



## **Recent advances in the fabrication of Chitosan-based films for food packaging applications**

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**Abstract :** Chitosan-based films have a great interest in the food packaging field due to their antimicrobial activity, physicochemical properties, biodegradability, and capacity for food conservation. Some alternatives studied by researchers to the fabrication of these films are the polymer blends and the incorporation of bioactive compounds, chitosan nanoparticles, and metallic nanoparticles. These materials give to packaging excellent mechanical and barrier properties, easy biodegradation, and activity against pathogens. In this review are presented the last advances related to chitosan-based films for food packaging applications of which are highlighted the mechanical properties, barrier properties, and antimicrobial activity.

### **Introduction**

Chitosan, a poly- $\beta$ -(1-4)-D-glucosamine derived from partial deacetylation of chitin, is a polysaccharide found in many insects, exoskeletons of marine invertebrates, fungi and some algae<sup>1-4</sup>. Chitosan is soluble in acidic aqueous solution and its solubility depends on deacetylation grade and molecular weight<sup>5</sup>. Chitosan have a high antimicrobial activity against bacteria and fungi<sup>6</sup>, and it is used in the fabrication of films for food packaging<sup>7</sup> and delivery systems of active compounds<sup>8,9</sup> due to its functional properties, biodegradability, biocompatibility, and nontoxicity. Some mechanisms proposed by researchers in order to explain the antimicrobial activity of chitosan are the alteration of metabolic activity, blocking of the genetic transcription, and the chelating ability<sup>5</sup>. However, this property may be impacted by factors as the degree of deacetylation and molecular weight of chitosan, microorganism type, pH, ionic strength, and solutes, which affect the reactivity of the amine group and the interactions with the cellular layer<sup>7</sup>.

Nowadays, food packagings not only must protect to food products from external influences that affect their integrity and nutritional value but also to be elaborated according to consumer requirements in a cost-effective way and with minimum environmental impact<sup>5</sup>. Polymers play a role very important in this application field because it has demonstrated their antibacterial response against pathogens<sup>10-16</sup> and utilization in the fabrication of plastic films (i.e., chitosan, polyvinyl alcohol (PVA), polyethylene terephthalate (PET), Polypropylene (PP), Polyethyleneglycol (PEG), polyethylene (PE), starch, cellulose, etc) for food packaging<sup>2,17</sup>. Also, polymer blends are a good option in this field since is possible to modify their chemical structure, improve their antimicrobial effect, and physical properties<sup>18</sup>. Some examples of chitosan-based films used as food packaging include polysaccharides, common plastics, crosslinking agents, plasticizer agents, nanoparticles, collagen derivatives, and bioactive compounds derived from plants and animals. Although, bio-based films have antimicrobial and antifungal activities and minimize the contamination by great volumes of plastics

materials<sup>7</sup>, they have limitations regarding their mechanical and barrier properties<sup>19</sup>. According to this, researchers have implemented strategies of the nanotechnology to overcome these issues<sup>20</sup>. Indeed, it has demonstrated that nanoparticles can improve the physicochemical and barrier properties in polymer matrix; interact with specific organics presents in the food, monitor food preservation, and prevent the photodegradation of plastics<sup>19,21,22</sup>. This review will present the last studies related to chitosan-based films used in food packaging applications including polymer blends, bioactive compounds, chitosan nanoparticles, and metallic nanoparticles, emphasizing in the antimicrobial activity, mechanical properties and barrier properties. The scheme presented in **Figure 1** shows aspects related to the fabrication of chitosan-based films for food packaging applications.

## 1. Polymer blends

Polymer blends are a good option in the films fabrication for food packaging because the properties of each component are taken advantage for creating a material with good tensile properties and a suitable barrier against the moisture, gases, and water. Recently, some researchers fabricated bilayer films from polysaccharides with a high barrier to gases, good mechanical resistance, and flexibility<sup>23</sup>. Also, the combination of natural and synthetic polymers as chitosan, starch and PVA have proved to be a good option in this field. A certain study demonstrated that chitosan and starch not only have a good chemical interaction, but also antimicrobial activity against pathogenic and non-pathogenic bacteria<sup>24,25</sup>, and mold<sup>26</sup>. Similarly, it was reported in this study that the use of these polymers with binding agents as glutaraldehyde produces a material with a high thermal stability. Another alternative in these cases is the physical crosslinking which ensures a strong inter-chain interaction<sup>27</sup>. On the other hand, in environmental applications, it has been demonstrated the use of chitosan/PVA hydrogels physically crosslinked for pollutants absorption<sup>28</sup>.

