Review

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Nanoreinforcement as a strategy to improve physical properties of biodegradable composite films based on biopolymers

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ABSTRACT

Food packaging is evolving from inert plastic to renewable biopolymer film that acts as barrier against gases, light radiation, and microorganisms, reducing food waste without environmental damage. Distinct starting systems were selected to prepare films: single polymer matrix, blend of polymers, cross-linked polymers, and emulsion-based matrix. The blend of polymers was one of the best approaches to improve mechanical and barrier properties of films, especially when one of the polymers was pectin, gelatin or xanthan gum. These polymers can form a gel and increase the viscosity of the starting systems leading to a more elastic matrix. Although some of these films showed potential to replace plastic materials, their physical properties were poor compared to plastics. Thus, several strategies were used to strengthen matrix building block connections or interactions between nanoreiforcement and matrix compounds with the aim of improving physical properties. Among metal oxides, TiO_2, ZnO, CaO, and MgO were the most studied, alone or in combinations with other reinforcements. Natural fillers, like chitosan and cellulose nanofibers were also added to improve the biopolymer’s performance. Several of these systems successfully extended the shelf life of food systems by retarding spoilage, showing great potential to improve food quality and reduce waste. However, most of the studies were carried out on a laboratory scale and it would be necessary to explore the feasibility of producing these films on an industrial scale.

Key words

Films, matrix, nanoload, metal oxides, natural fillers, cross-linking

1. Introduction

Plastic materials are used in food packaging for many applications since they increase the shelf life of products by protecting food during storage and transportation (Andrade-Del Olmo, Pérez-Álvarez, Hernáez, Ruiz-Rubio, & Vilas-Vilela, 2019). However, the accumulation of plastics in ecosystems is a great concern regarding the damage they cause to the environment and animal life (Akshaykranth, Venkatappa Rao, & Rakesh Kumar, 2020). Nowadays the packaging is evolving from inert plastic to antimicrobial, biodegradable, or edible biopolymer film packaging (Motelica et al., 2020a; Dash, Ali, Das, & Mohanta, 2019). Edible biodegradable coatings or films act as barriers against water vapor and degradation by oxygen or light radiation, reducing lipid oxidation and food waste (Umaraw, & Verma, 2017). Food-grade polymers have been developed as packaging films because they are safe and renewable resources (Zhang et al., 2019). Edible films have been made with various biopolymers, including proteins (soy, whey, milk), polysaccharides (starch, gums, mucilages), and lipids, alone or combined (Mohammadi, Mirabzadeh, Shahvalizadeh, & Hamishehkar, 2020). Other polymers such as chitosan, polylactic acid (PLA), carboxymethylcellulose, and sodium alginate have also been extensively researched due to their eco-friendly nature, biodegradability, film-forming ability, edibility, and non-toxicity (Han, & Wang, 2017; Hao et al., 2017; Rezaei, & Shahbazi, 2018; Hu et al., 2020; Motelica et al., 2021.

The physical properties of biodegradable films are mainly related to the biopolymer's self-aggregation capacity, which allows the formation of different types of network microstructures that lead to different mechanical and tensile properties. Biopolymer-based films have poor physical properties compared to the plastic films that they replace (Bujok et al., 2021). They have relatively low ultimate strength (σ_b) and elasticity (Young's modulus), especially in moisture-rich environments because of their inherent water susceptibility (Sadeghi-Varkani, Emam-Djomeh, & Askari, 2018). In addition to poor mechanical and tensile properties, some of these films only have limited abilities to block light (Li et al., 2011). Nowadays, appropriate inert barrier properties is not a sufficient condition for good performance. Actual trends require additional material functions, like antioxidant or antimicrobial activity, moisture controllers, gas absorbing, or flavor releasing; this is known as "active packaging" (Bujok et al., 2021). To improve the film's physical behavior, inorganic or natural fillers nanoparticles have been added to reinforce different matrices. Nanoparticles are hydrophobic in nature, and for this reason, they improve barrier properties against moisture, water vapor, and oxygen. In addition, the use of nanoparticles significantly improves the optical, mechanical, electrical, antimicrobial, and thermal properties of the resultant nanocomposite films (Hu et al., 2020; Sadeghi-Varkani, Emam-Djomeh, & Askari, 2018). Among the nanoparticles of metal oxides, the most studied are TiO_2, ZnO, CaO, and MgO (Dash, Ali, Das, & Mohanta, 2019; Arakha et al., 2015; Bindhu, Umadevi, Micheal, Arasu, & Al-Dhabi, 2016; Garcia, Shin, & Kim, 2018). They showed ability to reinforce film structure and were active against food-born pathogenic microorganisms (Bujok et al., 2021; Pušnik Crešnar et al., 2021). Addition of natural fillers such as chitosan (Mohammadi, Mirabzadeh, Shahvalizadeh, & Hamishehkar, 2020), and cellulose nanofiber (Ahmadi, Ahmadi, Alizadeh Sani, Ehsani, & Ghanbarzadeh, 2021), among others, were also reported to successfully improve biopolymer film's performance. This review is focused on the effects of nanoreinforcement (nanoparticles or nanofillers) on the physical properties of biodegradable or/and edible films. Films prepared from different starting systems were compared to show the effects of matrix component interactions on mechanical and barrier properties. Examples of the performance of these films in food systems are described in sections 2 and 3. Figure 1 shows the different starting systems selected to obtain films and the strategies used during preparation to improve their physical properties. These topics are described in detail in the following sections.

2. Metal oxide reinforcement

2.1. TiO_2-nanoparticles

Titanium dioxide (TiO_2) has been selected as reinforcement in a variety of systems because is an inert metal oxide. It is approved by the United States Food and Drug Administration (FDA) for use in human food and food contact materials, if the amount of titanium dioxide does not exceed 1% by weight of the food (Feng et al., 2019). Moreover, it has been widely used as a color additive in food and cosmetic applications to block light and give products a white appearance. Due to its photocatalytic activities, TiO_2 can be used to protect against foodborne microorganisms and allergens in the presence of ultraviolet radiation or when combined with an essential oil (Nasiri, Sani, Hakimzadeh, & Shahidi, 2019; Alizadeh Sani et al., 2022a). Besides, migration from the film is negligible which makes it safe for food packaging applications (Zhang, & Rhim, 2022). Among applications in food production, chitosan-TiO_2 composite edible inks have been prepared for screen-printing and for special customization or batch production of food or drug decorations (Wang, Qian, Li, & Ding, 2018). In coating applications, the effect of chitosan-based edible coating containing nanoparticles of TiO_2 on the postharvest quality of blueberries was evaluated during storage (Xing et al., 2021). The reported results showed that the chitosan/nano-TiO_2 composite coating could maintain the nutrient composition of blueberries while playing a significant role in preserving the quality of fruit at 0°C. TiO_2 was also added to PLA to prepare nanocomposite films with the aim of improving weight consistency, fruit firmness, color, and sensory quality of mangoes stored for 15 days at 20°C (Chi et al., 2019). PLA nanocomposite films were effective in delaying ripening during the entire storage period and maintaining postharvest quality of mangoes(delaying changes in color, total acidity, and vitamin C) for 15 days, thus increasing the market period.

2.1.1. Single-matrix starting systems

Table 1 shows several examples in which TiO_2 nanoparticles were added to improve the physical properties of films formulated with different matrix components. The properties selected were water vapor permeability and Young's modulus (E), a tensile parameter used to evaluate elasticity. Table 1 shows the values that these parameters reached when the optimum concentration of nanoreinforcement was used. From these examples it is possible to compare the effects on physical properties in different matrices. The concentration of reinforcement was a key value in formulations and extensively studied. The reinforcement interrupts matrix building blocks connections causing defects or pores in matrices. When TiO_2 was added to starch granules it promoted disruption of structure, increasing the amorphous starch portion (Phothisarattana & Harnkarnsujarit, 2022a). Besides, aggregation of TiO_2 particles was dependent on hydrogen bonding to polymer and increasing concentration of TiO_2 non-linearly increased the size of self-aggregates (Phothisarattana & Harnkarnsujarit, 2022a). However, depending on concentration, the positive interactions matrix/reinforcement could improve mechanical properties despite disruption of matrix structure. Among matrices studied, milk proteins films have been thoroughly investigated. Whey protein isolate (WPI) films were reinforced by adding TiO_2 nanoparticles at different concentration levels (0.1 to 2.0% TiO_2/WPI mass ratio) to a WPI solution-based system to control their physical properties through the concentration of TiO_2 (Li et al., 2011). The strategy was based on avoiding TiO_2 particle agglomeration in the film. When the concentration of TiO_2 nanoparticles was low (<0.25%), the reinforcement was homogeneously dispersed in the protein matrix and promoted tensile strength of the composite films. In contrast, higher concentrations of TiO_2 (>0.25%) enhanced the self-assembly of TiO_2-TiO_2 nanoparticles, which produced a decline in the tensile strength and an increase in water vapor permeability. According to the data reported, a concentration of TiO_2 from 0.25% to 0.5%

would be optimum for these films (Li et al., 2011, Table 1). Similar results were found for whey protein concentrate solution-based matrix. A concentration of 0.5% was the optimum value for reinforcement (Montes de Oca-Ávalos et al., 2020, Table 1). In agreement with these findings, studies on bio-nanocomposite films of *Lallemantia iberica* mucilage/TiO_2 showed a more uniform distribution of TiO_2 nanoparticles in the polysaccharide matrix at low dosages of TiO_2 nanoparticle, leading to improved mechanical, thermal, and barrier properties (Sadeghi-Varkani, Emam-Djomeh, & Askari, 2018). For sodium caseinate matrix the optimum reinforcement value was 0.5%, indicating that in this concentration TiO_2 was homogeneously distributed, and therefore the matrix contained fewer defects (Montes-de-Oca-Ávalos et al., 2018, Table 1).

Films prepared from whey protein solutions with TiO_2 nanoparticles added at concentrations of 10% or 15% were also studied (Al–Hadedee, Awahd, Mahmood, & Musa, 2020). Contrary to expectations, even at such high concentrations, TiO_2 nanoparticles improved the tensile and antimicrobial properties of the films. However, the addition of nanoparticles at such a high percentage changed film colors to a milky white. Additionally, the improvement found in physical properties did not encourage the use of such a high concentration of nanoparticles. For milk protein-based films reinforced with spherical nanoparticles there is a general agreement that 0.5% is the optimal concentration of reinforcement. Although most authors used spherical nanoparticles of P25, other geometries were also studied. Edible films based on whey protein nanofibrils reinforced with TiO_2 nanotubes or nanoparticles were prepared (Feng et al., 2019). The nanofibrils performed well in biodegradable films and showed ordered β-sheet structures leading to homogeneous structure and great antioxidant activity. The interactions between nanofibrils and nanotubes allow films to be obtained with good mechanical properties and great potential for application to various food products, such as raw and chilled meat (Feng et al., 2019, Table 1). The report showed the importance of reinforcement geometry on physical properties of films.

