Use of Titanium Dioxide (TiO2) Nanoparticles as Reinforcement Agent of Polysaccharide-Based Materials

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Keywords: hybrid material, functionalization, cross-linking agent, titanium dioxide, polysaccharides

Abstract:

In recent years, a strong interest has emerged in polysaccharide-hybrid composites and their potential applications, which have interesting functional and technological properties. This review summarizes and discusses the reported advantages and limitations of the functionalization of conventional and nonconventional polysaccharides by adding TiO2 nanoparticles as a reinforcement agent. Their effects on the mechanical, thermal, and UV-barrier properties as well as their water-resistance are discussed. In general, the polysaccharide?TiO2 hybrid materials showed improved physicochemical properties in a TiO2 content-dependent response. It showed antimicrobial activity against bacteria (gram-negative and gram-positive), yeasts, and molds with enhanced UV-protective effects for food and non-food packaging purposes. The reported applications of functionalized polysaccharide?TiO2 composites include photocatalysts (dye removal from aqueous media and water purification), biomedical (wound-healing material, drug delivery systems, biosensor, and tissue engineering), food preservation (fruits and meat), cosmetics (sunscreen and bleaching tooth treatment), textile (cotton fabric self-cleaning), and dye-sensitized solar cells. Furthermore, the polysaccharide?TiO2 showed high biocompatibility without adverse effects on different cell lines, indicating that their use in food, pharmaceutical, and biomedical applications is safe. However, it is necessary to evaluate the structural changes promoted by the storage conditions (time and temperature) on the physicochemical properties of polysaccharide?TiO2 hybrid composites to guarantee their stability during a determined time.

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Review

Use of Titanium Dioxide (TiO_2) Nanoparticles as Reinforcement Agent of Polysaccharide-Based Materials

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Abstract: In recent years, a strong interest has emerged in polysaccharide-hybrid composites and their potential applications, which have interesting functional and technological properties. This review summarizes and discusses the reported advantages and limitations of the functionalization of conventional and nonconventional polysaccharides by adding TiO_2 nanoparticles as a reinforcement agent. Their effects on the mechanical, thermal, and UV-barrier properties as well as their water-resistance are discussed. In general, the polysaccharide–TiO_2 hybrid materials showed improved physicochemical properties in a TiO_2 content-dependent response. It showed antimicrobial activity against bacteria (gram-negative and gram-positive), yeasts, and molds with enhanced UV-protective effects for food and non-food packaging purposes. The reported applications of functionalized polysaccharide–TiO_2 composites include photocatalysts (dye removal from aqueous media and water purification), biomedical (wound-healing material, drug delivery systems, biosensor, and tissue engineering), food preservation (fruits and meat), cosmetics (sunscreen and bleaching tooth treatment), textile (cotton fabric self-cleaning), and dye-sensitized solar cells. Furthermore, the polysaccharide–TiO_2 showed high biocompatibility without adverse effects on different cell lines, indicating that their use in food, pharmaceutical, and biomedical applications is safe. However, it is necessary to evaluate the structural changes promoted by the storage conditions (time and temperature) on the physicochemical properties of polysaccharide–TiO_2 hybrid composites to guarantee their stability during a determined time.

Keywords: polysaccharides; titanium dioxide; cross-linking agent; functionalization; hybrid material

1. Introduction

In recent years, the development of functional and eco-friendly materials with advanced properties as an alternative to replacing conventional nondegradable polymers has gained attention, particularly, for the polysaccharide-hybrid materials which exhibit diversified technological applications (antimicrobial agent, packaging material, water pollutant degradation, energy storage, and biosensors) [1,2]. Hybrid materials refer to combining two or more organic or inorganic components such as organic–organic (starch–cellulose), inorganic–inorganic (TiO_2–Ag), and organic–inorganic (starch–TiO_2) compounds, and they are synthesized by different routes such as covalent immobilization, electrostatic binding, and polymerization methods among others [3]. These synthetic routes are effective to fabricate polysaccharide-hybrid structures with enhanced technological properties and applications [3]. Currently, there is a special interest in combining organic compounds such as polysaccharides with inorganic compounds like titanium dioxide (TiO_2) to obtain hybrid materials with enhanced stability and new functionalities [4–7].