In studies performed by Zemljic and coworkers<sup>29</sup>, it was reported the adhesion of chitosan chains onto polyethylenetherephthalate (PET). According to this study, the presence of amine groups inhibits the activity of pathogens such as *E.coli*, *L. monocytogenes*, fungi *C.albicans*. As well, Lago et al.,<sup>30</sup> used chitosan, polyethylene, and PET to fabricate films with good mechanical properties and antimicrobial activity against coliform enterobacteria and mesophilic aerobic microorganism. Likewise, PEGylated chitosan has shown to be a good option in these applications because exhibits antibacterial activity and generates films more flexible<sup>31</sup>. In the same way, the incorporation of oleic acid to chitosan matrices causes a decrease in their tensile and barrier properties<sup>32</sup>. Finally, in another study was reported the antimicrobial activity of chitosan/PET/PP based films against *E.coli* and *B. subtilis*<sup>33</sup>. The results of this study demonstrated that this process was regulated by the release of chitosan of the plastic films, that in this case, it was increased with the temperature and acidity but decreased with the ion strength of the solution.

Considering the importance of the environmental impact caused by plastic materials, researchers have conducted comparative studies between PP and chitosan<sup>34</sup>. This study was realized in the different life stages of the materials. The results showed that in the case of chitosan, the acids and glycerin used in the extraction process and as plasticizer agent respectively, have an impact on fields as land use, mineral categories, and respiratory organics. While, in the case of PP, the environmental implications are related to carcinogens produced because of the incineration and landfill during the last life stage of this material. In accordance with the above, it is necessary the implementation of novel techniques or biotechnological alternatives that do not affect to environment<sup>35-38</sup>. In Table 1 and 4 are shown some results related to antimicrobial activity, mechanical properties and barrier properties of chitosan-based films that use polymer blends.

## 2. Incorporation of bioactive compounds

In a recent studies has been demonstrated that the polymeric mixture based on chitosan and bioactive compounds provide a barriers against water vapor and enhance the tensile properties of the films<sup>39-43</sup>. Some naturals subproducts with antioxidant, antibacterial, antifungal properties used in food packaging are: Maqui berry<sup>44</sup>, eugenol<sup>40</sup>, phenolic components<sup>41,45,46</sup>, Aloe vera<sup>47</sup>, nisin (NS), natamycin (NT), pomegranate (PE) and grape seed extract (GE)<sup>39</sup>, tea extracts<sup>42</sup>, anthocyanins which is used as indicators<sup>43</sup>, quercetin<sup>48</sup>, Benzoic and sorbic acid<sup>49</sup>, carvacrol<sup>50,51</sup> and mint or thyme essential oils<sup>52,53</sup>.

In Table 2 and 4 are shown some results related to antimicrobial activity, mechanical properties, and barrier properties of chitosan-based films that incorporate bioactive compounds.

### 3. Nanofillers

The incorporation of nanofillers into polymeric films has resulted be an excellent alternative obtaining a highly compact structure with better mechanical, thermal, and barrier properties.

Nanocomposites that include metallic nanoparticles exhibit an excellent antimicrobial response and good mechanical and barrier properties. Studies have established that the synergetic antibacterial action of chitosan and nanoparticles is owing to the effects produced by the action of each one and the change of nanoparticle surface chemistry<sup>54-56</sup>. The functional groups present in the structure of the nanocomposite can affect the chemical interaction between the nanofillers and the polymer chains. Therefore, the chemical affinity between functional groups of the polymer chains and nanofillers is indispensable for the improvement of the properties of the films. In studies performed by Zhang et al.,<sup>57</sup>, it was demonstrated that certain functional groups (i.e., COOH-, NH<sub>2</sub>-, and OH-) have a good chemical affinity with chitosan. On the other hand, mechanical and barrier properties in polymer films are improved with the presence of nanoparticles<sup>58</sup>. It has been reported that the incorporation of nanoclays into plastic films affects the mechanical properties (i.e., tensile, flexural and izod impact strength), and physicochemical characteristics, causing an increase of tensile strength, thermal stability, a decrease of gas permeability (i.e., oxygen, carbon dioxide, and nitrogen)<sup>59</sup>. Hence, many researchers are studying the effects that produce the incorporation nanofillers in polymer films used as food packagings. Some of nanofillers used are: chitosan nanoparticles, metallic nanoparticles, and nanoclays.

Chitosan nanoparticles are more advantageous than bulk chitosan because have a higher surface area and charge density that ease a good interaction with the surface of bacterial cells<sup>60</sup>. Researchers have evaluated the effect of chitosan nanoparticles incorporated into gum films<sup>61</sup>. Results of this study indicate that the antimicrobial activity of films is reduced with the increase of the size of nanoparticles. This is due to that nanoparticles large do not allow the contact with the bacterial membrane and the agglomeration reduces their surface charge. Also, chitosan nanoparticles can occupy the free volume in the system structure, improving aspects as the roughness, hydrophobicity, and vapor permeability. Similar results were obtained by others researchers. Chang et al.,<sup>62</sup> assessed the effect of chitosan nanoparticles incorporated in starch matrices. The results demonstrated that the compatibility between the materials improved the tensile strength, storage modulus, glass transition temperature, water vapor barrier and thermal stability. Hosseini et al.,<sup>63</sup> found that the incorporation of chitosan nanofillers in fish gelatin matrices causes a decrease of the water vapor barrier and produces stronger films with a decreased fracture strain. In another study performed by these researchers, it was demonstrated that the addition of essential oils into these polymer matrices improves the antimicrobial activity, crystallinity, and flexibility of the material<sup>64</sup>. Last, chitosan nanoparticles in cellulose matrices also promotes antimicrobial activity, better tensile and barrier properties, and oil resistance<sup>65</sup>.