Plant proteins were also used to prepare edible films. The effects of ultrasonic/microwave assisted treatment (UMAT) on physical properties of films prepared with soy protein isolate (SPI, 5.0 g/100 mL)/nano-TiO_2 (0, 0.5, 1.0, 1.5 and 2.0 g/100 mL) were studied (Wang et al., 2014, Table 1). The results showed that incorporation of nano-TiO_2 significantly improved films' tensile strength values (245% higher than the control), reduced water vapor permeability (72% lower than the control), and oxygen permeability values (58% lower than the control) at all TiO_2 concentrations and UMAT application times under 20 min. UMAT application improved the distribution of nanoparticles in the matrix, prevented nanoparticle aggregation, and increased intermolecular forces between nano-TiO_2 particles and soy proteins. The observed reductions in water vapor permeability of films containing nano-TiO_2 indicate that the addition of this nano reinforcement could be an effective strategy to enhance film performance and improve final product quality and shelf stability. This report also shows the importance of preparation method and conditions. UMAT application allowed to expose the functional groups of the protein and thus strengthen the connections between the building blocks of the film structure. Soy protein-based films showed similar mechanical and barrier properties than whey protein-based films, indicating that protein origin did not affect physical properties (Table 1). Positive interactions matrix/reinforcement were reported in both cases as well as an improvement in film performance. However, the use of vegetal protein may be an advantage from the environmental and economic points of view. Plant proteins are widely available and cheaper to produce than animal proteins.

Polysaccharides were successfully used to prepare biodegradable films aiming to replace plastics. To improve the physical properties of pullulan films, TiO_2 was added at different concentrations (Liu et al., 2019, Table 1). Pullulan, a water-soluble, fungus-like yeast exopolysaccharide, is a biodegradable, biocompatible, and edible polymer composed of maltotriose units linked to each other by α-(1- 6) glycosidic bonds. Pullulan films have poor physical-chemical properties. However, these may be improved by adding essential oils, nanoparticles, or by combining pullulan with other polymers. The films were formulated with a solution of 4g/100 mL of pullulan and 0 to 0.08g/100 mL of TiO_2. According to their results, pullulan film containing 0.04 g/100 mL of nano-TiO_2 had the best water vapor barrier and tensile strength. This TiO_2 concentration was ten times lower than the optimal concentration found for most systems, indicating the important role of polymer/nanoparticle interactions. A concentration as low as 0.04% is an advantage from both environmental point of view and suitability for food applications since it might be expected that migration of TiO_2 into food is neglectable. Other polymers such as chitosan were deeply investigated. To improve antioxidant and antimicrobial properties, chitosan films with addition of TiO_2 and/or anthocyanin-rich black plum peel extract were prepared (Zhang et al., 2019, Table 1). Although chitosan has excellent film-forming properties, the application of chitosan films is limited by its poor antioxidant and antimicrobial properties. However, the addition of nanoparticles and antioxidant extract greatly improved antioxidant, antimicrobial, and pH-sensitive abilities. The reinforced films had enhanced water vapor and UV–vis light barriers and greater mechanical strength, suitable for applications in food packaging. Regardless of whether the polymer is a protein or a polysaccharide, films made from them possess similar physical properties. E values reach up to 5 MPa and WVP values up to 5 x 10^{-10} g s^{-1} m^{-1} Pa^{-1} (Table 1). All these studies were performed in lab scale. It would be necessary to explore the possibility of scale-up the process and produce films in industrial scale.

2.1.2. Two-polymer starting systems

In addition of reinforcement with nanoparticles, other strategies to improve strength of matrix connections was the mix of polymers. More complex matrices formed by two polymers were also described. An edible nanocomposite packaging film containing simultaneously extracted protein-polysaccharide (biopolymers) from the marine red alga *Gracilaria lemaneiformis* and TiO_2 nanoparticles was studied (He, Huang, Lin, & Wang, 2017). Addition of TiO_2 reduced water vapor permeability, improved mechanical properties, and thermostability, as compared to a control sample without TiO_2. The studied nanocomposite films containing TiO_2 exhibited effective antimicrobial activity against both *E. coli* and *S. aureus*. Although promising results were obtained when the packaging was used to preserve cherry tomatoes, water vapor permeability was 10 times higher than for the other systems shown in Table 1 and the required TiO_2 concentration was ten times greater than typically used to achieve film improvement. A more successful two-polymer matrix was formulated with solution of sweet potato starch and lemon waste pectin. Films were prepared with a starch–pectin (3:1) ratio and reinforced with nanoparticles of TiO_2 incorporated at different concentrations (0.5%, 1%, 2%, 3%, and 4%) (Dash, Ali, Das, & Mohanta, 2019). The tensile properties of edible films without additives were considerably greater (at least 10 times) than the solution films reported in Li et al. (2011) and Wang et al. (2014), most likely due to the presence of lemon waste pectin in formulations, which interacted positively with starch to form a strong matrix (Table 1). Pectin also increased matrix viscosity which led to improved mechanical properties. Their results showed that although tensile properties of formulations without additives were good, the addition of TiO_2 nanoparticles to starch-pectin films in low concentrations (0.5 to 2%) improved the matrix properties. TiO_2 nanoparticles were evenly distributed in the matrix, improving thermal stability and mechanical properties, while decreasing water vapor permeability and solubility of the films, making them more suitable to replace synthetic plastic materials. Another strategy to improve biodegradable films physical properties is formulating the matrix with a blend of gelatin and κ-carrageenan. The films showed excellent physical properties and the highest E values were reported for films reinforced with TiO_2 (Alizadeh Sani, Tavassoli, Salim, Azizilalabadi, & McClements, 2022b, Table 1). Natural pigments (saffron or red barberry anthocyanins) were added to the films as pH-responsive color indicators and TiO_2 nanoparticles were included for light blocking. The performance of the films was proved by using them to monitor changes in the freshness of packaged fish during storage. Loss of freshness was evaluated as changes in film color, which was correlated to ammonia production during fish degradation. The presence of the anthocyanins and TiO_2 nanoparticles enhanced the bacteriostatic properties and inhibited oxidative reactions. Films were able to detect food deterioration and prolong shelf life, improving product quality and reducing food waste. The blend of a protein or polysaccharide-based film with a polymer able to form a gel such as gelatin led to very much improved mechanical and tensile properties. As interactions between polymers were positive, gelatin gel kept its strength and allow obtaining a more connected structure. Other polymer blends include a component which is an industrial waste. The re use of it in film formulations is appealing much attention since it makes packaging production more sustainable. Biodegradable film based on sour lemon peel were prepared with the aim of using the waste from lemon juice factories (Meydanju, Pirsa, & Farzi, 2022). Films were modified with xanthan gum and TiO_2–Ag nanoparticles. Addition of nanoparticles significantly increased thermal stability, antimicrobial activity, tensile strength and Young's modulus, and decreased water vapor permeability (Table 1). The presence of xanthan gum, which can form a gel, increased the E-modulus by at least five times compared to the matrix based on a single polymer (Table 1). The use of pectin, gelatin or xanthan gum in the formulation of the films showed a significant effect on the physical properties of the matrix (Table 1). The ability to form a gel of these compounds and to increase the viscosity of the starting systems led to a more elastic matrix, whose properties were further improved by the addition of TiO_2 nanoparticles. These mixtures are among the most successful strategies to obtain films capable of replacing plastic materials. To overcome the high sensitivity of native starch films to the environmental changes (humidity, temperature, and pH), cross-linked wheat starch-based ternary nanocomposite films with incorporation of sodium montmorillonite (3%–7% by weight) and TiO_2 (1%–4% by weight) nanoparticles were formulated (Yousefi, Savadkoohi, Zahedi, Hatami, & Ako, 2019). Among the nanocomposites studied, a ternary-based nanocomposite film containing 5% by weight of sodium montmorillonite and 1% by weight of TiO_2 (the maximum allowable amount in food, as stated by the FDA) exhibited the best performance and has the potential to be environmentally friendly packaging for food. Among the authors, polymer crosslinking is considered a very promising strategy to improve the physical properties of films, since it allows establishing strong connections between the components of the matrix. The covalent bonds that form between the polymers lead to a more homogeneous structure. However, in this example, the E and WVP values were close to those obtained for films based on a single polymer. There was no improvement in physical properties as a consequence of the crosslinking reaction.

2.1.3 Two-phase starting systems

Other alternatives to petroleum-based plastics were films starting from a two-phase system (coarse, conventional or nanoemulsions). Chitosan/starch films containing clove oil (3, 6, 9, or 12%) and TiO_2 (1, 3, 5, and 7%) nanoparticles were studied (Li et al., 2019). The system was composed of an aqueous phase containing both polymers and glycerol as plasticizer and a hydrophobic phase of clove oil and TiO_2 nanoparticles. TiO_2 reinforcement has been proved to eliminate oxygen in the packaging with the oxygen absorption efficacy depending on TiO_2 contents (Phothisarattana, Wongphan, Promhuad, Promsorn, & Harnkarnsujarit, 2021). The method selected for homogenization led to a dispersed phase formed by big droplets (~10 μm). This coarse emulsion was dried to give films a heterogeneous structure as reported in SEM images. Although droplet distribution was uneven, films with less than 9% of clove oil had an elongation at break, which was greater than the control without TiO_2 and clove oil, indicating that despite the inhomogeneity in structure, some tensile properties were improved in the presence of TiO_2 nanoparticles and clove oil. However, Young’s modulus was not reported in the manuscript, and it is therefore difficult to evaluate the effect on elasticity (Table 1). Films prepared from emulsions may have poorer physical properties than films prepared from solutions because the presence of a hydrophobic phase may interrupt matrix structure and weaken connections among the building blocks of structure. One strategy to improve the physical properties of emulsion-based films may be the selection of a preparation method that reduces droplet size in the dispersed phase (Table 1). In sodium caseinate/sunflower oil films, tensile properties improved when the starting emulsion was homogenized using high-speed homogenization followed by sonication. With this two-step method the droplet sizes were within the conventional emulsion range (0.2 to 0.6 μm). The homogeneous structure of films led to a higher Young’s modulus for conventional emulsion-based film than for solution-based film (Montes-de-Oca-Ávalos et al., 2018). For whey protein concentrate films, nanoemulsions performed better than conventional emulsions, allowing including a hydrophobic phase without worsened physical properties (Montes de Oca-Ávalos et al., 2020). For nanoemulsion-based films, elasticity was comparable to that of solutions-based films. For most systems, the negative effect on tensile properties that may have a hydrophobic phase diminished with decreasing droplet size. The presence of a hydrophobic phase during formulation has the additional advantage that it may dissolve bioactive compounds of lipophilic nature such as carotenes or vitamin, giving food products functionality by promoting health benefits.

