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Additives for Realistic Biodegradable Cellulose-based Film with Mechanical and Antibacterial Properties

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Abstract. Developing the biodegradable and renewable materials in the food packaging industry has become one of the most important topics in modern society, where has attracted a lot of efforts in this field. In this review, we have discussed the additives that used to regulate the mechanical and antimicrobial properties by blending into cellulose and its derivatives. Cellulose is one of the best biomass composites for film formation with resource abundance and biodegradability. To realize the further benefits of cellulose and its derivatives in the food packaging manufacture, there are still a quantity of opportunities in improving the practicality and cost of the additives.

1. Introduction

Petroleum-based plastics have attracted a great deal of attention on account of the advantages of low cost, low density and easy processing, which provides great impact for the human society. The market has demonstrated huge demand on the plastic products, and the applications have been widely developed in electronic devices, machinery, food manufacturing and many other industries. Among the aforementioned application, plastic consumables in the food industry, especially the products like disposable tableware, straw, plastic bags, packaging film, etc., will cause serious plastic pollution to the environment. Hundreds of years should be taken to completely degrade the disposable plastic products. To address this challenge, bio-degradable cellulose-based materials have been extensively investigated and utilized in the food industry by reason of its nontoxicity, natural abundance and biodegradability. However, the realistic performance such as mechanical properties and antibacterial properties are still unable to overwhelm the plastic products, which limits the widespread applications of the cellulose-based materials. Therefore, a lot of efforts have been input to develop the additives of improving the performance in mechanical property and antibacterial property, where are the key competence of biodegradable cellulose-based films for realizing the practical applications.

2. Additives for Mechanical Property

The mechanical property is an important factor for bridging the practical application to biodegradable cellulose-based materials. Various additives have been investigated to regulate the mechanical property. An important strategy is the incorporation of nanomaterials, which have been demonstrated to effectively strengthen the performance of biopolymer-based membrane layer. Inorganic raw material TiO_2 can be used as a food additive to achieve the super hydrophobicity, thermal stability and mechanical properties, which is a good candidate as additive in the materials of food industry.[1][2] Shao et.al. mixed nano titanium dioxide (TiO_2) and bovine bone collagen (BC) as reinforcing substances into hydroxypropyl methyl cellulose (HPMC), and formed food packaging materials with good mechanical, barrier and thermal properties by solution pouring method (Figure 1a). Nano TiO2 is linked to HPMC and BC hydroxyl groups by hydrogen bonding through hydrophilic groups on the surface. The change of hydrogen bond can resist the stress change process during stress loading and release, so the tensile strength (TS) and elongation (EAB) of HPMC/BC/0.04 TiO_2 sample reach 26.48 MPa and 50.24%, respectively, which increase by 24.49% and 23.0% compared with pure HPMC sample. [3] Fonseca et.al discussed that the regulation of TiO_2 nanoparticle concentrations in HPMC-TiO_2 nanocomposite film, which can affect the dispersion in cellulose (matrix), and the direct effect of its dispersion is on the heat resistance, barrier and mechanical properties of the sample. For the film covering 2 wt% TiO_2, it increases the intensity of tensile stress by 13% and elongation by 23%.[4].