Abdollahi et al.,<sup>53</sup> found that a good chemical interaction between nanoclays, chitosan, and rosemary essential oils (REO) not only promotes the antimicrobial response and antioxidant effect but also improves the mechanical and barrier properties. Evenly, similar results were obtained by others researchers. Lavorgna et al.,<sup>66</sup> indicated that the use of silver-Montmorillonite nanoparticles as filler into chitosan matrices improves the chemical and physical structure of the nanocomposites (i.e., thermal stability, mechanical strengths, and water uptake) and promotes antimicrobial activity against *Pseudomonas* spp. Giannakas et al.,<sup>67</sup> reported the use of nanoclays as filler in chitosan/PVA films. According to this study, the presence of nanoclays and PVA in the system enhances the stiffness and the strength of the material and, provides a water and oxygen barrier. Rubilar et al.,<sup>68</sup> reported that the incorporation of a type of modified bentonite (cloisite@30B) as nanofiller in chitosan-acetate films increases tensile properties and the elongation at break, and at the same time, decreases water solubility and water vapor transmission rate (WVTR) at the material.

Silica and metallic nanoparticles also are used as nanofillers in bionanocomposites. It has demonstrated that the addition of nanosilica in chitosan/PVA films reinforces the physical properties of the material and enhanced the barrier against water and gases<sup>69</sup>. These effects also are observed in films composed by nanosilicon carbide dispersed/chitosan. Nanosilicon carbide can decrease the gases permeability, improve the thermal stability and chemical resistance; and increase tensile strength of the films<sup>70</sup>. At the same time, the incorporation of nanosilica and a crosslinking agent inside of this type of nanocomposites can enhance the water and heat resistance, and increase the fluorescence of the material. However, a decrease their crystallinity due to changes in their structure is presented<sup>71</sup>.

In studies performed by Wei et al.,<sup>72</sup> was demonstrated high antibacterial activity against *Escherichia coli* (Gram negative) and *S. aureus* (Gram positive) in chitosan films with silver nanoparticles incorporated. In other applications, also have been tested the antibacterial activity of this system against *E. coli* by the electrochemical deposition of silver nitrate and chitosan onto metallic substrates<sup>73</sup>. Similarly, studies have evidenced the use of chitosan/PVA blends as substrates for the formation of silver nanoparticles<sup>74</sup>. Chitosan/silver nanocomposites with broad spectrum of antimicrobial activity can be obtained by green synthesis<sup>75,76</sup>. Youseff et al.,<sup>7</sup> fabricated nanocomposites from chitosan with silver and gold nanoparticles with good antibacterial activity. In this case, metallic nanoparticles were synthesized by means of a biosynthesis process and after were incorporated into the polymer matrix.

Azizi et al.,<sup>78,79</sup> indicated that fillers composed of cellulose/ZnO and cellulose/ZnO-Ag improve mechanical and physical properties of chitosan-PVA films. In this study, an increase in tensile strength and modulus; and thermal stability were evidenced. Also, this system exhibited adverse effects against *salmonella choleraesuis* and *staphylococcus aureus* demonstrating their antibacterial activity against pathogens. Similarly, in another study was demonstrated the feasibility of films that include chitosan, carboxymethylcellulose, and ZnO nanoparticles on the shelf life of white soft cheese<sup>80</sup>. In a study reported by Demitry et al.,<sup>81</sup> was evidenced the inhibitory activity against *S. stolonifer* of a system composed to chitosan and cinnamaldehyde. Also, it was shown an improvement mechanical properties by incorporating graphite nano-stacks in the system, since the presence of the nanoparticles allowed a better interaction between the polymeric chains. Zanuja et al.,<sup>82</sup> demonstrated that nanocomposites formed by zinc oxide nanoparticles, neem essential oil, and chitosan polymer have suitable characteristics to be used as food packagings. This is due to the interactions between the bio-active group of phenol, the functional groups of chitosan and the nanoparticles prevent coagulation, promote flexibility, decrease water absorption, increase the thickness, and inhibit the photo-degradation process of the material. Finally, a recent study reported the biophysical stimulation of chitosan/PVA/TiO<sub>2</sub> films using a treatment of high hydrostatic pressure (HHP)<sup>83</sup>. In this study was observed that the HHP treatment on the nanocomposite promoted a good chemical interaction between the polymers chains and lower migration of the nanoparticles in the material. In Table 3 and 4 are shown some results related to antimicrobial activity and mechanical and barrier properties of chitosan-based films that incorporate nanofillers.