Titanium dioxide (TiO_2) is a versatile material with interesting characteristics (biocompatible, chemical stability, high reactivity, electrochemical properties, low cost, and safe production) [2,8–10] used as a photocatalyst for water-dye degradation [11]. It is employed as a white colorant in the food and pharmaceutical industries [11]. Furthermore, TiO_2 exhibits UV-protection and antimicrobial properties [12,13]. Moreover, TiO_2 is widely used to develop energy storage systems like lithium-ion batteries and dye-sensitized solar cells [2,14–16]. Recently, TiO_2 has been used as a physical cross-linking agent to improve the technological and functional properties of polysaccharide-based materials [17–19].

In the last decade, the use of TiO_2 as a reinforcement agent of polysaccharide-based materials has been explored [5,11,20]. Teymourpour et al. [6] reported that the soybean polysaccharide biocomposite reinforced with TiO_2 showed good antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*. Ahmadi et al. [21] developed a carboxymethyl cellulose film cross-linked with TiO_2 with improved UV-protective effects. Urruela-Barrios et al. [5] fabricated alginate-gelatin hydrogels combined with TiO_2 for tissue regeneration. Tunma [22] fabricated an active packaging with the cassava starch–TiO_2 composite for banana and tomato preservation. Khodadadi et al. [23] reported that the pectin–TiO_2:Cu composite is effective for methyl orange dye removal. Nonetheless, Khanmirzaei and Ramesh [24] fabricated a rice starch/ionic liquid/TiO_2 nanocomposite for solar cell applications. Furthermore, the incorporation of TiO_2 in different polysaccharide matrixes (carboxymethyl cellulose; starch; sodium alginate; agar; and a combination of k-Carrageenan, xanthan gum, and gellan gum) had a positive impact on their mechanical, thermal, and physicochemical properties, which exhibit potential industrial applications [17,20,25–27].

This review summarizes the advantages and limitations that the use of TiO_2 nanoparticles as a reinforcement agent offers during the development of polysaccharide-based hybrid materials and provides an overview of the effect of diverse polysaccharide compounds reinforced with TiO_2 on the antimicrobial activity and water treatment, potential food packaging material, pharmaceutical, and biomedical applications.

2. Hybrid Materials

The functionalization of organic materials through introduction of inorganic (metallic or metal oxide) nanoparticles is a strategy widely used to fabricate hybrid materials with enhanced properties, which has increased considerably in the last five years [3]. Hybrid materials, in particular, organic–inorganic materials, are commonly prepared using polysaccharides in combination with inorganic nanoparticles like TiO_2 [8,28], where the most common method for their preparation is the evaporative casting-plate via mechanical stirring (Figure 1a) and chemical or physical surface deposition (Figure 1b) [29]. Furthermore, the hybrid materials are classified as class I (organic and inorganic presenting noncovalent interactions) or class II (organic and inorganic exhibiting covalent interactions) depending on the intra- and intermolecular interactions among the organic matrix and cross-linking agent [3].

In general, cross-linking agents (glutaraldehyde, polyethylene glycol, calcium carbonate, and TiO_2) tend to limit interaction of the polymer chains with water molecules and provide structural integrity during exposure to a defined pressure and moisture conditions [3]. It could react with the available functional groups (–OH and –NH_2) present in the organic matrix. Nonetheless, the type and concentration of the reinforcement agent determine the effects (positively or negatively) in the technological and functional properties of the organic compound [30]. TiO_2 has the potential to enhance the properties of polysaccharide-based films such as starch (from potato, corn, and rice), sodium alginate, carboxymethyl cellulose, pullulan, agar, gums (k-Carrageenan, xanthan gum, and gellan), and chitosan, as is discussed below.