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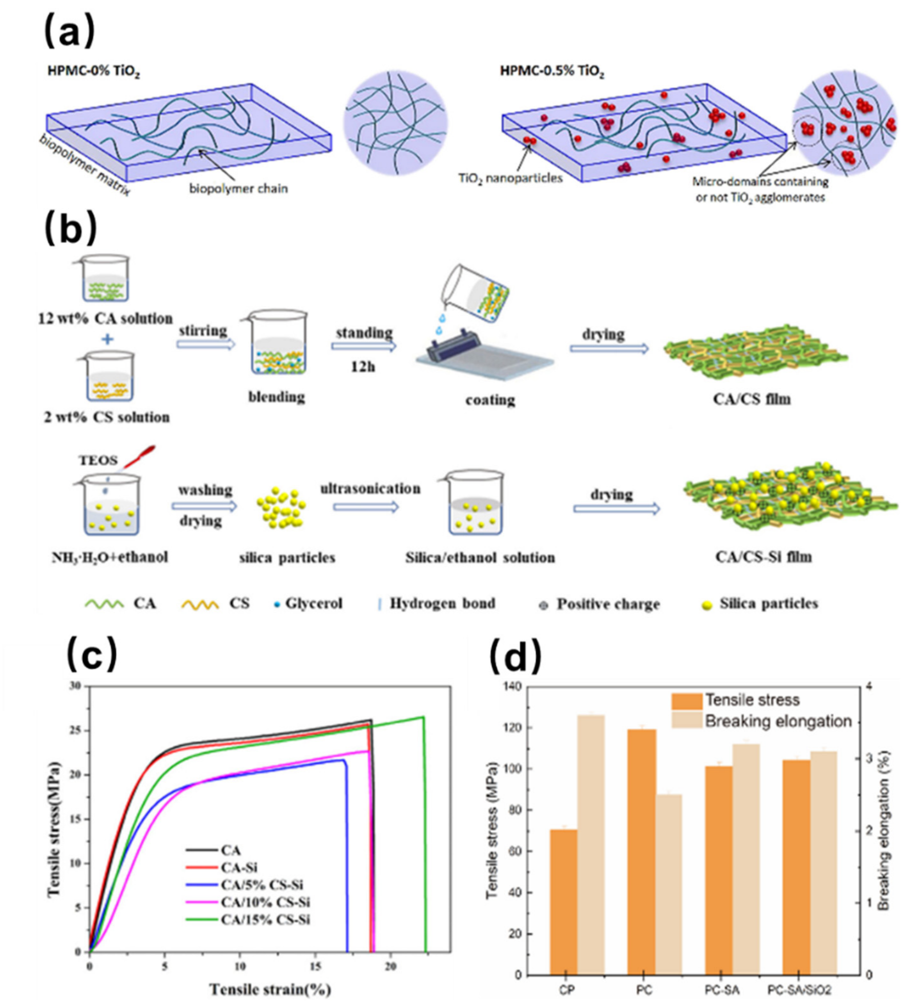

Figure1. (a) Physical structure diagram of HPMC composite membrane added with titanium dioxide. Reproduced with permission from ref3. (b) Process diagram of preparing CA/CS Si composite membrane. (c) Stress-strain curves of composite films with different chitosan proportions. Reproduced with permission from ref5. (d) Elongation at break of degradable cellulose based super hydrophobic antibacterial materials. Reproduced with permission from ref6.

Silica is also a popular additive to food as an anticoagulant in various products because of its nontoxicity and high stability. Zhou et.al have prepared bio-based plastic film with modified oxygen-resistance and hydrophobicity with bio-sed cellulose acetate (CA), using chitosan and silica particles as blending components (Figure.1b). The mechanical capacity of the membrane could be increased by 2.8 times of tensile stress and 25.6 times of tensile strain (Figure.1c).[5] Jiang et al. used nano silica (SiO_2) modified stearic acid (SA) as the hydrophobic layer and mixed polylactic acid (PLA) and cinnamaldehyde (CIN) as the barrier layer to prepare a composite degradable hydrophobic packaging with excellent barrier performance on cellulose paper. Due to the rigid polymer in the composite film layer, the tensile stress strength of PC-SA/SiO_2 is as high as 104.3MPa (Figure 1d).[6] Rukmanikrishnan et al. took hydroxyethyl cellulose (HEC) as the substrate and combined silver nanoparticles, SiO_2 nanoparticles and K-Carrageenan to improve the mechanical properties of the film layer. According to the tensile stress-strain curve, the addition of nano SiO_2 particles increases the tensile strength of the composite film by 42.69% and the elongation by 23%. [7]

In addition, various organic nanoparticles can provide different strategies for the construction of nanocomposites, which have been proven with good stability and biocompatibility. Zhang et.al proposed a simple and low-cost method for preparing super hydrophobic coatings by spraying edible beeswax and coInee lignin, which serve to connect cellulose, enabling plants to obtain excellent structural strength. The composite coating surface has shown a structure like the leaf surface. The beeswax coated coffee lignin forms supramolecular bond with the substrate to improve the adhesion of the coating to the substrate and the thermal stability of the overall coating. After a period of heating and washing, the water contact angle of the coating can remain above 150° (Figure 2a). [8][9] He et.al constructs an antibacterial surface on cellulose lignin film through hydrogen bond and electrostatic interaction (Figure.2b). The tensile strength can achieve 75.90 MPa, which is significantly higher than commercial polyolefin film and other biopolymer composite films (Figure.2c). This can be attributed to the internal voids where the laminated structure with more benzene rings with rigid structures can regulate the tensile strength and toughness.[10] Dhar et.al have delivered a exceptional method of using alkali lignin (AL) as an intelligent additive agent for in situ bacterial cellulose (BC) fermentation. AL nanoparticles were compounded with BC substrate through strong intermolecular hydrogen bonds, and the sacrificial hydrogen bonds at the bonding surface of AL and BC were dynamically broken and reconstructed with the increase of the load of AL nanoparticles (Figure 2d). With the improvement of the interaction between the two interfaces, the self-assembled AL structure can effectively dissipate at the boundary of AL and BC to improve the strength and toughness of the biomass film. [11]