#### 4. Mechanical and barrier properties

Polymeric films with good mechanical properties enable preservation, handling, and improvement of the quality of foods<sup>84</sup>. The mechanical properties are of interest in the fabrication of plastic films because is important to know the force or elongation necessary that cause deformation or breaking point in the material<sup>85</sup>. Some of the mechanical properties most studied of chitosan-based films are Tensile stress, Young Modulus, elongation at break, Elastic Modulus, Ultimate Elongation, and Specific Deformation. These properties are dependent on the material type used in the fabrication of the films.

Similarly, polymeric films with good barrier properties allow extending the shelf life of food products. The barrier properties (i.e., Water Vapor Permeability, Gas vapor Permeability and, Moisture Content, Solubility) are essential in the design of foods packaging<sup>23</sup>. Suitable barrier properties and release rate are obtained by controlling solubility and diffusivity in the films<sup>86</sup>. These properties can be affected by the incorporation of fillers since these increase the distance of the tortuous path around the filler particles and reduce the cross-sectional area between them<sup>87,88</sup>.

Researchers have incorporated bioactive compounds and nanoparticles to modify the physicochemical properties of the plastic films. Important findings have demonstrated that the moisture content and yellowness of chitosan-based films is reduced by incorporating chitosan nanoparticles. In this case, nanoparticles occupy the free volume of the polymeric matrix and create physical barriers<sup>61</sup>. Also, the presence of the chitosan nanoparticles in the polymeric matrix reduces the interaction between protein chains. This effect causes in the material, a decrease the elongation at break<sup>63,70</sup>, a reduction the mobility of their chains, and the restricting the entrance of water molecules<sup>62,89,63</sup>. Also, the hydrophobicity of chitosan induces the aggregation of nanoparticles inside of polymeric matrix and causes a decrease in the transparency of the films<sup>63</sup>. Metallic nanoparticles also can affect the properties of the films because they increase their lightness<sup>53</sup> and transparency<sup>67,82</sup>. Then, depending the food type, the above would affect the functionality of the packaging.

Mechanical and barrier properties also can be affected by the use of plasticizers<sup>61</sup>, essential oil<sup>64</sup> and acids<sup>45</sup>, since these agents can increase the inter-chain spacing of the polymer, reduce the stiffness of the proteins, and modify the transparency of the material. Next, in Table 4 are presented some results related to characteristics of these properties for chitosan-based films reported in recent studies.

## 5. Antimicrobial activity

Antimicrobial activity of chitosan-based films can be summarized in the following aspects<sup>5,7,60,54-56</sup>:

- Reactivity of the amine group, degree deacetylation and molecular weight of chitosan.
- Characteristics as: pH, ionic strength, and solutes.
- Antioxidant, antibacterial, and antifungal properties of bioactive compounds incorporated in polymer matrix.
- Higher surface area and charge density of chitosan nanoparticles incorporated in polymer matrix
- Synergistic antibacterial action between chitosan and the metallic nanoparticles.

In Tables 1-3 are presented the antimicrobial activity of chitosan-based films against some type of microorganisms.

## 6. Conclusions

The implementation of Chitosan-based films in food packaging applications became in a new strategy to elaborate biodegradable materials with high antimicrobial activity. This type of material could potentially replace non-biodegradable plastics. However, their widespread use has been limited by their poor mechanical properties and barrier properties. Due to this, different strategies have been implemented to overcome these limitations, for example, the use of polymer blends, crosslinking agents, plasticizer agents, nanoparticles and bioactive compounds.

Some important results have evidenced that polymer films that include crosslinking agents have suitable thermal stability, flexibility, barrier properties, and antimicrobial activity. Also, certain bioactive compounds provide antimicrobial activity, barriers against water vapor and good tensile properties of the films. Last, the incorporation of Nano fillers give to the films a more compact structure with better mechanical, thermal, and barrier properties. Future directions in this topic will be focusing on the last item and will be considered the effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of the films and the evaluation of antimicrobial activity.