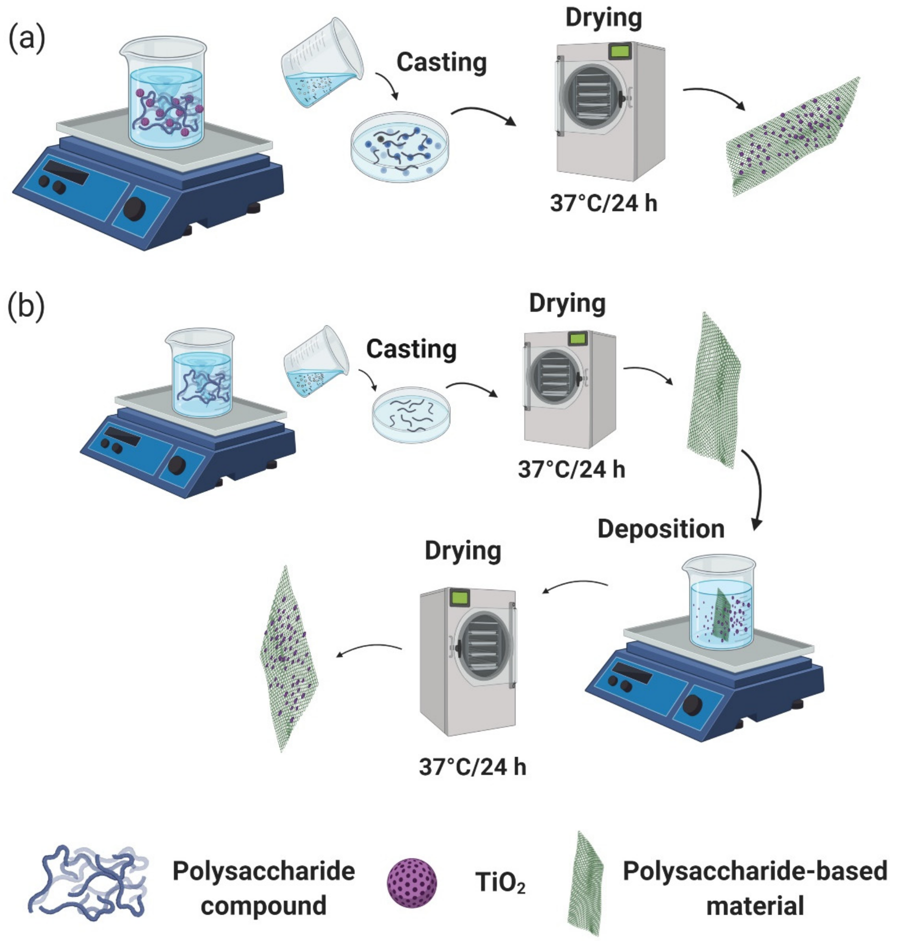

Figure 1. Mechanical stirring (**a**) and chemical deposition (**b**) methods for polysaccharide-hybrid material preparation (adapted from Anaya-Esparza et al. [1], Miyazaki et al. [29], and Tang et al. [31]) (Figure created in Biorender.com).

3. Polysaccharide–TiO_2 Hybrid Materials

Polysaccharides are biopolymers composed of monosaccharides connected by glycosidic bonds [3]. They are obtained from different sources (plants, animals, algae, and microbial) and exhibit a wide range of applications because they are low cost, abundant, biodegradable, edible, and biocompatible with numerous organic and inorganic compounds [3]. However, most of their potential applications are limited by their poor physical properties (high solubility, low water barrier ability, low thermal stability, poor gas permeability, and mechanical resistance). Thus, their functionalization is necessary [32]. Moreover, nano-TiO_2 can improve the physicochemical (Figure 2) and functional properties of polysaccharide-based materials like starch, sodium alginate, carboxymethyl cellulose, chitosan, pullulan, agar, k-Carrageenan, xanthan gum, and gellan gum-based materials [1,5,17,20–22,33]. Figure 3 summarizes the main applications of polysaccharide-based materials functionalized with TiO_2 nanoparticles.