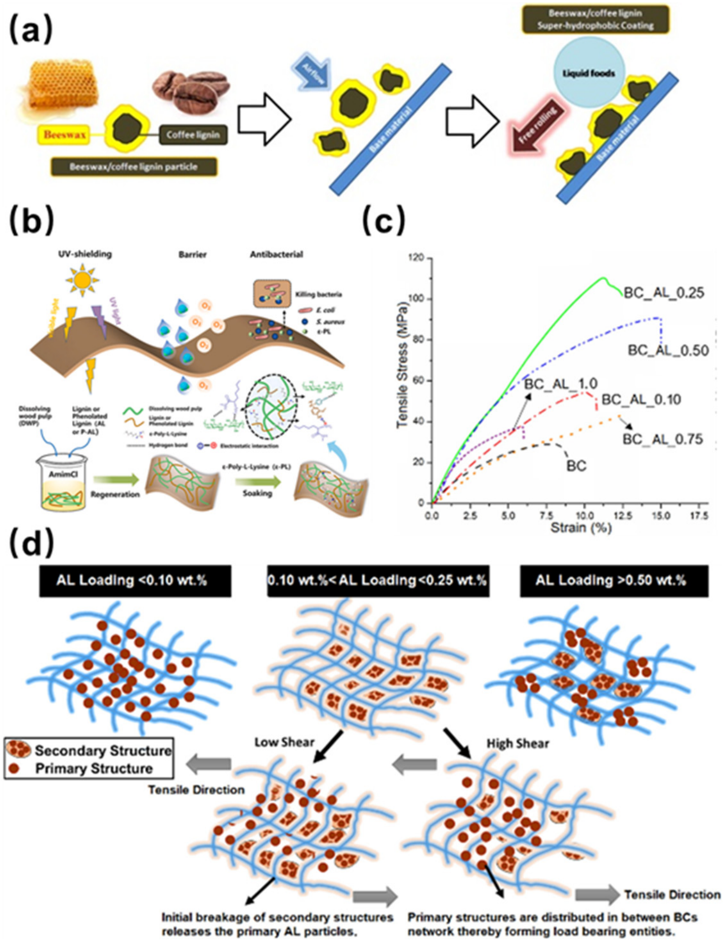

Figure2. (a) Enhancement mechanism of coffee lignin in heat resistant edible super hydrophobic coating. Reproduced with permission from ref8. (b) Schematic diagram of multi-functional cellulose lignin membrane. (c) Engineering stress-strain diagram of BC/AL membrane. Reproduced with permission from ref10. (d) The mechanism of the bearing capacity of the aluminum particle structure formed by the self-assembly method, and their reinforcement effect under different concentrations of aluminum load. Reproduced with permission from ref11.

3. Additives for Antibacterial Properties

The element essence of organic nanoparticle lignin is based on carbon. Representative investigations have seen that the carbon-based derivatives can improve the mechanical capacity of the cellulose film. Apart from that it demonstrates the antibacterial properties. Wu et.al have used the in-situ polymerization of carboxymethyl cellulose (CMC) to modify graphene oxide (GO), in which urea (U) was the intermediate of amination process to obtain uniform graphene oxide monolayer dispersion (GC). The antibacterial mode of composite film was modified from overload mode to contact active antibacterial mode, and the antibacterial ability of the composite membrane against Escherichia coli and Staphylococcus aureus increased by 23.8% and 25.6%, respectively, compared with the control group. [12]

Chitosan is the most widely used organic antibacterial agent in the food film, which is generated by deacetylated modification of chitin. Chitin is plentiful widely distributed in the natural world, and its reserves are the second largest natural polymer after cellulose. High molecular weight chitosan dissolved in acid will form a cationic bio-flocculant, with the high molecular chains densely distributed on the cell surface, affecting the metabolism of bacteria, thus playing the role of sterilization and bacteriostasis. Chitosan with low molecular weight penetrates into bacteria through porous cell wall, destroys the colloidal state of cell contents, causes flocculation deformation, or directly interferes with electronegative RNA and DNA and other genetic material, inhibits bacterial reproduction and leads to bacterial death.