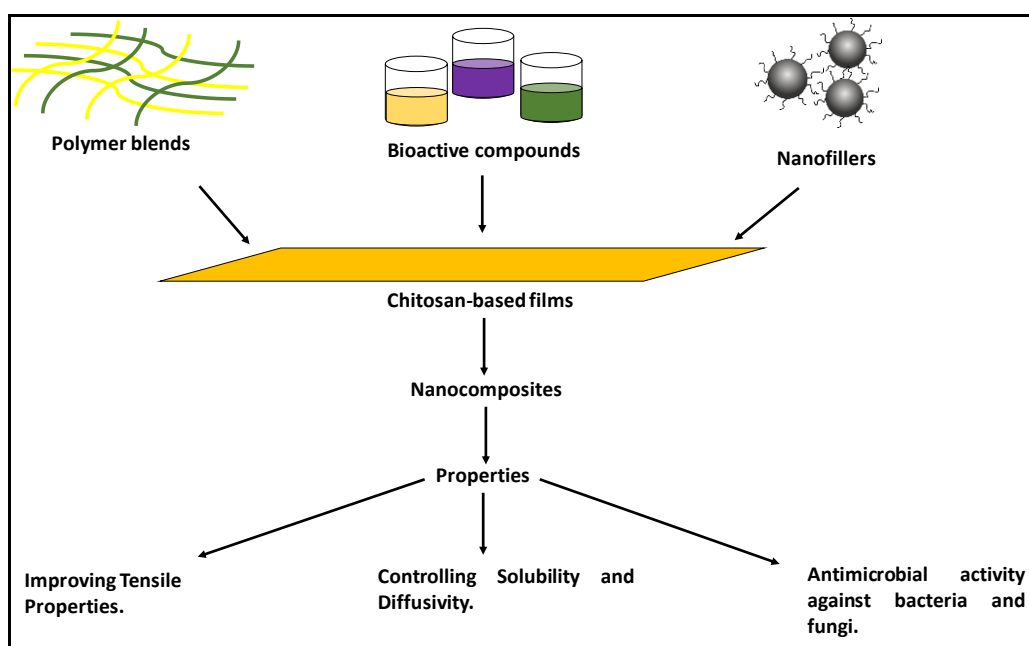


Figure 1. Strategies for the fabrication of Chitosan-based films

**Table 1.** Mechanical properties, Barrier Properties and Antimicrobial activity of chitosan-based films using polymer blends

Chitosan-Polymer	Young Modulus (YM), Tensile Stress (TS), Elongation at break (EB), Elastic Modulus (EM)	Water Vapor Permeability (WVP), Oxygen Permeability (OP), Moisture content (MC), Solubility (S), CO <sub>2</sub> Permeability (CP)	Antimicrobial Activity
Ch-Starch-PVA <sup>24</sup>	-----	-----	Bacillus subtilis
Ch-Starch <sup>25</sup>	-----	-----	Salmonella enterica Escherichia Coli
Ch-Starch <sup>26</sup>	-----	-----	Saccharomyces cerevisiae Aspergillus Flavus Lactobacillus acidophilus
Ch-PET <sup>29</sup>	-----	-----	Salmonella enterica, Campylobacter spp., Escherichia coli, Listeria Monocytogenes and Fungi Candida albicans
Ch- Polyamide 66/6 Ch- PE-PET <sup>30</sup>	~ 800 MPa (YM) ~ 40 MPa (TS) ~ 1% (EB)	-----	Coliform enterobacteria and Mesophilic aerobic microorganism.
Ch-Tara gum <sup>61</sup>	58.44 ± 3.23 MPa (TS) ~ 45 % (EB)	12.94 ± 0.15 % (MC) 10.37 ± 2.31 % (S) 0.419 ± 0.027 g-mm/m <sup>2</sup> -hr-KPa (WVP)	Escherichia Coli and Staphylococcus aureus
Ch-Fish gelatin <sup>63</sup>	11.28 ± 1.02 MPa (TS) 32.73 ± 7.38 % (EB) 467.2 ± 49.63 MPa (EM)	65.19 ± 2.32 % (S) 0.884 ± 0.127 g-mm/m <sup>2</sup> -hr-KPa (WVP)	-----
Ch-FucoPol <sup>23</sup>	38% (EB) 137 MPa (EM)	0.75 × 10 <sup>-11</sup> mol/ms-Pa (WVP) 0.47 × 10 <sup>-16</sup> mol-m/m <sup>2</sup> -s-Pa (OP) 5.8 × 10 <sup>-16</sup> mol-m/m <sup>2</sup> -s-Pa, (CP)	-----
PEGylated Ch-PEG <sup>31</sup>	~ 70 MPa (YM)	-----	Escherichia Coli
Ch-PET-PP <sup>33</sup>	-----	-----	Staphylococcus aureus, Bacillus subtilis, and Escherichia coli
Ch-Fish gelatin <sup>64</sup>	6.72 – 3.28 MPa (TS) 151.82 – 87.20 % (EB) 276.60 – 153.75 MPa (EM)	0.525 – 0.683 g-mm/m <sup>2</sup> -h-KPa (WVP)	Staphylococcus aureus, Listeria monocytogenes, Salmonella enteritidis and Escherichia coli
Ch-Cellulose-Glycerol <sup>65</sup>	60.8 ± 5.17 MPa (TS) 3.12 ± 0.12 GPa (YM) 3.85 ± 0.38 % (EB)	8.591 X 10 <sup>-10</sup> ± 2.1 X 10 <sup>-10</sup> g/m-s-Pa (WVP)	Staphylococcus aureus, Escherichia coli, and yeast Saccharomyces cervisiae