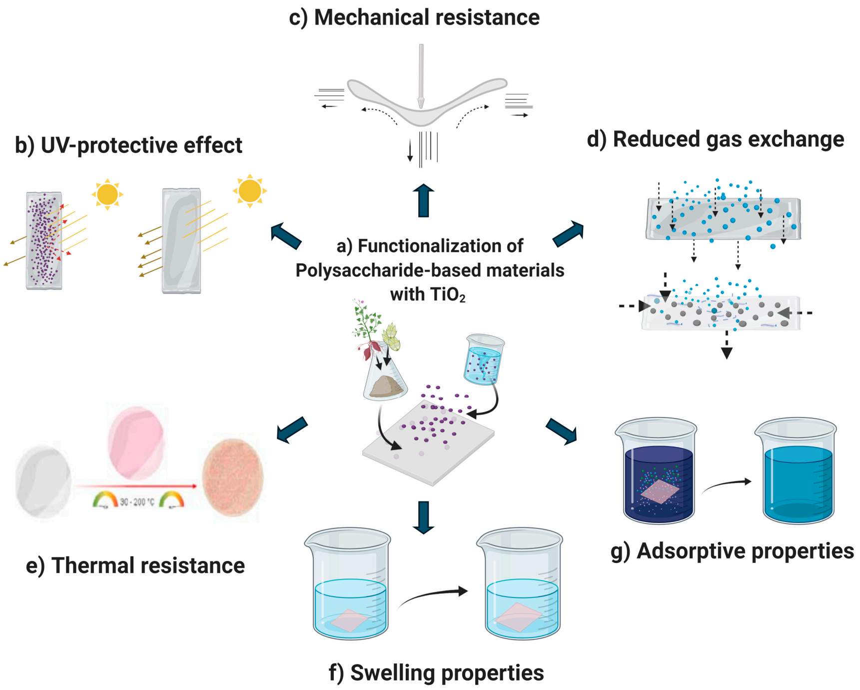

Figure 2. Schematic representation of the functionalization of polysaccharide-based materials with TiO_2 (**a**) and their effects on the UV-blocking (**b**), mechanical (**c**), gas exchange (**d**), thermal (**e**), swelling (**f**), and adsorptive (**g**) properties (adapted from Hou et al. [34], Goudarzi et al. [35], de Moura et al. [36], and Dai et al. [37]) (Figure created in Biorender.com).

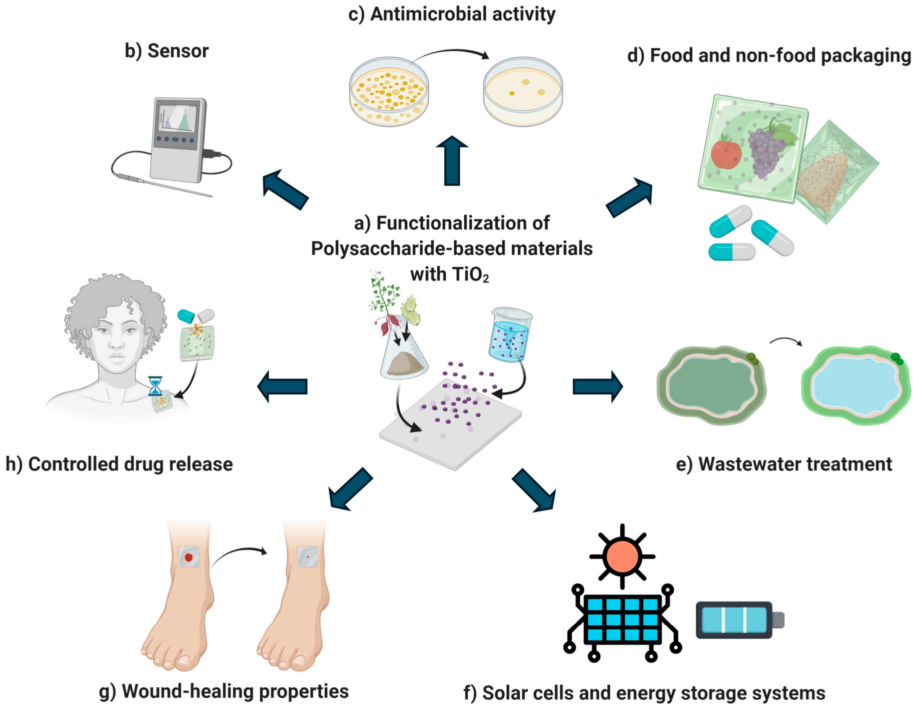

Figure 3. Schematic representation of the functionalization of polysaccharide-based materials with TiO_2 (**a**) and their main applications: sensor development (**b**), antimicrobial activity (**c**), food and non-food packaging (**d**), wastewater treatment (**e**), solar cells and energy storage systems (**f**), wound-healing (**g**), and controlled drug release (**h**) (adapted from de Moura et al. [36], Dai et al. [37], Ismail et al. [38], and Al-Morakam [39]) (Figure created in Biorender.com).