2.2. ZnO-nanoparticles

ZnO is an inexpensive material that can be prepared via several techniques to obtain different structures, including nanorod, nanotubes, nanoneedle, nanoleaf, nanoflower or nanosheet (Shimpi, Rane, Shende, Gosavi, & Ahirrao, 2020). ZnO, prepared as micro or nanostructures, has been widely studied due to its diverse applications in physics, chemistry, electrical engineering, and material science. It has also been used as an additive by cosmetic, pharmaceutical, and medical industries (Mishra, & Adelung, 2018). Nanostructured ZnO films with rod-like morphology were successful in photocatalytic degradation with visible light of non-biodegradable indigo-carmine dye (Shimpi, Rane, Shende, Gosavi, & Ahirrao, 2020). In addition to biodegradable properties, ZnO nanofillers present antimicrobial activity and are considered Generally Regarded as Safe (GRAS) by the FDA (US Food and Drug Administration) to be used in plastics and food contact materials with a specific migration limit of 25 mg Zn/kg of food (Mishra, & Adelung, 2018; EFSA, 2016).

2.2.1. Single-matrix starting systems

To compare the nanoreinforcement physical effects on different matrix, a selection of the obtained E parameter's and WVP values was summarized in Table 2. Among polymers for food packaging, poly lactic acid (PLA) has been thoroughly investigated. PLA is an aliphatic polyester, primarily produced by industrial polycondensation of lactic acid and/or ring-opening polymerization of lactide (Castro-Aguirre, Iñiguez-Franco, Samsudin, Fang, & Auras, 2016). Despite being more expensive than polyolefins, PLA has aroused great interest because it is a natural derivative (Marra, Silvestre, Duraccio, & Cimmino, 2016). This polymer is a good alternative to plastic materials because it is safe for contact with food, biocompatible, compostable, biodegradable, flexible, highly transparent to visible light, and easy to obtain on a large scale (Akshaykranth, Venkatappa Rao, & Rakesh Kumar, 2020, Valerini et al., 2018). To extend PLA uses in different applications, it has been blended with different fillers like fibers, or with micro- and nanoparticles. Biocomposite films of PLA with 1, 3 and 5 % of ZnO nanoparticles have been prepared with the aim of evaluating mechanical, barrier, and antimicrobial (against *Escherichia coli*) properties (Marra, Silvestre, Duraccio, & Cimmino, 2016, Table 2). Films were characterized by a good dispersion of ZnO nanoparticles in PLA matrix and good mechanical and barrier properties. The film containing a nanoparticle concentration of 1% showed the best E value obtained of all matrices studied (Table 2). Excellent tensile properties to replace plastics materials were achieved with a single polymer matrix and a simple preparation method. The fact that it may be produced in large scale makes PLA an ideal solution. Among the concentrations selected in this study (Marra, Silvestre, Duraccio, & Cimmino, 2016), the PLA film with 5% ZnO was the best formulation, showing excellent antimicrobial activity against *Escherichia Coli* (reduction was 99.99 already after 24 h). Another study also reported that films with over 3% of ZnO nanoparticles exhibited a complete growth inhibition of *E. coli* (Kim et al., 2019). Studies evaluating the effect against *Staphylococcus aureus*–code of 1431 (ATCC 25923) described similar results, indicating that films containing ZnO are potential synthetic plastics replacements with excellent UV protective and antibacterial properties (Nasab, & Tabari, 2018). Biodegradable films with ZnO were also able to reduce total viable counts in packaged meat, while reducing the degree of lipid oxidation (Phothisarattana, Wongphan, Promhuad, Promsorn, & Harnkarnsujarit, 2022). From the antimicrobial point of view, the optimum values of nanoparticle concentration were very high compared to the levels needed for TiO_2 nanoparticles (Chi et al., 2019). None of these reports include migration studies, which should be necessary to prove suitability for food packaging at these high concentrations.

Using a reinforcement of nanorods, nanocomposite films with ZnO submerged in the PLA matrix were prepared by solvent casting (Zhang et al., 2017). Although with this preparation method good activity as antibacterial, antimicrobial, and anti UV blocking agent was obtained, the active surface of ZnO was limited since nanorods were placed on bulk. To overcome this limitation, PLA films have been coated with aluminum-doped zinc oxide nanoparticles to functionalize their surface (Valerini et al., 2018). The approach was successful, and the coated films exhibited strong antibacterial activity against *Escherichia coli*. In a simpler and more economic approach, ZnO nanorods were grown on the surface of the PLA substrates, using a hydrothermal method at an optimum temperature of 70°C (Akshaykranth, Venkatappa Rao, & Rakesh Kumar, 2020). This preparation method led to higher surface activity, obtaining a material with good antibacterial properties. The effects of processing parameters on physical properties of PLA/ZnO nanocomposite films were reported (Cui et al., 2021, Table 2). Various ultrahigh-pressure treatments (0, 200 and 400 MPa) were selected to analyze their effects on the microstructure and thermal, barrier, and mechanical properties of films. The water vapor permeability value of the film containing 5% ZnO and treated at 400 MPa was the lowest, reduced by 47.3% compared with that of pure PLA film. Young's modulus increased significantly with ultrahigh-pressure application compared to the untreated film. However, E value for the film containing 10% ZnO nanoparticles was lower than for films containing lower amounts of nanoparticles (1%), indicating the advantage of using lower concentrations of nanoparticles, regarding tensile properties (Table 2). Lower concentrations could be even safer for food packaging and more environmentally friendly. More studies relating food migration and nanoparticles concentration could be useful to stablish suitability for food packaging.

Non-hazardous ZnO nanoparticles were also added to other polymers. Polycaprolactone was used to prepare biodegradable antimicrobial nanocomposites films (Bujok et al., 2021, Table 2). A nanoparticles content of up to 3.0% led to a homogeneous film. Addition of ZnO nanoparticles to the polymer matrix resulted in a significant decrease of water vapor permeation (46%), induced bactericidal effects against the food- born pathogenic bacterium *E. coli* and enhanced biodegradation rate of the prepared nanocomposite film. However, Young's modulus values were significantly lower than for PLA films values (Table 2), indicating that although ZnO nanoparticles improved films in some respects, matrix properties were very relevant. The strength of matrix building blocks connections is a determinant factor for mechanical and tensile properties. It depends on polymer nature and polymer treatment during preparation method and may be modified by formulation. Several single polymer-based matrices were also described. Poly(butylene succinate) as matrix was also reinforced with ZnO nanoparticles (Petchwattana, Covavisaruch, Wibooranawong, & Naknaen, 2016). The films had good antibacterial properties; unfortunately, the mechanical properties were worsened by the addition of ZnO. Better results were found with bagasse cellulose-based films with ZnO nanopillars on the surface (Xie, Pan, & Cai, 2022). Films were prepared via chemical crosslinking together with a hydrothermal process for in-situ growth of ZnO nanoparticles. The obtained films possessed excellent mechanical properties, oxygen and water vapor barrier properties, biodegradability, and low migration of Zn^{+2}, and performed well for food preservation, especially for *Staphylococcus aureus* (gram-positive bacteria) and *Escherichia coli* (gram-negative bacteria). The report showed the relevance of matrix/nanoreinforcement interactions and nanoparticles placement achieved by the selected method of preparation. As with PLA, starch is also a polymer of great interest because it has a well-documented capacity to create flexible nanocomposites and is inexpensive. However, their mechanical properties and water vapor resistance are poorer than the ones of conventional synthetic films. This problem was overcome by blending starch films with ZnO nanoparticles (Mirjalili, & Ardekani, 2017). Starches of different origins have been investigated. Buckwheat starch films containing concentrations from 1.5 to 4.5% of zinc oxide nanoparticles were formulated to avoid *Listeria monocytogenes* growth on mushrooms (Kim, & Song, 2018). The film containing 3% ZnO nanoparticles had the best physical properties of all. It was successfully applied to fresh-cut mushrooms, indicating its potential for food packaging. Janeng starch was used to prepare films reinforced with addition of ZnO, in concentrations of 1, 3, and 5%, and glycerol as plasticizer. Addition of ZnO improved physical properties of film compared to the control without ZnO. Results showed that films with higher ZnO concentrations had better thermal resistance as analyzed by DSC (Amni, Ismet, Aprilia, Mariana, & Akbar, 2020). Bionanocomposite film based on basil seed mucilage, a hydrocolloid containing high molecular weight polysaccharides, and ZnO nanoparticles was studied, and its physical, permeability, mechanical, thermal, and antimicrobial properties were described (Foghara, Jafarian, Zomorodi, Khosrowshahi asl, & Nasiraei, 2020). The film without ZnO did not show antibacterial properties, while the addition of ZnO increased trends in antibacterial activity with increasing content of nanoparticles. Addition of 0.25% ZnO resulted in improvement of physical properties. However, Young's modulus value was considerably lower than for other bionanocomposite films, indicating poorer mechanical properties (Table 2). Basil seed mucilage-based films had E values close to the ones obtained for protein-based films reinforced with TiO_2 (Table 1). Polyvinyl alcohol-based films with various loading contents (1, 3 and 5 wt %) of ZnO nanoparticles and thicknesses (70, 100, and 130 μm) were analyzed by microstructural, mechanical, antibacterial, and physical properties (Ahangar, Abbaspour-Fard, Shahtahmassebi, Khojastehpour, & Maddahi, 2015). ZnO nanoparticles were homogenously distributed in the polymer matrix; as a result, barrier properties of films were enhanced. Regarding tensile properties, Young´s modulus was in the order of a single polymer-based matrix added with TiO_2 (Table 1). Similar results were found when ZnO nanoparticles modified with folic acid were added to polyvinylalcohol-based films (Mallakpour, & Lormahdiabadi, 2020). Most single polymers-based films showed poor tensile properties and it is expected that they have a poorer performance than plastic films. PLA and polycaprolactone are the only polymers that allow preparing films with excellent tensile properties using simple methods. Among single polymer-based films, proteins films were also reinforced with ZnO. Semolina, a high gluten type of wheat flour, was reinforced with ZnO nanorod and nano-kaolin in diverse ratios (1:4, 2:3, 3:2, and 4:1 %, Jafarzadeh et al., 2017). For these films, oxygen permeability decreased as ZnO nanorods contents increased, while heat sealability improved as nano-kaolin content increased. ZnO narorods and nano-kaolin blend fillers improved the functionality of the semolina-based edible films by enhancing physical properties and antibacterial activity, compared to the films without reinforcements. Similar results were found for films based on wheat gluten reinforced with ZnO nanoparticles (Rezaei, Pirsa, & Chavoshizadeh, 2020). Pure gluten film had no antimicrobial effect, but films containing zinc oxide nanoparticles showed a significant inhibitory effect on bacteria and fungi. Soy protein isolate films incorporated with ZnO nanoparticles were prepared for food packaging (Tang et al., 2019). Nanoparticle concentrations varied from 0.01 to 0.2%. Addition of ZnO improved tensile, oxygen barrier, and antimicrobial properties. Thermal stability of film was also enhanced compared to the pure soy protein isolate film. Sodium caseinate based- films containing microcapsules of Melissa officinalis essential oil in concentrations of 0, 5 or 10% w/v were reinforced with 0, 0.01, or 0.03 % w/v of ZnO nanoparticles (Sani, Marand, Alizadeh, Amiri, & Asdagh, 2021). The effects of reinforcement were optimized by a central composite design. Microcapsules and nanoparticles were homogeneously distributed in the protein film. The nanocarriers proved to be compatible with sodium caseinate matrix and improved antioxidant and antibacterial properties. Other one-polymer matrices were also investigated. Bionanocomposites based on chitosan and incorporated with nanoparticles of ZnO were prepared (Priyadarshi, & Negi, 2017; Gomes Lauriano Souza et al., 2020; Krishnan et al., 2020). The ZnO nanoparticles added as fillers in the chitosan films improved water barrier and mechanical properties. Their bioactivity was characterized by performing in vitro and in situ studies (Gomes Lauriano Souza et al., 2020). The food matrix employed to test films was fresh poultry meat. When films were used as primary packaging, the samples presented a decrease of deterioration speed, evaluated as preservation of the initial reddish color and as a reduction on the oxidation process and microbiological growth. The added nanoparticles enhanced the antibacterial and antioxidant properties of the films, improving their performance. Although single polymer-based films were successful to extend food shelf life, the mechanical and tensile properties were still poor and other strategies should be used to improve films physical properties. All these studies were performed in lab scale. Larger-scale studies are needed to prove that these materials can be synthesized on an industrial scale. It would also be important to test whether it is possible to prepare these films using the industrial facilities already installed.