Chitosan (Ch), Polyvinyl alcohol (PVA), Polyethylene (PE), Polyethylene terephthalate (PET), Polyethylenglycol (PEG), and Polypropylene (PP)

**Table 2. Mechanical properties, Barrier Properties and Antimicrobial activity of chitosan-based films that incorporate bioactive compounds.**

Chitosan-Bioactive Compounds	Young Modulus (YM), Tensile Stress (TS), Elongation at break (EB), Elastic Modulus (EM), Ultimate Elongation (UE), Specific deformation (SD)	Water Vapor Permeability (WVP), Oxygen Permeability (OP), Moisture content (MC), Solubility (S), CO <sub>2</sub> Permeability (CP)	Antimicrobial Activity
Ch-Maqui berry extracts <sup>44</sup>	-----	-----	Listeria innocua, Serratia marcescens, Aeromonas hydrophila, Achromobacter denitrificans, Alcaligenes faecalis, Pseudomonas fluorescens, Citrobacter freundii and Shewanella putrefaciens.
Ch-Aloe Vera <sup>47</sup>	-----	-----	Botrytis cinerea
Ch- Ferulic acid (FA) Ch- Ethyl ferulate (EF) <sup>45</sup>	FA: 58.3 ± 2.1 MPa (TS), FA: 6.8 ± 2.1 % (UE) FA: 3920 ± 625 MPa (YM) EF: 58.7 ± 2.7 MPa (TS), EF: 7.3 ± 2.4 % (UE) EF: 3755 ± 580 MPa (YM)	FA: 3.9 ± 0.15 g/Pa-s-m x 10 <sup>-10</sup> (WVP) EF: 3.6 ± 0.25 g/Pa-s-m x 10 <sup>-10</sup> (WVP) FA: 0.6 ± 0.1 cm <sup>3</sup> / Pa-s-m 10 <sup>-10</sup> (OP) EF: 0.8 ± 0.2 cm <sup>3</sup> / Pa-s-m 10 <sup>-10</sup> (OP)	-----
Ch-Nisin-Natamycin-Pomegranate-grape seed extract <sup>39</sup>	-----	-----	Mesophilic bacteria and yeast and mold.
Ch-Eucalyptus globulus essential oil <sup>46</sup>	-----	15.95 ± 1.27 % (MC) 13.19 ± 1.03 % (S)	Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, Candida albicans and Candida parapsilosis.
Ch-Tea extracts <sup>42</sup>	~ 30 MPa (TS) ~ 10 % (EB)	11.51 ± 1.53 × 10 <sup>-11</sup> g/m-s-Pa (WVP) 75.03 ± 0.91 % (S)	
Ch-PVA-Anthocyanins <sup>43</sup>	3.53 MPa (EM) 26.8 % (SD) 9.6 MPa (TS)	-----	-----
Ch-Galic acid <sup>90</sup>	-----	7.230 ± 0.55 g-mm/d-m <sup>2</sup> -Kpa (WVP)	-----
Ch-Galic acid <sup>41</sup>	~ 9 – 17 MPa (TS) ~ 15 – 25 % (EB)	-----	Escherichia coli L monocytogenes

Ch-Eugenol-TPF <sup>40</sup>	153 ± 0.23 MPa (TS) 41.03 ± 77.1 MPa (YM) 10.71 ± 62.38 % (EB)	4707.38± 83.55 g-mil/m <sup>2</sup> -day-atm ((WVP) 229.06 ± 3.34 cc-mil/m <sup>2</sup> -day-atm (OP)	-----
Ch-Benzoic acid-Sorbic acid <sup>49</sup>	-----	-----	Escherichia coli, Staphylococcus aureus Bacillus cereus, and Ps. fluorescens
Ch-Cyclodextrin-Carvacrol <sup>50</sup>	-----	-----	Mesophiles, psychrophiles, Pseudomonas spp., enterobacteria, lactic acid bacteria, yeasts, and fungi
Ch-Gelatin- mint or thyme essential oils <sup>52</sup>	-----	-----	L. monocytogenes and L. monocytogenes
Ch-Carvacrol <sup>51</sup>	-----	-----	Bacillus subtilis, Escherichia coli, Listeria innocua, and Salmonella enteritidis



**Table 3. Mechanical properties, Barrier Properties and Antimicrobial activity of chitosan-based films that incorporate nanofillers.**