3.1. *Starch–TiO_2 Hybrid Material*

Starch is one of the most versatile polysaccharides with relevant applications. However, their hydrophilic nature limits their uses [26]. Therefore, the addition of inorganic compounds like TiO_2 into the starch matrix is a feasible strategy for development of functional starch-based materials with improved physicochemical properties for food and non-food packaging, photocatalyst, biomedical, and solar cell applications [3,40], as listed in Table 1.

Table 1. Effect of TiO_2 incorporation on starch matrix properties.

Application	Method/Presentation	* Composition	Relevant Results	Ref.
Food and non-food packaging	Evaporative casting/Film	Rice starch (3 g 100 mL^{-1}), TiO_2 (1% of total solid content), glycerol (1.5 g)	TiO_2 enhanced antimicrobial activity and physicochemical properties of rice starch-film.	[4]
Food and non-food packaging	Evaporative casting/Film	Corn starch (40% *w/v*), PVA (60% *w/v*), glycerol (30% *w/v*), TiO_2 (5% *w/v*)	The thermal resistance of corn starch/PVA composite was improved by adding TiO_2.	[7]
Food and non-food packaging	Evaporative casting/Film	Potato starch (60%), glycerol (40%), TiO_2 (2.5% of total mixture)	TiO_2 increased the hydrophobicity of the starch-film and improved their mechanical and thermal properties.	[19]
Food and non-food packaging	Evaporative casting/Film	Cassava starch (NI), TiO_2 (0.01% *w/w*), glycerol (NI)	The fruits treated with the hybrid film exhibited longer shelf life than that treated with petroleum-based films.	[22]
Food and non-food packaging	Condensation polymerization/Film	Corn starch (10 g 100 mL^{-1}), TiO_2 (3% of total solid content), glycerol (8 mL), HCl 0.1M (12 mL)	The hybrid material showed high-pressure resistance.	[25]
Food and non-food packaging	Evaporative casting/Film	Corn starch (16 g 100 mL^{-1}), TiO_2 (10%), glycerol (8 g)	The thermal resistance of starch-based film increased by adding TiO_2.	[26]
Food and non-food packaging	Evaporative casting/Film	Wheat starch (2 g 50 mL^{-1}), TiO_2 (4% of total solid content), glycerol (50% w/w of starch)	TiO_2 improved the thermal, mechanical, water-related, and UV-barrier properties of starch-based films.	[27]
Food and non-food packaging	Evaporative casting/Film	Starch (6 g), poly(ε-caprolactone) (100 g), TiO_2 (6 g), glycerin (18 g), ethyl alcohol (600 mL)	The starch–PCL–TiO_2 composite showed improved physicochemical properties compared to the starch–PCL film.	[32]
Food and non-food packaging	Evaporative casting/Film	Corn starch (5 g 100 mL^{-1}), TiO_2 (3%), glycerol (0.5 g)	The composite reinforced with TiO_2 showed improved mechanical properties.	[41]
Food and non-food packaging	Evaporative casting/Film	Starch (2.5 g 100 mL^{-1}), PVA (2.5 g 100 mL^{-1}), TiO_2 (0.03 g), glycerol (0.5 g)	The hybrid film showed bacteriostatic activity against *E. coli* and *L. monocytogenes* and favorable photocatalytic properties on methylene blue dye.	[32]
Food and non-food packaging	NI/Nanofluids	Corn starch (NI), PVA (NI), TiO_2 (NI)	The rheological behavior of the starch–PVA film-forming solution is influenced by TiO_2 concentration.	[33]
Food and non-food packaging	Evaporative casting/Film	Maize starch (2 g 37 mL^{-1}), PVA (2 g 38 mL^{-1}), TiO_2 (0.05% of total solid content), glycerol (1.2 g)	Starch–PVA–TiO_2 exhibited improved thermal, mechanical, and optical properties.	[42]
Food and non-food packaging	Evaporative casting/Film	Corn starch (10 g 100 mL^{-1}), PVA (10 g), TiO_2 (1% *w/w*) glycerol (3.5 g)	The mechanical properties of corn starch–PVA film were improved by adding TiO_2.	[43]
Food and non-food packaging	Evaporative casting/Membrane	High amylose starch (10 g 100 mL^{-1}), PVA (6 g 150 mL^{-1}), TiO_2 (1% w/w), glycerol (3 g 100 mL^{-1})	TiO_2 enhanced the antimicrobial activity and mechanical properties of the starch–PVA membrane.	[44]
Food and non-food packaging	Evaporative casting/Film	Wheat starch (5 g 100 mL^{-1}), TiO_2 (3% *w/w*), glycerol (40% *w/w*)	The functional properties of the starch/TiO_2 composite could be positively modified by a low UVA exposure time.	[35]