Song et al. obtained cellulose-chitosan lemon film (C-Chx-F) by easily coating the surface of cellulose with a chitosan citric acid complex (Figure.3a). This membrane will seriously damage the structure of Staphylococcus aureus, with the inhibition rate ranging from 88.25 ± 4.23% to 97.19 ± 1.38% (Figure.3b).[13]

Using similar strategy, Lai et.al produced food grade polyelectrolyte composite membrane (hydroxypropyl methylcellulose grafted chitosan and carboxymethyl cellulose sodium) through electrostatic interaction, and the growth of common bacteria such as Escherichia coli and Staphylococcus aureus was not observed below the membrane.[14]

Curcumin is another promising organic antibacterial agent to deliver high antibacterial properties in the food film. Curcumin with autooxidation can oxidize to form a variety of intermediates with good biological activity, so as to obtain its own bacteriostatic and bactericidal properties. At present, studies have proved that curcumin combined with other antibacterial substances can form a good synergistic antibacterial effect, including traditional antibiotics, strong metal antibacterial agents, biological conjugate antibacterial agents, etc. Compound bacteriostatic agents show high sensitivity to bacteria and enhanced absorption capacity.[15] Zhang et al. added chitosan to Tempo-oxidized cellulose nanofibers grafted with curcumin, and prepared CGTOCNF bio-nano composite membranes by type casting. The number of indentured Escherichia coli on CGTOCNF decreased by 72.97% after 24 hours, indicating that the composite could effectively inhibit the polymerization of filamentous temperature-sensitive protein Z(FtsZ).[16] Li et al. discussed the development of a food-safe Sargassum cellulose nanofibre (SCNF) from large quantities of common seaweed using a high efficiency and low energy method as a substrate for disposable tableware (Figure 3c). As tableware is used for a long time in many humid environments, the cellulose substrate is immersed in curcumin solution to improve the antibacterial effect on aflatoxin for food safety (Figure.3d).[17] Yang et.al have developed a multi-fiber composite film combining the curcumin (Cur) microsphere nanoparticles with bacterial cellulose nanofibers (BCNF)/chitin nanofibers (CNF) by in-situ hybridization. The antibacterial rate of the composite membrane against Escherichia coli was 63% and the inhibitory effect against Staphylococcus aureus was 74%.[18]