2.2.2. Combination of nanoparticles reinforcement

As a different strategy to improve physical properties, metal nanoparticle reinforcements were combined (Motelica et al., 2020b). This idea was based on the hypothesis that grouping more antimicrobials agents in the same packaging may result in a synergic effect, which could lead to either better antimicrobial activity against a wider spectrum of spoilage agents, or to the use of a lower required quantity of antimicrobials. For the films, the selected matrix was chitosan reinforced with ZnO nanoparticles. Some of these films also contained Ag nanoparticles loaded in citronella essential oil and added in different concentrations. Films prepared with both metal nanoparticles showed a stronger effect and broad-spectrum antimicrobial activity compared to the single loaded film, confirming the initial hypothesis. Further studies on antibacterial activity of a set of chitosan-metal oxide films or chitosan-modified graphene (oxide) films were reported (Wrońska et al., 2021). Two foodborne pathogens were selected: *Campylobacter jejuni* ATCC 33560 and *Listeria monocytogenes* 19115. Films showed excellent biological activity compared to chitosan films with low cytotoxicity, showing the potential of loaded films for food packaging. However, combination of nanoreinforcement did not significantly improve physical properties. Improvement of matrix structure by blending or crosslinking polymers proved to be more promising as described below.

2.2.3. Two-polymer starting systems

Another strategy to overcome the poor physical properties (low tensile strength and high degree of water absorption) of biopolymers is blending them with other polymers. Ethylene vinyl alcohol was blended with chitosan and reinforced with ZnO nanoparticles (Sadeghi, & Shahedi, 2016). The presence of ethylene vinyl alcohol in the composite improved barrier properties, transparency, and mechanical properties. On the other hand, chitosan enhanced the antimicrobial properties of the film. Addition of ZnO nanoparticles reduced the adverse effects of glycerol. The developed nanocomposite provided better properties and fewer adverse effects of plasticizer on matrix film than the single film-based polymer. Similar results were found by blending gelatin with β-glucan (Sherafatkhah Azari, Alizadeh, Roufegarinejad, Asefi, & Hamishehkar, 2021). The ZnO nanoparticles (up to 5%) and β-glucan added to gelatin-based matrix led to a film with potential for food packaging due to its unique features. Blends with Mahua oil-based polyurethane and chitosan, incorporated with different proportions of ZnO nanoparticles have also been used to prepare biodegradable films (Saral Sarojini, Indumathi, &

Rajarajeswari, 2019). The performance of the films to be used as food packaging materials was analyzed, quantifying their ability to increase the shelf life of film-wrapped carrot pieces. Three different nanocomposite films with 0.75:0.25 ratio polyurethane/chitosan and 1, 3 or 5% ZnO were prepared by solvent casting method. Data reported showed that the thermal stability and tensile strength of the composite film were greater than those of individual-polymer based film and that the blended films physical properties were improved through nano ZnO reinforcement of the polymeric matrix. Results of cytotoxic study proved the films were safe for contact food packaging. Besides, they proved to be efficient at protecting wrapped carrot pieces. For the blended film containing 3% ZnO, the shelf-life period was extended up to 9 days. Following a similar approach, composite films with a blend of chitosan and cellulose acetate phthalate were formulated (Indumathi, Saral Sarojini, & Rajarajeswari, 2019). The films were reinforced with ZnO nanoparticles added in concentrations from 2 to 7.5%. The data reported showed that the thermal stability and barrier properties of the films increased with increasing amount of nano ZnO. The antimicrobial effects of films were tested on black grapes. The film with 5% of ZnO extended the shelf life of product to up to 9 days. Chitosan was also blended with gelatin (Kumar et al., 2020). The biocomposite films were reinforced with ZnO nanoparticles of 20-40 nm prepared by a green method. The particles size was in the range of all reported values for nanoreinforcement metal particles, which usually are from commercial origin. The films were developed to replace plastics materials with a biodegradable alternative for postharvest packaging of fresh fruits and vegetables. The biocomposites containing 2% and 4% ZnO nanoparticles showed a compact, smooth, and heterogeneous surface compared to the control (chitosan-gelatin without reinforcement) films, good antibacterial activity, and were a good alternative to replace synthetic plastic packaging. Other nanocomposite films were prepared with a mixed matrix of gelatin and polyvinyl alcohol reinforced with functional nanoparticles of TiO_2 and ZnO embedded in 4A-Zeolite (Azizi-Lalabadi, Alizadeh-Sani, Divband, Ehsani, & McClements, 2020). Gelatin is used to prepare biodegradable packaging materials because of its film-forming properties, non-toxicity, and biodegradability. However, it has low barrier and mechanical and tensile properties. Thus, the functional properties of gelatin films were improved by incorporating polyvinyl alcohol and functional particles within them. A comparison of physical properties between gelatin/polyvinyl alcohol film and the film reinforced with 1% and 1.5% of ZnO nanoparticles is shown in Table 2. The reinforced films had E values three times higher than the control without additives. The report proved that the structural, optical, mechanical, barrier, and antimicrobial properties of the prepared films could be modulated by controlling the type and concentration of nanoparticles employed. Addition of ZnO improved water vapor barrier and tensile properties, and elasticity as indicated by the increase in Young's modulus value. Addition of TiO_2 had a lower effect on physical properties than the addition of ZnO, and reinforcement with a mix of both oxides together did not improve the performance of film compared to that of the film added with ZnO only. The best tensile and water vapor barrier properties were found for the film containing a concentration of ZnO of 1.5% (Table 2). The gelatin/polyvinyl alcohol matrix had tensile properties like polycaprolactone matrix, showing that polymer blend is a powerful strategy to improve physical properties and enhance performance of biodegradable films. A starch/kefiran blend was also reported. ZnO nanoparticles (20-30 nm) in concentrations of 1%, 3%, and 5% were added to starch/kefiran nanocomposite (Babaei-Ghazvini, Shahabi-Ghahfarrokhi, & Goudarzi, 2018). Kefiran, a microbial and water-soluble exo-polysaccharide, has been investigated for packaging applications in the last decade. Addition of nano ZnO increased Young's modulus of the specimens studied and improved other physical properties (Table 2). However, physical properties values measured for starch/kefiran reinforced films were significantly lower than the ones of films prepared with gelatin/polyvinyl alcohol, showing the relevance of interactions among building blocks of matrix structure (Table 2). E values indicated that attractive forces were lower for starch/kefiran than for gelatin/polyvinyl alcohol and less positive interactions among components took place. Polyvinyl alcohol/pluronic blends loaded with ZnO nanoparticles also proved promising for preparing nanocomposite films for packaging in contact with food (Amin, Partila, Abd El-Rehim, & Deghiedy, 2020). The composites exhibited broad-spectrum antimicrobial activity against bacterial pathogens, and fungi, and the activity increases with increasing concentrations of ZnO nanoparticles (5 to 25%). ZnO nanoparticles also improved microbiological properties in other composite blended films. A biodegradable film composed of thermoplastic starch (5%) and polyethylene (93%), containing ZnO nanoparticles (2%), showed high inhibitory activity against both *Staphylococcus aureus* and *E. coli* bacterial strains, indicating improvement in formulation achieved by addition of ZnO nanoparticles (Saemi, Taghavi, Jafarizadeh-Malmiri, & Anarjan, 2021). Interactions among matrix components and reinforcement are usually studied by FTIR spectroscopy. The shift of the signals in the infrared spectrum proves the interactions between the components of the matrix and the new signals that may appear could indicate the formation of some chemical bond. Only a few reports described matrix structure by small angle X-ray scattering (SAXS). The interpretation of the SAXS curves with various mathematical models allows the quantification of structural elements of the matrix.

