earth and Environmental Science*, 492, 012043. doi:10.1088/1755-1315/492/1/012043.
[56] Escamilla-García, M., Calderón-Domínguez, G., Chanona-Pérez, J.J., Mendoza-Madrigal, A.G., Di Pierro, P., García-Almendárez, B. E., Amaro-Reyes, A. and Regalado-González, C. (2017) Physical, Structural, Barrier, and Antifungal Characterization of Chitosan–Zein Edible Films with Added Essential Oils. *International Journal of Molecular Science*, 18, 2370; doi:10.3390/ijms18112370.
[57] Zhang, S., Zhang, M., Fang, Z. and Liu, Y. (2017) Preparation and Characterization of Blended Cloves/Cinnamon Essential Oil Nanoemulsions. *LWT-Food Science and Technology*, 75, 316–322. https://doi.org/10.1016/j.lwt.2016.08.046.
[58] Noshirvani, N., Ghanbarzadeh, B., Garrat, C., Rezaei, M. and Hashemi, M. (2017) Cinnamon and Ginger Essential Oils to Improve Antifungal, Physical and Mechanical Properties of Chitosan-Carboxymethyl Cellulose Films. *Food Hydrocolloids*, 70, 36–45. https://doi.org/10.1016/j.foodhyd.2017.03.015.
[59] Andrade Martins, Y.A., Borges Sandre, M.F., Ferreira, S. V., Silva, N. M., Toledo Leão, P.V., Oliveira Filho, J. G., Rocha Plácido, G., Leão, K. M., Soares Nicolau, E., Buranelo Egea, M. and Pereira da Silva, M. A. (2020) Edible Films of Whey and Cassava Starch: Physical, Thermal, and Microstructural Characterization. *Coatings*, 10, 1059. doi:10.3390/coatings10111059.
[60] Arnon, H., Zaitsev, Y., Porat R. and Poverenov, E. (2014) Effects of carboxymethyl cellulose and chitosan bilayer edible coating on postharvest quality of citrus fruit, *Postharvest Biology and Technology*, 87, 21–26. https://doi.org/10.1016/j.postharvbio.2013.08.007
[61] Pl & acido, G. R., da Silva, R. M., Cagnin, C., Cavalcante, M. D., da Silva, M. A., Caliari, M. A., de Lima, M. S. and do Nascimento, L. E. (2016) Effect of chitosan-based coating on postharvest quality of tangerines (Citrus deliciosa Tenore): Identifcation of physical, chemical, and kinetic parameters during storage, African Journal of Agricultural Research, 11(24), 2185–2192. Doi: 10.5897/AJAR2014.9355
[62] Otoni, C.G., Avena-Bustillos, R.J., Olsen, C.W., Bilbao Sáinz, C. and McHugh, T.H. (2016) Mechanical and water barrier properties of isolated soy protein composite edible films as affected by carvacrol and cinnamaldehyde micro and nanoemulsions. *Food Hydrocolloids*, 57, 72–79. https://doi.org/10.1016/j.foodhyd.2016.01.012
[63] Chen, F. and Chi, C. (2021) Development of pullulan/carboxylated cellulose nanocrystal/tea polyphenol bionanocomposite films for active food packaging. *International Journal of Biological Macromolecules*, 186, 405-413. https://doi.org/10.1016/j.ijbiomac.2021.07.025
[64] Ni, Y., Shi, S., Li, M., Zhang, L., Yang, C., Du, T., Wang, S., Nie, H., Sun, J., Zhang, W. and Wang, J. (2021) Visible light responsive, self-activated bionanocomposite films with sustained antimicrobial activity for food packaging. *Food Chemistry*, 362. https://doi.org/10.1016/j.foodchem.2021.130201
[65] Jha P. (2020) Effect of plasticizer and antimicrobial agents on functional properties of bionanocomposite films based on corn starch-chitosan for food packaging applications. *International Journal of Biological Macromolecules*, 160, 571-582. https://doi.org/10.1016/j.ijbiomac.2020.05.242

[66] Goudarzi, V. and Shahabi-Ghahfarrokhi, I. (2018) Photo-producible and photo-degradable starch/TiO_2 bionanocomposite as a food packaging material: Development and characterization. *International Journal of Biological Macromolecules*, 106, 661-669. https://doi.org/10.1016/j.ijbiomac.2017.08.058