Table 1. *Cont.*

Application	Method/Presentation	* Composition	Relevant Results	Ref.
Food and non-food packaging	Evaporative casting/Film	Tapioca (65.8%) or wheat (65.8%) starch, TiO_2 (6%), glycerol (28.2%)	The effect of TiO_2 as a reinforcement agent depends on the type of starch.	[45]
Food and non-food packaging	Evaporative casting/Film	Wheat starch (1 g 100 mL^{-1}), TiO_2 (5% *w/w*), glycerol (40% *w/w*)	TiO_2 incorporation increases the hydrophobicity and UV-blocking ability of starch film.	[39]
Food and non-food packaging	Evaporative casting/Film	Wheat starch (68.1%), TiO_2 (3%), glycerol (28.9%)	The preparation method influences the functional properties of starch-based hybrid materials.	[46]
Food and non-food packaging	Evaporative casting/Film	Potato starch (1 g 100 mL^{-1}), TiO_2 (1% *w/w*), glycerol (40% *w/w*)	TiO_2 improved the thermal, water-related, and UV-barrier properties of starch-based films.	[47]
Food and non-food packaging	Evaporative casting/Film	potato starch (NI), TiO_2 (1% *w/w*)	The hybrid film showed enhanced UV-blocking properties.	[48]
Food and non-food packaging	Evaporative casting/Film	Wheat starch (5 g 100 mL^{-1}), kefiran (2 g 100 mL^{-1}), TiO_2 (3% *w/w*), glycerol (40% *w/w*)	The functional properties of the starch/kefiran/TiO_2 composite could be positively modified by a low UVA exposure time.	[49]
Food and non-food packaging	Evaporative casting/Film	Sago starch (4 g 100 mL^{-1}), CEO (2%), TiO_2 (5% *w/w*), glycerol (40% *w/w*)	The hybrid film had antimicrobial activity against *E. coli*, *S. Typhimurium*, and *S. aureus* and improved UV-barrier properties.	[50]
Food and non-food packaging	Evaporative casting/Film	Cassava starch (70 g 100 mL^{-1}), TiO_2–Al_2O_3 (2:1), glycerol (30% *w/w*)	Starch–TiO_2:Al_2O_3 showed enhanced physicochemical properties compared with the starch–TiO_2 hybrid film.	[51]
Food and non-food packaging	Evaporative casting/Film	Yellow dent corn starch (5 g 100 mL^{-1}), TiO_2:Ag (4% *w/w*), glycerol (1.9% *w/w*)	Starch–TiO_2:Ag exhibited antimicrobial activity against *E. coli* and *S. aureus*; it was enhanced in 70 and 40%, respectively, compared with the starch–TiO_2 hybrid film.	[52]
Photocatalysis	Evaporative casting/Film	Starch (5 g 100 mL^{-1}), PVA (5 g 100 mL^{-1}), TiO_2 (8%), glycerol (40%)	The hybrid film showed photocatalytic degradation of bisphenol A and 2,4-D.	[53]
Photocatalysis	Evaporative casting/Film	Starch (4 g 100 mL^{-1}), TiO_2 (0.08 g 100 mL^{-1})	The hybrid film showed a low-moderate antibacterial effect against *S. aureus*.	[54]
Photocatalysis	Evaporative casting/Film	Corn starch (1 g 100 mL^{-1}), PVA (1 g 100 mL^{-1}), PMMA-co-AM (0.6 g 100 mL^{-1}), TiO_2 (0.2 g), glycerol (0.8 g)	The hybrid film exhibited photocatalytic properties against methylene blue and acetaldehyde.	[55]
Biomedical	Evaporative casting/Hydrogel membrane	PVA (5 g), starch (3.5 g), g–C_3–N_4 (0.1 g), Ag–TiO_2 (0.7 g), water (80 mL)	In an animal model, the hybrid membrane had better wound-healing properties than a conventional cotton gauze wound dressing.	[56]
Biomedical	Evaporative casting/Composite	Wheat starch (56.2%), TiO_2 (10%), vancomycin (10%), glycerin (23.8%)	The composite exhibited antimicrobial activity and controlled drug release.	[57]
Solar cell	Evaporative casting/Nanocomposite	Rice starch–lithium iodide (65:35%), TiO_2 (2 wt.% of total solid content)	TiO_2 enhanced the conductivity of the starch/ionic liquid composite.	[24]