From these models, sizes of structural elements and distances among them may be calculated. This more powerful approach should be applied to more systems since a deeper knowledge of structure characteristics will help understand and predict mechanical and tensile properties of matrix and design strategies to improve films physical properties.

In addition to blending, polymers may also be cross-linked to make a denser and more connected matrix. Tragacanth, an anionic natural polysaccharide, and polyvinyl alcohol were successfully cross-linked with citric acid to obtain films with good antioxidant and antibacterial properties (Janani, Zare, Salimi, & Makvandi, 2020). The resulting nanocomposite films had higher soil degradation rates than the tragacanth-based films, showing that the cross-linking of both polymers had several advantages. The best antioxidant activity was found in the film containing 5% of ZnO nanoparticles and 3% ascorbic acid. The cross-linked films proved to be promising materials to avoid environmental pollution, and to prevent microbial growth and lipid oxidation in fatty foods. Phenyllactic acid grafted chitosan was prepared by a free radical induced reaction (Li, Sun, Zhu, Wang, & Xu, 2018). The protecting effect of the biodegradable film was tested on Taiwan green jujube. The weight loss and rotting rates of the treated fruits were reduced after 21 days of storage, indicating that the film was effective in delaying postharvest loss of fruits. In addition, a higher retention of total phenol, ascorbic acid, malondialdehyde, and total soluble solids in green jujube was also reported. Phenyllactic acid grafted chitosan reinforced film showed great potential to improve the quality and safety of fruits during storage. However, as E modulus was not reported it is difficult to evaluate the effect of preparation method on tensile properties and the possibility of using the film in industrial scale. Although some cross-linking compounds such as citric acid proved to be efficient to bond polymers, cross-linking potential should be evaluated in deeper extent, proving that the covalent bonds were actually formed in matrices. Measurements of molecular weight of polymers forming the matrix could be a way to determine the cross-linking reaction extent. Very few reports succeeded proving cross-linking and as it is such a promising strategy more research on this subject should be done.

2.2.4. Multilayer films

Active packaging refers to a system that interacts with the product to prolong its shelf life and enhance its safety (Adilah, Jamilah, & Hanani, 2018). More complex films for advanced packaging applications were developed by preparing bi or multilayer films that release antibacterial and antioxidant compounds to food. The L-isomer of polylactic acid was blended with ZnO nanoparticles (Andrade-Del Olmo, Pérez-Álvarez, Hernáez, Ruiz-Rubio, & Vilas-Vilela, 2019) . The nanoparticles were placed in the bulk region of the matrix. Additionally, the polymer was superficially modified by the deposition of chitosan and β-cyclodextrins containing carvacrol. These two materials were placed layer-by-layer on PLA/ZnO films surface. These prepared multilayer films had improved biological properties due to the bactericide effect of ZnO nanoparticles, the contact killing capacity of chitosan, and the antibacterial and antioxidant properties of carvacrol released from β-cyclodextrins (more than 95 % of totally released carvacrol was released within 14 days). Multilayer films composed of chitosan and sodium alginate, with addition of carboxymethyl chitosan-ZnO nanoparticles in each layer were prepared by casting layer by layer. Films were dehydrated at 50°C until the surface was firm but still adhesive (Wang et al., 2019). The antibacterial effects of the films were tested in red grapes. The red grapes were covered by films and stored at 37 °C for 7 days. The films were removed to photograph, and positive results were obtained. The red grapes maintained their shape, and their surface remained smooth. Although films were successful to extend red grapes shelf life, its elasticity was not quantified. Without E values, it is difficult to compare tensile properties with other reinforced matrices and to evaluate the advantages of using films with such a complex formulation. Active films based on a bilayer system in which each layer was prepared with a different method were successfully formulated (Estevez-Areco, Guz, Candal, & Goyanes, 2020). The outer layer was obtained by flat die extrusion followed by calendering and consists of a composite film of thermoplastic starch and ZnO nanorods. The inner layer was made of poly(vinyl alcohol) containing rosemary polyphenols and was deposited on one side by electrospinning and hot pressing. This bilayer material had differentiated activities in each phase: rosemary extract was released to food simulants and ZnO nanorods prevented E. Coli growth on external surface. As expected, incorporation of ZnO nanorods as reinforcement improved the mechanical properties of films. Addition of the inner increased Young's modulus by 51% and decreased the water vapor permeability by 42% compared to values for the outer layer film without ZnO nanorods. Parameters values for the bi-layer film are shown in Table 2. The reported values corresponded to a material with good physical properties that performed better than starch/kefiran/ZnO films, showing that polyvinyl alcohol had more positive interaction with starch than kefiran. In addition to reinforcement concentration and geometry, compatibility of polymers due to positive interactions is also a key factor to consider for formulating films.

2.2.5. Two-phase starting systems

Emulsions are another alternative for preparing active films. The lipid phase may dissolve antibacterial or antioxidant agents as well as valuable molecules like vitamins or essential lipids. Chitosan biopolymer was used as matrix to prepare films reinforced with ZnO nanoparticles in concentrations of 0, 1 or 3%, and with Melissa essential oil as lipid phase in 0, 0.25 or 0.5 % (Sani, Pirsa, & Tağı, 2019). The film with the best physical properties and transparency had a concentration of ZnO nanoparticles of 1.0% and Melissa essential oil of 0.35% (Table 2). This film had also good antibacterial properties despite the low barrier vapor reported. As shown in Table 2, various matrices and preparation strategies were successful in obtaining biodegradable films that show potential to replace plastic materials, being the most successful PLA and polycaprolactone and the blends of gelatin or starch with polyvinyl alcohol. The performance of these matrices was even improved by ZnO nanoreinforcement, which enhanced physical properties in all cases.

2.3. CaO nanoparticles

CaO nanoparticles were investigated in less extend than other nanoparticles. They were added to different polymers to improve their performance in different applications, especially in medical studies. Surface functionalization of biodegradable poly-ε-caprolactone nanofibers was performed to obtain a material useful as scaffolding for bone and soft-tissue engineering (Permyakova et al., 2019). In food applications, coatings of poly(vinyl acetate–co–vinyl alcohol) latex added with CaO nanoparticles at concentrations of 50, 100, and 150 $mg \cdot L^{-1}$ were applied to reduce losses in cucumbers postharvest. The fruits were stored in a chamber at 10°C and visual and physical parameters were measured over time. Addition of nanoparticles to the coating at the selected concentrations had positive effects on visual quality and appearance, and antioxidant and pigment content of the fruits. According to SEM studies, the CaO nanoparticles were located at the bottom zone of the film. For this reason, reinforcement was in contact with the cucumber fruit. A possible explanation is that Ca interactions due to its positive charge generated bridges that improved material stability and reduced water interaction, generating a more hydrophobic material. The reinforcement applied extended the shelf-life of cucumbers up to 24 days postharvest (Cid-Lopez et al., 2021).

Regarding films formulation, sodium alginate-based films were also reinforced with CaO. Sodium alginate is a natural polymer extracted from brown seaweed. It is a promising material for food packaging that contains units of mannuronic and guloronic acids (Kim, Baek, & Song, 2018). Edible films based on sodium alginate had ZnO or ZnO/CaO nanoparticles added in four different concentrations (0.1, 0.5, 1 and 5 g/L). According to the report, the mechanical, barrier, and optical properties were improved by cross-linking between alginate molecules and nanoparticles. This hypothesis was not proved in the study and surprisingly, contrary to expected in a cross-linking reaction, the best properties were achieved with concentrations of 0.1 and 0.5 g/L, the lowest concentrations selected. In both cases, values of tensile strength and elongation at break were very close to the values of the control film without nanoparticles, showing a very low effect on physical properties. Water vapor permeability worsened with the addition of nanoparticles. The presence of CaO in ZnO/CaO nanoparticles did not show additional beneficial effects on physical properties compared to the effect of ZnO nanoparticles. The main contribution of the article was the release analysis of metal oxides from the film. The studies performed using food simulants showed that when the concentration of ZnO and ZnO/CaO nanoparticles were 0.5 g/L they remain trapped in the alginate gel, limiting their release into the intestinal media. Values of migration from both ZnO and ZnO/CaO nanocomposite films with 0.5 g/L nanoparticles concentration were below the limit of 25 mg per Kg of food simulant stablished by the FDA for Zn migration. These findings indicated that films formulated with 0.5 g/L nanoparticles were safe for use in food applications (Aristizabal-Gil et al., 2019).

2.4. MgO nanoparticles

Magnesium oxide nanoparticles have been used as active antimicrobials and catalyst materials, as well as packaging materials. In the food industry, they attracted much attention due to their strong antibacterial activity, thermal stability, and low cost. MgO nanoparticles show food-grade security and have several desirable properties, including absorption ability, surface and nucleating effects, and the ability to provide polymers with high mechanical strength (Swaroop, & Shukla, 2018). Different matrices based on a single polymer have been used to prepare biodegradable films reinforced with MgO nanoparticles. Polyvinyl alcohol films were prepared adding MgO nanoparticles in a concentration of 2% to improve their performance in packaging. There was a strong interfacial attraction through hydrogen bonding between the oxygen atom of MgO nanoparticles and the hydroxyl group of the polymer matrix, which modified the mechanical properties that were better for the reinforced film than for the polyvinyl alcohol film. Distribution of nanoparticles was homogeneous, which also contributed to the best mechanical behavior of the reinforced film. The reported results showed great potential for MgO to improve physical properties of polymers (Venugopal et al., 2015). Regardless of the nanoreinforcement employed, the E-modulus for the nanoreinforced polyvinyl alcohol film was of the order of magnitude of the E-modulus value of another single polymer-based matrix, such as proteins (Tables 1 to 3). When polyvinyl alcohol was mixed with other polymers such as starch or gelatin, the tensile properties were better than those of the polymer-based film alone, demonstrating the relevance of the interactions between the matrix components. It also highlights the success of the strategy of blending polymers to improve physical properties. PLA-based films were reinforced with MgO nanoparticles in concentrations up to 4%. Compared to the tensile strength and oxygen barrier properties of the film without nanoparticles, the 2% reinforced film showed the best performance (up to 29% and 25%, respectively) and good antibacterial properties. In addition, the prepared PLA films were transparent and able to block UV radiation, showing excellent properties as food packaging material compared to other polymers (Swaroop, & Shukla, 2019, Table 3). These films were successfully produced on a large scale, using a sustainable method that included an industrial level melt-processing setup. This equipment allowed the production of blown PLA/MgO nanocomposites for food packaging (Swaroop, & Shukla, 2019, Table 3). Chitosan was also used to prepare nanocomposite films with MgO nanoparticles. Optimal mechanical behavior was found with a MgO concentration of 5%, which led to a Young's modulus 38% higher than in the polymer without nanoparticle addition. The nanocomposite films showed remarkable thermal stability, and better moisture and flame-retardant barrier properties, which make them more suitable for packaging (De Silva, Mantilaka, Ratnayake, Amaratunga, Nalin de Silva, 2017). Similar results were reported for MgO/carboxymethyl chitosan nanocomposite films (Wang, Cen, Chen, & Fu, 2020, Table 3). Concentrations as low as 1% were enough to improve physical properties and show antimicrobial activity against *Listeria monocytogenes* and *Shewanella baltica*.