Chitosan-Nanofiller	Young Modulus (YM), Tensile Stress (TS), Elongation at break (EB), Elastic Modulus (EM), Ultimate Elongation (UE), Specific deformation (SD) Fracture strength (FE)	Water Vapor Permeability (WVP), Oxygen Permeability (OP), Moisture content (MC), Solubility (S), CO <sub>2</sub> Permeability (CP) Water vapor transmission rate (WVTR)	Antimicrobial activity
Ch/PVA-SiO <sub>2</sub> <sup>69</sup>	20.6 (TS) 227 (YM)	-----	-----
Ch-MMT nanoclays-REO <sup>53</sup>	65.71 – 74.41 (TS)	(0.30 – 0.47) x 10 <sup>-10</sup> g/m-s-Pa (WVP) 3.01 – 4.83 % (EB)	L. monocytogenes, S. agalactiae Escherichia coli, L Putida, and L lactis
Ch/PVA-CNCs-ZnO <sup>78</sup>	153.2 ± 1.8 (TS) 932 ± 36 (YM) 3.2 ± 0.7 (EB)	-----	Salmonella choleraesuis and Staphylococcus aureus
Ch/PVA-CNCs-ZnO -Ag <sup>79</sup>	0.205 GPa (TS) 1.20 GPa, (YM)	-----	Salmonella choleraesuis and Staphylococcus aureus
Ch-Ag <sup>55</sup>	-----	-----	Escherichia coli and Staphylococcus aureus
Ch-Ag <sup>75</sup>	-----	-----	Staphylococcus aureus and Pseudomonas aeruginosa
Ch- SiC <sup>70</sup>	~ 7 – 25 (TS)	~ 2- 6 (OP) Lit-cm <sup>2</sup> /min	-----
Ch-Nano zinc oxide/ Neem essential oil <sup>82</sup>	30 – 70 (TS) 7 – 16 (EB)	~ 0.41 – 1.57 mg/cm <sup>2</sup> /h (WVP)	Escherichia coli
Ch/Cinnamaldehyde- Graphite <sup>81</sup>	2.2 – 3.8 (EM) GPa 62 – 90 (FE) 6 – 13 % (EB)	-----	Rhizopus stolonifer
Ch/PVA-Nanoclays (NaMMT and org-MMT) <sup>67</sup>	2289 – 3816 (YM) 6.30 – 16.13 (EB)	~ 0.5 – 2 g/h- m <sup>2</sup> x 10 <sup>-6</sup> (WVP) ~ 0.6 – 3.5 cm <sup>3</sup> /m <sup>2</sup> /day (OP)	Escherichia coli
Ch/ PVA-TiO <sub>2</sub> <sup>83</sup>	6.53 – 17.15 (TS) 50.5 – 68.48 (EB)	3.47 – 4.84 x10 <sup>-12</sup> g-cm/cm <sup>2</sup> -s-Pa (WVP) 1.25 – 1.59 cm <sup>3</sup> /m <sup>2</sup> -s-Pa (OP)	Escherichia coli, S. enterica, L. monocytogenes, and S. aureus

Ch/Acetate- Cloisite®30B) <sup>68</sup>	49.6 – 66.3 (EB) 6.7 – 9.0 (TS)	4.60 – 6.68 X10 <sup>-18</sup> Kg m/m <sup>2</sup> -s-Pa (WVP) 1.81– 2.34 x 10 <sup>-3</sup> (WVTR)	-----
Ch/CMC- ZnO <sup>80</sup>	6.8 – 12.6 x 10 <sup>6</sup> (Pa) (TS)	-----	Staphylococcus aureus, Pseudomonas aeruginosa, and Escherichia coli, Candidia albicans

Rosemary essential oil (REO), Montmorillonite (MMT), cellulose nanocrystals(CNCs), zinc oxide (ZnO), Glutaraldehyde (GL), hydrophilic sodium–montmorillonite (NaMMT), organically modified montmorillonite (org-MMT), Carboxymethylcellulose (CMC), Nano silicon carbide (SiC)

Table 4. Important results related to the mechanical and barrier properties of Chitosan-based films