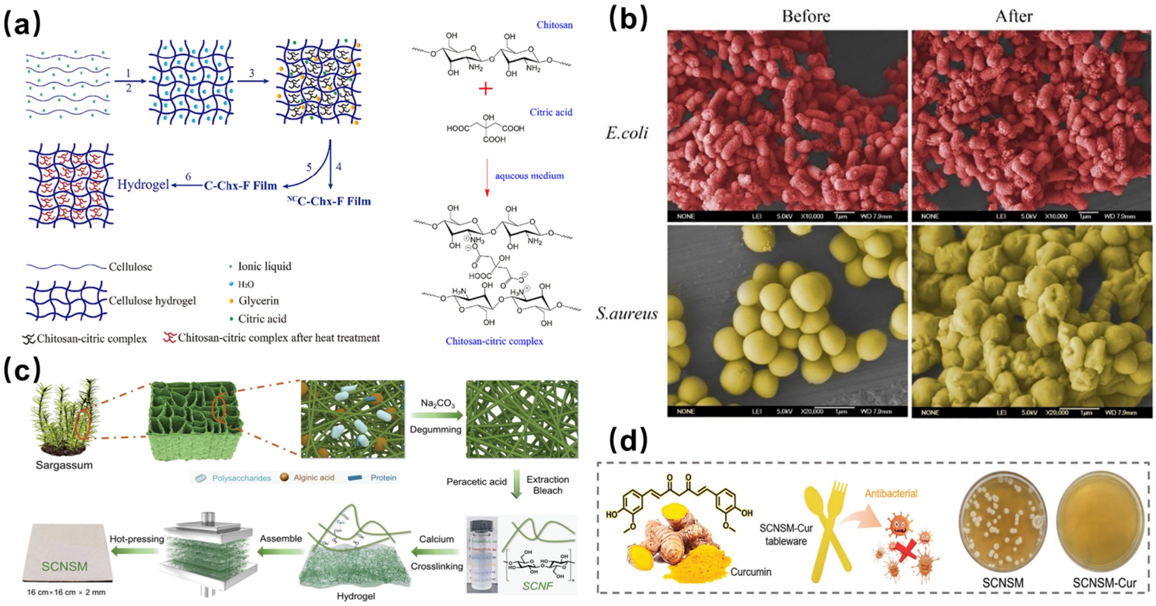

Figure3. (a) Schematic diagram of preparation of NCC-Chx-F membrane: 1. Soaking in deionized water to remove excess ionic liquid. 2. Recombination and regeneration of cellulose. 3. Immersing in chitosan citric acid solution with glycerin. 4. Dry at 23 ℃. 5. Vacuum drying at 80 ℃. 6. Soak in water to form ion crosslinked chitosan citric acid complex. (b) Electron microscopic observation of Escherichia coli and Staphylococcus aureus cells before and after membrane contact. Reproduced with permission from ref13. (c) Schematic diagram of SCNF extraction process and preparation of Sargassum fiber bulk material. (d) Comparison photo of antibacterial test of curcumin-loaded Sargassum fiber disposable tableware. Reproduced with permission from ref17.

Among a variety of organic antibacterial agents, the antibacterial activity of cinnamaldehyde is also very prominent comparing the effects of chitosan, curcumin. Liu et.al have mixed the cinnamon oil (CNO) lotion stabilized by oxidized cellulose nanofibers (OCNF) and curcumin (Cur) into gelatin/chitosan (GC) mixed membrane structure to prepare a multifunctional active intelligent biomass composite film. The antibacterial inhibition zone of GC membrane and Cur-GC membrane is less than 50 mm^2. After the addition of the Pickering lotion loaded with CNO, the antibacterial performance against E.coli and S.aureus is from 34.27 ± 3.65 mm^2 to 192.13 ± 14.52 mm^2 and 34.58 ± 2.15 mm_2 to 202.82 ± 10.23 mm^2, respectively. These results have shown the excellent antibacterial ability of cinnamaldehyde in food film.[19]

Besides the organic additives, there is also combination of inorganic carbon-based derivatives and inorganic metal nanoparticles to build an antibacterial film. Jamr ó z et.al have described multi-walled carbon nanotubes (MWCNTs), graphene oxide (GO), silver nanoparticles (Ag NPs) and other nano-fillers as reinforcement materials in furan cellulose membranes (FUR) (Figure 4a). The nanocomposite membranes prepared by this strategy have different antibacterial abilities against pathogenic bacteria and fungi. [20]

In addition, the inorganic metal nanoparticles are also sufficient to resist the invasion of bacteria for the food films. Positive silver ions interact with negative microbial cell membranes by electrostatic forces, and this effect is widely used in the development of antibacterial products. When the cell wall structure of bacteria and fungi is damaged by silver nanoparticles, they lose their barrier function. Kanikireddy et al. used mint leaf extract as a reducing agent to destabilize Ag NPs in CMC - Guar gum substrate. The membrane formed by these substances had more than 80% inhibition effect on ten kinds of foodborne disease pathogens such as Salmonella enterica, Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa, Staphylococcus aureus, Candida albicans, Micrococcus coastal, Fusarium oxysporum, Salmonella typicum and Bacillus subtilis within 8 hours. [21] Ren et.al prepared the nano-cellulose-fibrils/Ag-nanoparticles nanocomposite films doped with silver nanoparticles (Ag NPs) from nano cellulose fibrils (NCF) isolated from bamboo parenchyma cells (Figure.4b). The maximum inhibition zone for Salmonella typhi and Escherichia coli of this effective nanocomposite films was 13.5 ± 0.8 mm and 7.5 ± 0.3 mm respectively (Figure.4c).[22]