* Material composition was based on the best-reported results. NI: no information; PVA: polyvinyl alcohol; PCL: poly(ε-caprolactone; 2,4-D: 2,4- dichlorophenoxyacetic acid.

3.1.1. Food and Non-Food Packaging Applications of Starch–TiO_2 Hybrid Material

Most of the investigations reported in the literature for the corn starch–TiO_2 hybrid composite are focused on developing eco-friendly food and non-food packaging alternatives to existing conventional plastic packaging [26]. The reinforcement of starch film with TiO_2 promotes an increase in mechanical and thermal properties with higher degradation temperature (344 °C) compared with starch-based film (230 °C) in a dose-dependent response [7], and it exhibited high-pressure resistance (8.39 N/mm^2)

compared with the starch film (3.63 N/mm^2) [25]. Wang et al. [41] reported that the mechanical properties of the hybrid film could be influenced (negatively or positively) depending on the TiO_2 content. Moreover, the increasing hydrogen bonds and electrostatic interactions (between the –OH groups of the starch and the Ti^{2+} atoms) in the hybrid film are responsible for the improved properties. Furthermore, the starch–TiO_2 hybrid film exhibited low–moderate antibacterial activity against *S. aureus*, but not against *E. coli* [54].

Additionally, corn starch may be combined with polyvinyl alcohol (PVA) and reinforced through TiO_2 addition to fabricate ternary-hybrid films (starch–PVA–TiO_2) with enhanced functional and technological properties [58]. The addition of TiO_2 in the starch/PVA matrix improved its thermal (increased) and water resistance (increased), and moisture and oxygen (reduced) permeability through hydrogen, Ti=C bonds, and attractive electrostatic forces, where nano-TiO_2 may promote the formation of a compact and dense structure, acting as an obstacle to the diffusion of water and oxygen molecules through a hybrid film without altering the starch/PVA structure [58,59].

Kochkina and Butikova [42] mentioned that the incorporation of TiO_2 into a starch/PVA film improves their physicochemical properties and extends their functionalities. The addition of TiO_2 in small quantities (0.1% *w/w*) into a biodegradable corn starch/PVA film did not alter its structure. However, it promotes intermolecular interaction through hydrogen-bond formation, improving its thermal stability (from 190 to 230 °C) and water vapor permeability (decrease from 12.6 to 5.39×10^{-7} g/m h Pa) as well as improving its mechanical (tensile strength from 16.22 to 21.11 MPa) and UV-barrier properties. Similar findings were reported during evaluation of the mechanical (tensile strength increased) and physicochemical (swelling degree increased) properties in a corn starch/PVA film reinforced with TiO_2 nanoparticles [43].