Among matrices studied, different types of polybutylene films were described. MgO/Ag (silver) nanoparticles were incorporated into poly(butylene succinate-co-terephthalate) matrix to prepare nanocomposite films via solvent casting (Zhang et al., 2021, Table 3). The film reinforced with nanoparticles in a 3% concentration presented the optimal performances in physical and antibacterial properties. To test the films, cherry tomatoes were packed, and weight loss rate, firmness, and microorganism counts were evaluated with time. The film with 3% nanoparticles showed the best preservation abilities, having the packed cherry tomatoes with the lowest weight loss rate and highest firmness of all samples. After 7 days of preservation, the number of microorganisms on the uncovered sample was nearly five times higher than that on the sample covered with the film reinforced with 3% nanoparticles (Zhang et al., 2021). Poly(butylene adipate-co-terephthalate) was also used to prepare reinforced films with MgO nanoparticles coated with cetrimonium bromide (Wang, Cui, Fan, Li, & Liu, 2021, Table 3). In agreement with poly(butylene succinate-co-terephthalate) films behavior, the best nanoparticles concentration was 3%. At contents higher than 5% there was nanoparticle aggregation. The presence of coated nanoparticles enhanced antibacterial efficiency against Gram-positive bacterial *S. aureus*. The optimum values reported for MgO nanoreinforcement for most films studied were higher than for reinforcement with TiO_2 (Table 1). These studies did not include migration tests to different simulants. It would be a contribution to carried out these tests to ensure the safety of using MgO as nanoreinforcement in packaging. A few approaches using more complex matrix with two polymers have also been investigated. The modification of starch with proteins is one strategy used to improve starch films performance. Films based on modified starch and albumin were reinforced with MgO nanoparticles in concentrations varying from 0 to 5%. Addition of MgO increased films thickness and decreased water vapor permeability. The films with MgO showed good antioxidant and antibacterial properties (Hosseini, Pirsa, & Farzi, 2021). Considering the improvement in the physical properties that occur when a mixture of polymers is used to formulate the matrix, it would be a contribution if there were more studies that describe the structure of complex matrices and the interactions between the components of the matrix. In this way, mixtures could be found that could be processed in the plants installed to manufacture plastics.

Films based on emulsions as starting systems were also described. Chitosan/MgO nanocomposite films containing clove essential oil also showed improved physical properties compared to chitosan-based films. The presence of clove essential oil also provided good antibacterial activity against *Staphylococcus aureus* (Sanuja, Agalya, & Umapathy, 2014). Physical and antibacterial properties of protein films were also modified by adding a lipid phase. The structure of wheat gluten film was modified by including Heracleum persicum essence, magnesium oxide nanoparticles and polypyrrole in the formulation. According to the reported results, addition of the essence and polypyrrole modified gluten film structure, improving the barrier to gases and antioxidant activity. Despite the starting systems had two-phases, water and lipid phases, the physical properties were improved compared to the one phase system. The presence of the lipid phase allowed incorporating antibacterial compounds that improved film performance. These films showed potential to be used for active and intelligent packaging of foods (Fazeli, Alizadeh, & Pirsa, 2022).

3. Nanofillers from natural origin

In addition to metal oxide nanoparticles, natural nanofiller may also be added to improve physical properties of films. Chitosan nanofiber is one of the most studied nanofillers for the reinforcement of biopolymer films. It has excellent physical properties including surface to volume ratio, biodegradability, high mechanical strength, and antimicrobial activity. Production is also easy and cost-effective (Kalantari, Afifi, Jahangirian, & Webster, 2019). It may be obtained from sources such as coconut crab (*Birgus latro*) shell waste by ionic gelation method to be used in different food packaging applications (Rasulu, Praseptiangga, Joni, & Ramelan, 2019). Among the uses described for chitosan nanofiber, novel active packaging films based on whey protein isolate (WPI) incorporated with chitosan nanofiber and nano-formulated cinnamon oil were developed (Mohammadi, Mirabzadeh, Shahvalizadeh, & Hamishehkar, 2020, Table 4). Fourrier Tansform Infrared (FT-IR) and scanning electron microscopy (SEM) experiments were used to prove that distribution of chitosan nanofiber throughout the film was homogenous. Because of matrix homogeneity, the addition of chitosan nanofiber improved the barrier against water vapor. This bio-nanocomposite film proved to be an excellent barrier against gases and damage caused by light and UV radiation. The film showed a decrease around 12% in water vapor permeability compared to the film prepared from a solution of WPI alone (control, Table 4). Although Young's modulus decreased 25% compared to the control, its value was still good (Table 4). Added nanofiller and nanoparticles may negatively influence physical properties; however, these complex films have the potential to incorporate antioxidant and antimicrobial agents (Alizadeh Sani, Ehsani, & Hashemi, 2017), and nutraceutical bioactive compounds in their matrix that may provide beneficial effects for packaged products. The better functionality of the film given by the possibility of containing antioxidants or releasing active compounds compensates for the decrease in the values of the tensile parameters. Another advantage for using nanofibers is that it is unlikely that they migrate to food. Other matrices were also reinforced with chitosan. Although gelatin is widely used in food packaging, the fragility and low flexibility of its films and its poor physical properties have limited its applications. Chitosan nanoparticles of spherical shape were added to reinforce a fish gelatin matrix in concentrations of 0 to 8%. They caused a remarkable increase in the tensile strength and elastic modulus, and a significant decrease of water vapor permeability (50% decline at 6% filler, Table 4). Higher concentrations of fillers led to nanoparticle aggregation (Hosseini, Rezaei, Zandi, & Farahmandghavi, 2015; 2016). Although the film has excellent tensile properties, the concentration of nanoparticles is very high, and it should be proved that they are safe in these amounts. Similar results were found when cupuassu puree/pectin matrix was reinforced with chitosan nanoparticles. Nanoparticles improved barrier and mechanical properties, leading to better food packaging materials (Melo, Nunes, Otoni, Aouada, & de Moura, 2019). Chitosan was also added to gelatin-based films in nanofibers geometry. The nanocomposite film reinforced with ZnO had better mechanical and barrier properties than the gelatin film alone (Amjadi et al., 2019a, Table 4). Nanofibers increase E modulus even in higher extent than nanoparticles, showing the relevance of reinforcement geometry. This effect is most likely due to the fact that the structure of the nanofiber-reinforced films is denser and less permeable than that of the nanoparticle-reinforced films. The use of reinforcement with different geometries opens new possibilities for food packaging. The wrapping with this film significantly decreased the growth of bacteria in chicken fillet and cheese samples (Amjadi et al., 2019b). The same effect in gelatin-based films as for reinforcement with chitosan nanofibers or nanoparticles was obtained by adding other filler such as amino-functionalized montmorillonite or cellulose. Biodegradable gelatin-based edible films physical properties were improved using nanoparticles of amino functionalized montmorillonite in a concentration of 0.12% as filler, and different amounts of dialdehyde xanthan gum as cross-linking agent (Ge et al., 2017). The selected nanofiller has a hydrophilic nature and is environmentally friendly. Mechanical and barrier properties improved with increasing cross-linking degree expressed in percentage, showing the relevance of matrix bonds in structural and mechanical properties (Table 4). This is an example in which cross-linking reaction was successful to improve tensile properties because of the covalent unions among matrix components that dialdehyde xanthan gum caused. E modulus was very high, and it is very likely that this film could be prepared in facilities where plastics are manufactured.

Cellulose nanofibers have a diameter in the nanoscale (around 3 nm) and a length in the micron scale, showing both crystalline and amorphous sections. They can be produced by different methods depending on the intended application. A matrix based on gelatin was reinforced with cellulose nanofibers as nanofiller (Ahmadi, Ahmadi, Alizadeh Sani, Ehsani, & Ghanbarzadeh, 2021). Nanoparticles of Se and ZnO were added to films as antibacterial and antioxidant agents. As evidenced by FTIR and

SEM techniques, dispersion of Se and ZnO nanopaticles was good, as were interactions with the biopolymer matrix. As shown in Table 4, the elasticity and water barrier properties of films with added ZnO were good for active packaging of perishable foods. These types of films will decrease food waste and improve food quality, making films production more sustainable. In several systems, nanofibers proved to perform better as a reinforcement than nanoparticles. Most likely the fact that one dimension is in the nanoscale but the other is in the microscale allowed stronger interactions among matrix molecules and reinforcement, leading to excellent tensile properties. Performance of other polymers was also enhanced with nanocellulose. Films based on tapioca starch/chitosan added with disintegrated bacterial cellulose nanofibers obtained from a film of nata de coco were prepared.A content of dried nanofibers of 0.136 g/100 g film led to the system with the best mechanical properties (Abral et al., 2021). In addition to nanoreiforcement effects, the films were formulated with a blend of polymers with positive interactions that also contributed to their physical properties. Pectin-based biodegradable films were improved with crystalline nanocellulose in concentrations of 2, 5, and 7% (Chaichi, Hashemi, Badii, & Mohammadi, 2017). The best results in terms of mechanical and water barrier properties were obtained with the addition of 5% nanocrystals. Cellulose nanocrystals were also used to reinforce chitosan nanoparticles/beeswax emulsion-based films (Wardhono et al., 2019). The reported results showed that the interaction between cellulose nanocrystals and chitosan molecules improved films physical and thermal properties. Addition of beeswax (a dispersed lipid phase) enhanced water barrier properties but deteriorated mechanical properties. However, a beeswax concentration of 25% led to films suitable for food packaging. Other natural fillers coming from vegetal waste also attracted attention since they make production of films more sustainable, forming part of a circular economy. Pectin is a non-toxic, biodegradable, edible biopolymer, with good gelation capacity. For these reasons it is considered a good matrix for edible film production. It is also a renewable resource that may be obtained from plant tissues. Pectin edible films with powder fillers obtained from red cabbage and beetroot were prepared for edible, active coloring, food packaging applications. The films should be used for foods with pHs between 4 and 8 and for products with shelf life of 30 days (Otálora González, De'Nobili, Rojas, Basanta, & Gerschenson, 2021). Nanocomposites based on carrageenan have been investigated due to their good biodegradability. They were added with natural montmorillonite at different concentrations (Sanchis et al., 2017). The modified films developed could be used for biodegradable and edible packaging films, or biomedical applications.