Chitosan-based films	Mechanical Properties	Barrier Properties	Principal characteristics
Ch- Polyamide 66/6 Ch- PE-PET <sup>30</sup>	The films presented a decrease of Young modulus, Elongation at break, and Tensile strength.	-----	A poor affinity between the polymer chains induced a decrease of Young modulus, Elongation at break, and Tensile strength of the material.
ChNps (Chitosan Nanoparticles)- Tara gum <sup>61</sup>	Chitosan nanoparticles enhanced the Young modulus and storage modulus, but decreased the Elongation at break, and Tensile strength of the material.	Chitosan nanoparticles reduced the moisture content and the solubility.  Plasticizer increased the WVP.	Chitosan nanoparticles promoted a structure more compact reducing the moisture content.  The amine group present in the structure of Chitosan decreased the solubility in the films.  Plasticizers favor the adsorption of water molecules.
Fish gelatin – ChNps (Chitosan Nanoparticles) <sup>63</sup>	Chitosan nanoparticles increased the elastic modulus and decreased the elongation at break	CSNPs decreased in water solubility  CSNPs decreased the WVP of the films.	The presence of chitosan nanoparticles in the polymeric matrix resulted in a stiffer material and brittleness.  The affinity between polymeric chains induce the formation of strong hydrogen bonds which not facilitates the entrance of water molecules.
PEGylated chitosan- PEG <sup>31</sup>	PEGylated chitosan decreased the Young Modulus.	-----	PEG chains incorporated within polymeric matrix act as plasticizer.
Fish gelatin/Oregano oil- Ch <sup>64</sup>	Oregano oil increase EAB and decreased the TS and the EM.	Oregano oil reduced the water vapor permeability (WVP).	Oregano promoted a material more flexible, less resistant, and with low WVP.
Cellulose-ChNps <sup>65</sup>	Chitosan Nanoparticles decreased strain at break and increased tensile strength and Young's modulus	Chitosan nanoparticles did not enhance the WVP of the films.	The affinity between polymeric chains increased the tensile strength of the material.  The presence of hydroxyl groups and carboxylic groups in the structure of the cellulose affect the transport of water vapor in the material.

**Table 5. Important results related to the mechanical and barrier properties of Chitosan-based films**

Chitosan-based films	Mechanical Properties	Barrier Properties	Principal characteristics
Ch- ferulic acid (FA) Ch- ethyl ferulate (EF) <sup>45</sup>	FA and EF decreased tensile strength of the films	FA or EF decreased WVP and oxygen permeability.	FA or EF limited the chain mobility in the material. FA- or EF- reduced the number of water absorption sites (NH <sub>2</sub> , OH). The crosslinking between oxidation products and chitosan chains reduced oxygen permeability of the material.
Ch- Eucalyptus globulus essential oil <sup>46</sup>		Eucalyptus Globulus essential oil decreased the moisture in the films.	The affinity between chitosan and the essential oil caused the formation of covalent bonds which limited the interactions between the polymeric chain and the water molecules.
CH- Tea extracts <sup>42</sup>	Tea extracts decreased the tensile strength and elongation at break.	Tea extracts decreased WVP and increased the solubility.	Tea extracts affected the crystalline structure of the material and hydrogen intermolecular bonding of the films.
Ch-Eugenol-TPF <sup>40</sup>	Chitosan nanoparticles and eugenol-loaded chitosan nanoparticles decreased the tensile strength, modulus and elongation at break of the films.	Chitosan nanoparticles and eugenol-loaded chitosan nanoparticles increased oxygen permeability, decreased water vapor permeability, and enhanced radical scavenging activity.	The agglomeration of the nanoparticles inside polymeric matrix resulted in films more brittle.
Ch-MMT nanoclays/REO <sup>53</sup>	MMT nanoclays increased the tensile strength.	MMT nanoclays decreased water solubility MMT nanoclays and REO decreased WVP	The interactions between chitosan and MMT nanoparticles stabilize the structure of the films causing lower solubility. Uniform dispersion of MMT nanoclays inside chitosan matrix enhanced tensile strength of the films.  The crosslinking between REO and Chitosan and the hydrophobic nature of REO caused lower water solubility.  Ordered dispersed nanoparticles and the presence of REO decreased WVP  REO gave plasticity to the films.
Ch-PVA-Nanoclays(NaMMT and org-MMT) <sup>67</sup>	Nanoclays decreased the strain at break and increased the stiffness and strength.	Nanoclays decreased water solubility and gases permeability	-----

**Table 6. Important results related to the mechanical and barrier properties of Chitosan-based films- continuation**

Chitosan-based films	Mechanical Properties	Barrier Properties	Principal characteristics
Ch- acetate- nanoclay (cloisite®30B) <sup>68</sup>	Nanoclays increased the elongation at break and tensile strength.	Nanoclays decreased WVTR, crystallinity, water solubility and moisture content	-----
PVA/Ch/CNCs/ZnO <sup>78</sup>	CNCs/ZnO increased the tensile strength and modulus and decreased the elongation at break.	-----	CNCs/ZnO and blend matrix had strong interactions which limited the matrix motion and increased the rigidity in the material.
PVA/Ch/CNCs/ZnO-Ag <sup>79</sup>	the tensile yield strength and Young's modulus increased	-----	-----
Ch- tNano zinc oxide/ neem essential oil <sup>82</sup>	Nanoparticles and oil increased tensile strength and elongation at break	Nanoparticles and oil decreased water solubility and WVP	Nanoparticles and oil increased the hydrophobicity. Nanoparticles and oil reduced the brittleness of the film and increased the flexibility of the material.
Ch-cinnamaldehyde-graphite <sup>81</sup>	Graphite increased the tensile strength and modulus	-----	Graphite in the CS-CA films led to higher values of tensile Strength and modulus due to the increase in chain entanglements.

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