Zinc oxide nanoparticles (ZnO NPs) is also another important type of inorganic nanoparticles being used as the additives in food films. Possible mechanisms of the antibacterial activity induced from ZnO NPs: 1. Zinc ions can penetrate the cell wall to react with the content of cytoplasm, which would kill bacteria. 2. The electrostatic direct interaction between ZnO NPs and bacterial surface leads to structural changes or bacterial deactivation. 3. Active oxygen species produced by zinc oxide can damage the integrity of bacterial cell membranes.[23] Roy et al. mixed ZnO NPs into soybean protein isolate (SPI) and cellulose nanocrystals (CNC) to form SPI/CNC@ZnO nanocomposite films. Based on ZnO nanoparticles, the composite membrane showed excellent antibacterial activity against both gram-negative E.coli and Gram-positive S.aureus. [24]

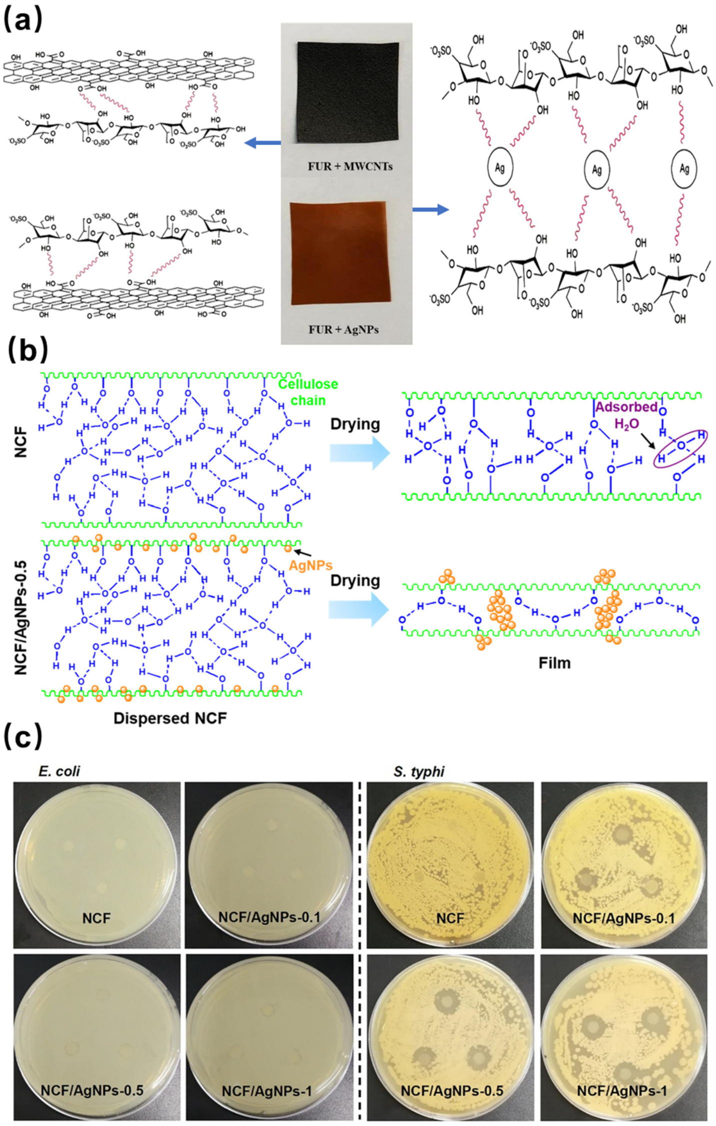

Figure4. (a) Schematic diagram of potential interactions between MWCNTs, Ag NPs and furan cellulose membrane. Reproduced with permission from ref20. (b) Schematic interactions during the formation of NCF based films. (c) Optical picture of the antibacterial effect of NCF-based materials against Escherichia coli and Staphylococcus aureus. Reproduced with permission from ref22.

4. Additives for Antibacterial Properties

One of the most important challenges in modern society is to develop the biodegradable and renewable materials in the food packaging manufacturing. In this review, we have discussed the mechanical and antimicrobial properties regulated by the blending of cellulose and its derivatives with additives. Cellulose is one of the best biomass composites for film formation with resource abundance and biodegradability. However, the development of biomass composite films still requires more advances and regulations to be introduced and applied at a commercial level. Nanoparticles that improve the mechanical capacity of the film are needed to reach a specific size, and a single source of additives to improve their antimicrobial properties is also necessary in the industry. To realize the further benefits of cellulose and its derivatives in the food packaging fabricating, there are still a large amount of opportunities in improving the practicality and cost of the additives. In the future, more additives from natural sources should be studied to further improve the practicality of cellulose-based smart food packaging materials.

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