There are many examples of natural fillers used in starch- based films. Films based on starch from different origin (tuber, cereal, and legume) were reinforced with cellulose nanocrystals in different amounts (2 and 5% on dry basis; Montero, Rico, Rodríguez-Llamazares, Barral, & Bouza, 2017). Physical properties were very much affected by the amylose/amylopectin ratio in starch, which affected matrix connections. The reinforcing effect of filler as evidenced by the increase of storage modulus was more prevalent in starch with a higher content of amylopectin chains. The film based on potato starch reinforced with 5 % of cellulose nanocrystals was the best alternative for short-shelf-life applications. Complex films were prepared by blending the polymer with montmorillonite, using different concentrations of montmorillonite and ZnO nanoparticles (Vaezi, Asadpour, & Sharifi, 2019). Among all the films obtained, the nanocomposite with 3 and 0.7 % amounts of montmorillonite and ZnO, respectively, had the best performance. It had well-moderated mechanical behavior in plastic and elastic regions, and good barrier and optical properties compared to starch film. Biodegradable films based on starch were also reinforced with wheat and corn hulls at a filler concentration of 5% (Ali et al., 2017). The granulated particles had particle sizes from 0.065 to 0.200 mm. The compatibility of both fillers with the matrix was good since all of the components were hydrophilic in nature and exhibited polar behavior. For this reason, the materials showed good tensile properties as evidenced by E (Young's modulus, Table 4). Besides films were fully biodegradable and safe for food packaging. From the mechanical point of view, wheat and corn hulls were the most successful fillers reported for starch, showing the relevance of interactions matrix/reinforcement and the hydrophilic or lipophilic nature of components selected for films formulations. Corn starch-based films were filled with several nano-clays and blueberry extract (Gutierrez & Alvarez, 2018). The aim was to prepare edible and intelligent (pH-sensitive) bionanocomposite films with improved properties. However, the films showed no sensitivity to pH and mechanical properties were poorer than ones achieved in other systems. Better results were obtained with films based on starch from guinea arrowroot tubers and grape waste flour and extract as natural fillers (Gutiérrez, Herniou-Julien, Álvarez, & Alvarez, 2018, Table 4). The edible film containing grape waste flour as a natural filler proved to be pH-sensitive and showed a decrease in the hydrophilic nature. Rice and hydroxypropyl cassava starch mixture, agar, and maltodextrin were blended to prepare biodegradable films (Wongphan, & Harnkarnsujarit, 2020). Physical properties of films were governed by polymer networks and interactions. Agar formed a continuous network inside the starch matrix while maltodextrin acted as a filler. In percentages higher than 40% it reduced mechanical strength because it interrupted matrix connections. The physical properties for the 40% maltodextrin film were good compared to other starch-based films (Table 4). The report shows the potential of blending polymers as a strategy to improve films performance. Tapioca starch-based films containing rice bran microparticles, with or without natamycin and nisin (natural antimicrobials), were prepared (Berti, Jagus, & Flores, 2021). Addition of rice bran improved mechanical properties but did not modify water barrier properties The natural preservatives diffused through the film as evidenced by zones of inhibition formed in the halo test against Saccharomyces cerevisiae and Listeria innocua (Berti, Jagus, & Flores, 2021). Cassava starch films reinforced with 1.5% beet powder as a natural filler were prepared, and their physical, chemical, and mechanical properties were studied (Otálora González, Flores, Basanta, & Gerschenson, 2020, Table 4). The films were also subjected to the application of a corona treatment. The surface of polymeric material was treated with a unit which generates an electric field that produced a spark. The addition of the filler led to a decrease in solubility and hydrophilicity, and an improvement in water barrier properties. By adding a filler or applying a treatment, it was possible to modify the properties of the films to obtain better performance in food packaging. Mixing of nanoparticles in polymer produced via extrusion possibly gave diverse results according to the mixing characteristics and interaction between nanofillers and matrices, resulting in either reinforcements or network destruction of polymeric matrices (Phothisarattana, & Harnkarnsujarit, 2022b). This report shows the relevance of the selected preparation method that strongly affects interactions among components and matrix building blocks connections. The obtained structure will strongly influenced the physical properties of films.

From the reports in the literature, it can be seen that there are various strategies to improve the physical properties of biodegradable films. Not all are successful on all systems and there is no general rule that applies to everything. However, some approaches that improved the physical properties in some matrices can be highlighted. In the first place, the treatment of the polymeric surface or of the bulk molecules is very relevant since these procedures allow the modification of functional groups of molecules, exposing them to the environment and favoring their interaction with other components of the matrix. Secondly, the formulation of matrix plays a key role in films performance. Although there are matrices based on a single polymer that have very good physical properties, some polymer mixtures have given better results. The positive interactions between them have substantially improved the tensile properties. However, it is difficult to predict which blend will be successful. To know the physical properties, the behavior of each pair of polymers must be studied. There are very few matrices whose structures are described in detail. This quantitative description of the structural elements would be important to predict the behavior of a polymer mixture. Third, polymer crosslinking allows the formation of covalent bonds that lead to better tensile and mechanical properties. Although promising, cross-linking reactions did not prove to be effective in enhancing physical properties in all systems studied. The cases in which improvements in physical properties were not achieved show that this reaction should be explored in more depth to demonstrate that it has actually occurred and to what extent it occurred. Techniques such as Gel Permeation Chromatography would be a powerful tool for this purpose. Fourth, the addition of nanoreinforcements improves the physical properties with respect to non-reinforced matrices. In most cases, both metal oxides and natural fillers showed great potential to improve the physical behavior of films. The combination of strategies (preparation method, formulation, cross-linking, and nanoreinforcement) allow enhanced biopolymers performance for application in food packaging.

4. Conclusion

Physical properties of films were related to matrix building blocks connections. Single polymer-based matrixes usually showed poorer properties than blended or cross-linked polymers, especially if one of the polymers was pectin or gelatin. The introduction of a lipid phase to a hydrophilic polymer usually worsened mechanical properties. However, matrix performance could be enhanced by reducing droplets size or using a processing method that led to stronger interactions among matrix molecules. In very few systems has the structure been quantified and described in detail. Knowledge of the size of the matrix building blocks and the distances between different structural elements would be very useful in predicting the tensile and mechanical properties of biodegradable/edible films. Although biopolymers showed poorer physical properties than plastic materials, they might be improved by adding reinforcement in films formulations. Biodegradable or edible films were successfully reinforced with metal oxide nanoparticles or natural nanofillers. Nanoreinforcements were homogeneously distributed and had positive interactions with matrixes. For these reasons, film mechanical and barrier properties were enhanced compared to the properties of matrixes without reinforcement. Other attributes such as antioxidant or antimicrobial activity were also improved by nanoreinforcements. In most systems, nanoparticles were effective in small amounts (lower than 1 %). The reinforced films were effectively extended the shelf-life of several food systems, retarding spoilage and preventing food waste. However, most of the systems were studied in laboratory scale and it should be necessary to perform scale-up studies to prove that films may be prepared in industrial scale.

CRediT authorship contribution statement

Nurys Tatiana Hoyos Merlano: Investigation.

Virginia Borroni: Investigation. Writing - Review & Editing

María José Rodríguez Batiller: Investigation.

Roberto Jorge Candal: Visualization. Writing - Review & Editing

María Lidia Herrera: Writing - Original Draft.

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Figure captions

Fig. 1 Starting systems and improvement strategies to enhance matrix performance

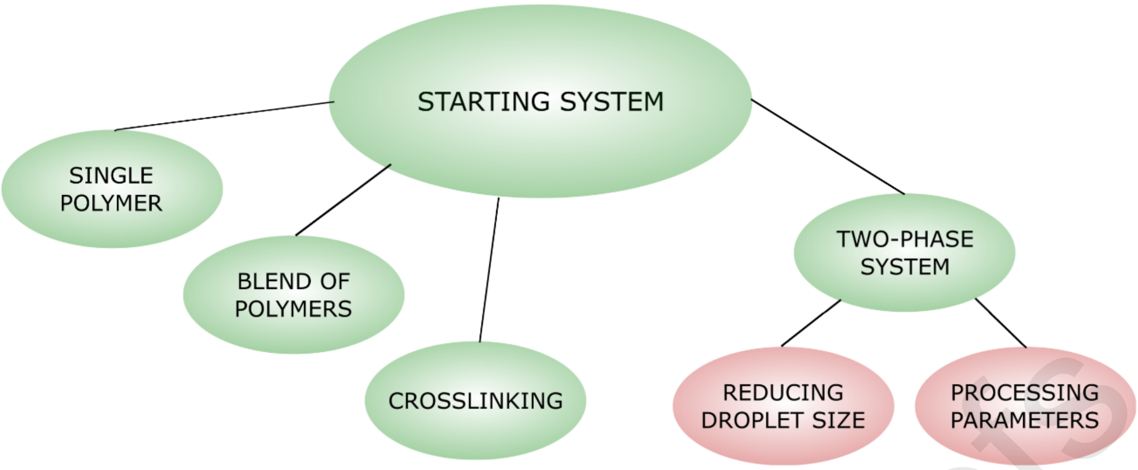

STARTING SYSTEM
SINGLE POLYMER
BLEND OF POLYMERS
CROSSLINKING
TWO-PHASE SYSTEM
REDUCING DROPLET SIZE
PROCESSING PARAMETERS

Table 1. Physical properties of edible biodegradable films reinforced with TiO_2 nanoparticles.

Starting systems	TiO_2 (%)	Young Modulus (E, MPa)	Thickness (µm)	Water vapor permeability x 10^{-10} ($g\ s^{-1}\ m^{-1}\ Pa^{-1}$)	Reference
Solution of whey protein isolate	0.5	12.8 ± 2.3	101 ± 4	3.19 ± 0.11	Li et al., 2011
Solution of whey protein concentrate	0.5	20.6 ± 0.3	380 ± 50	1.03 ± 0.16	Montes de Oca-Ávalos et al., 2020
Solution of sodium caseinate	0.5	1.5 ± 0.3	170 ± 30	3.33 ± 0.25	Montes-de-Oca-Ávalos et al., 2018
Solution of whey protein nanofibrils	1.0	---	144 ± 35	4.40 ± 0.22	Feng et al., 2019
Solution of soy protein isolate	0.5	7.3 ± 1.2	185 ± 4	4.40 ± 0.31	Wang et al., 2014
Pullulan film	0.04	---	---	1.8 ± 0.3	Liu et al., 2019
Chitosan/ anthocyanin-rich black plum peel extract	0.5	---	71 ± 2	5.12 ± 0.37	Zhang et al., 2019
Protein-polysaccharide from a marine alga	5.0	---	32 ± 1	43.81 ± 0.32	He, Huang, Lin, & Wang, 2017
Solution of sweet potato starch/lemon waste pectin	0.5	305.4 ± 2	150 ± 3	2.52 ± 0.03	Dash, Ali, Das, & Mohanta, 2019
Gelatin/κ-carrageenan	1.0	653 ± 8	101 ± 13	0.23 ± 0.02	Alizadeh Sani, Tavassoli, Salim, Azizilalabadi, & McClements, 2022b
Sour lemon peel Powder/xanthan gum	0.05	100 ± 0	250 ± 12	0.82 ± 0.01	Meydanju, Pirsa, & Farzi, 2022
hybrid sodium montmorillonite/ wheat starch	1.0	1.1 ± 0.1	112.2 ± 2.9	4.78 ± 0.85	Yousefi, Savadkoohi, Zahedi, Hatami, & Ako, 2019
Coarse emulsion chitosan–starch/clove oil	1.0	---	68 ± 7	1.30 ± 0.02	Li et al., 2019
Conventional emulsion sodium caseinate/sunflower oil	0.5	6.3 ± 1.6	180 ± 20	4.51 ± 0.18	Montes-de-Oca-Ávalos et al., 2018
Conventional emulsion whey protein concentrate/corn oil	0.5	16.2 ± 0.6	400 ± 40	0.51 ± 0.04	Montes de Oca-Ávalos et al., 2020
Nanoemulsion whey protein concéntrate/corn oil	0.5	19.4 ± 1.3	440 ± 50	0.87 ± 0.03	Montes de Oca-Ávalos et al., 2020

Table 2. Physical properties of edible biodegradable films reinforce with ZnO nanoparticles.

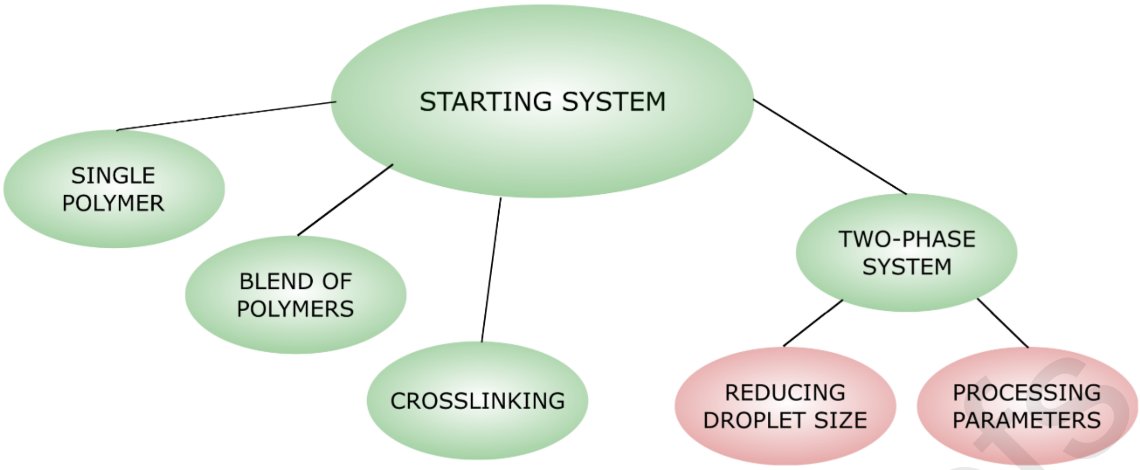
Starting systems	ZnO (%)	Young Modulus (E, MPa)	Thickness (µm)	Water vapor permeability x 10^{-10} (g s^{-1} m^{-1} Pa^{-1})	Reference
Polylactic acid/ZnO particles	1.0	3640 ± 110	---	2.5 ± 0.1	Marra, Silvestre, Duraccio, & Cimmino, 2016
Polylactic acid/ZnO particles	10.0	1158 ± 52	---	1.6 ± 0.3	Cui et al., 2021
Polycaprolactone/layered ZnO nanoparticles	1.0	634 ± 22	---	1.8 ± 0.6	Bujok et al., 2021
Basil seed mucilage/ZnO	0.5	1.27 ± 0.02	120 ± 0.12	0.6 ± 0.0	Foghara, Jafarian, Zomorodi, Khosrowshahi asl, & Nasiraei, 2020
Polyvinyl alcohol/ZnO	1.0	15.3 ± 0.31	130 ± 0.00	0.4 ± 0.1	Ahangar, Abbaspour-Fard, Shahtahmassebi, Khojastehpour, & Maddahi, 2015
Gelatin/polyvinyl alcohol	---	183.3 ± 2.0	160 ± 10	0.8 ± 0.1	Azizi-Lalabadi, Alizadeh-Sani, Divband, Ehsani, & McClements, 2020
Gelatin/polyvinyl alcohol/ZnO	1.0	519.8 ± 1.5	210 ± 0	0.5 ± 0.0	Azizi-Lalabadi, Alizadeh-Sani, Divband, Ehsani, & McClements, 2020
Gelatin/polyvinyl alcohol/ZnO	1.5	587.8 ± 1.7	270 ± 10	0.5 ± 0.1	Azizi-Lalabadi, Alizadeh-Sani, Divband, Ehsani, & McClements, 2020
Starch/kefiran/ZnO	1.0	31.30 ± 1.19	130 ± 0.00	2.2 ± 0.2	Babaei-Ghazvini, Shahabi-Ghahfarrokhi, & Goudarzi, 2018
Phenyllactic Acid Grafted Chitosan/ZnO	0.1	---	35.7 ± 8.7	3.0 ± 0.1	Li, Sun, Zhu, Wang, & Xu, 2018
Chitosan/ sodium alginate/carboxymethyl chitosan-ZnO nanoparticles	0.05	---	40.25 ± 0.55	0.6 ± 0.1	Wang et al., 2019
Starch containing ZnO nanorods/ poly(vinyl alcohol) containing rosemary polyphenols	1.0	70 ± 10	180 ± 13	1.7 ± 0.4	Estevez-Areco, Guz, Candal, & Goyanes, 2020
Chitosan/Melissa officinalis essential oil/ZnO nanoparticles	1.0	---	200 ± 7	8.6 ± 0.1	Sani, Pirsa, & Tağı, 2019

Table 3. Physical properties of edible biodegradable films reinforce with MgO nanoparticles.

Starting systems	MgO (%)	Young Modulus (E, MPa)	Water vapor permeability x 10^{-10} (g s^{-1} m^{-1} Pa^{-1})	Reference
Poly(Vinyl Alcohol)	2.0	18.5 ± 0.3	---	Venugopal et al., 2015
Polylactic	2.0	2,470.0 ± 75	0.00638	Swaroop & Shukla, 2019
Carboxymethyl chitosan	1.0	77.2 ± 1.1	---	Wang, Cen, Chen, & Fu, 2020
Poly(butylene succinate-co-terephthalate)	3.0	---	0.161	Zhang et al., 2021
Poly(butylene adipate-co-terephthalate)	3.0	48.81 ± 3.15	---	Wang, Cui, Fan, Li, & Liu, 2021

Table 4. Physical properties of edible biodegradable films reinforce with natural nanofillers.

Starting systems	Nanofiller	Young Modulus (E, MPa)	Thickness (µm)	Water vapor permeability x 10^{-10} (g s^{-1} m^{-1} Pa^{-1})	Reference
Whey protein isolate/chitosan nanofiber/nano-formulated cinnamon oil	Chitosan	74 ± 7	---	1.6 ± 0.1	Mohammadi, Mirabzadeh, Shahvalizadeh, & Hamishehkar, 2020
Fish gelatin/chitosan nanoparticles	Chitosan	453 ± 65	62 ± 1	0.7 ± 0.0	Hosseini, Rezaei, Zandi, & Farahmandghavi, 2015
Gelatin/chitosan nanofiber/ZnO nanoparticles	Chitosan	520 ± 17	110 ± 3	6.2 ± 0.3	Amjadi et al., 2019a
Gelatin/amino-functionalized montmorillonite	Amino functionalized montmorillonite	992 ± 12	---	5.1 ± 0.3	Ge et al., 2017
Gelatin/cellulose nanofiber/ZnO nanoparticles	Cellulose	810 ± 70	108 ± 4	0.2 ± 0.1	Ahmadi, Ahmadi, Alizadeh Sani, Ehsani, & Ghanbarzadeh, 2021
Starch	Rice bran	69 ± 5	---	1.7 ± 0.3	Berti, Jagus, & Flores, 2021
Starch	Wheat and corn hulls	478 ± 14	151 ± 2	---	Ali et al., 2017
Starch	Nano-clays	26 ± 0	970 ± 70		Gutiérrez, Herniou-Julien, Álvarez, & Alvarez, 2018
Starch/agar	Maltodextrin	220 ± 17	---	1,1 ± 0.2	Wongphan, & Harnkarnsujarit, 2020
Starch	Beetroot	---	460 ± 20	6.8 ± 0.3	Otálora González, Flores, Basanta, & Gerschenson, 2020


STARTING SYSTEM
SINGLE POLYMER
BLEND OF POLYMERS
CROSSLINKING
TWO-PHASE SYSTEM
REDUCING DROPLET SIZE
PROCESSING PARAMETERS

- Biodegradable/edible films from renewable sources show poor physical properties
- Films were reinforced with TiO_2, ZnO, CaO, and MgO or natural nanofillers
- Preparation methods strongly modified matrix building blocks connections
- Performance was improved by formulation, cross-linking, and nanoreinforcement
- Films showed great potential to improve food quality and reduce waste