Liu et al. [44] informed that incorporation of TiO_2 (0.6%) in a high-amylose starch/PVA-based membrane promoted a decrease in the optical transmittance with an increase in the mechanical (tensile strength to 9.53 MPa and elongation at break to 49.5%) properties of the film. The compatibility of high-amylose starch and TiO_2 were due to the formation of hydrogen and C–O–Ti bonds. They argued that TiO_2 could be adsorbed in the starch granule surface by the TiO_2–amylose (changes in the intensity and profile peaks in the range of 900–1000 cm^{-1} of the FTIR spectra) interactions that improve the miscibility of the starch/PVA structure. Furthermore, the compatibility of the TiO_2 with a starch matrix is OH availability-dependent; however, an excessive concentration of TiO_2 (>1% *w/w*) in the polymeric matrix could negatively affect the physicochemical properties of the starch/PVA films. Furthermore, the hybrid membrane showed that moderate antimicrobial activity performed by an agar test diffusion assay against *E. coli* (inhibition zone of 12.26 mm) and *S. aureus* (inhibition zone of 10.22 mm), which was attributable to the ability of TiO_2 to restrain the growth of bacteria due to its photocatalytic properties. Similar trends were reported by Lin et al. [58], who informed that a starch/PVA/TiO_2 (0.03% *w/w*) hybrid composite exhibited bacteriostatic activity against *E. coli* and *Listeria monocytogenes*, but the effect was dependent on the strain and TiO_2 content. Likewise, Ahmed et al. [56] found that the addition of TiO_2 nanoparticles in a PVA–starch–g–C_3–N_4–Ag hydrogel membrane enhanced the antibacterial activity against *E. coli* (inhibition zone of 37.33 mm) and *S. aureus* (inhibition zone of 33.25 mm).

Additionally, starch obtained from nonconventional sources like wheat, rice, tapioca, cassava, potato, and sago has been functionalized with TiO_2 nanoparticles to fabricate hybrid packaging materials. However, although nano-TiO_2 can act as a physical cross-linking agent of starch-based film, the type of starch matrix will have a significant impact on the properties of hybrid films [60].

Furthermore, in a wheat starch-based film, TiO_2 acts as a physical cross-linker agent improving its thermal stability (mass loss of 50% at 289 °C), UV-barrier (blocking >99% of UV-light), mechanical (an increase of tensile strength and Young's modulus), and water-related properties with a decrease in water vapor permeability and an increase in the hydrophobicity of the hybrid material [27,45]. However, a high amount of TiO_2 negatively affects the mechanical properties of the film, and the preparation method of the wheat starch–TiO_2 hybrid material strongly influences their physicochemical properties and potential applications [46].

The functionalization of potato starch-based films adding TiO_2 nanoparticles promotes an increase in its hydrophobicity, enhancing its water-related, mechanical, thermal, and UV-barrier properties. These facts were attributable to the stable formation of hydrogen bonds between oxygen in TiO_2 and hydrogen in C–O–H of starch, which decreases the possible active sites for water molecule retention and thermal decomposition of the starch composite [19,47]. Another root vegetable starch source for making hybrid materials is the cassava [22]. Tunma [22] developed an active packaging with the cassava starch–TiO_2 composite aimed to enlarge the shelf life of bananas and tomato fruits, finding that banana (14 days) and tomatoes (21 days) packaged in the hybrid films extended their shelf life beyond that of those packaged with petroleum-based films (5 and 10 days, respectively). Furthermore, the active material showed antibacterial activity against *Bacillus cereus* and *E. coli* through bacterial membrane alteration.

Malathi and Singh [4] informed that a rice starch-based film reinforced with TiO_2 exhibited antimicrobial activity against *E. coli* (a reduction >90% of viable cells) under UV-light (4 h), but the effect was dose-dependent, attributed to the photocatalytic activity of TiO_2 that may promote a membrane cell alteration, affecting cell viability and cell growth. Moreover, the presence of TiO_2 in the organic matrix improved the water vapor permeability, solubility, tensile strength, and elongation. According to the authors, TiO_2 can act as a physical cross-linking agent restringing segment rotation and molecular mobility between starch chains and water molecules through hydrogen bonding or O–Ti–O and C–O–Ti bonding, enhancing the physicochemical properties of the hybrid film.

Additionally, starch has been combined with other organic matrices (pectin, kefiran, cinnamon essential oil, and poly(ε-caprolactone)) and reinforced with TiO_2. Dash et al. [48] developed a biodegradable starch–pectin–TiO_2 film with enhanced UV-barrier properties for UV-sensible food and non-food compounds preservation (i.e., ascorbic acid). The addition of TiO_2 promotes a decrease in the moisture content, solubility, and moisture uptake with an increase in the thermal properties of the hybrid film in a dose-pendent manner. On the other hand, they reported that the mechanical properties of the hybrid film were negatively affected by the presence of nano-TiO_2 and mentioned that, at high concentrations, TiO_2 acts as an anti-plasticizer agent reducing the water molecule movement into the polymeric matrix, affecting the flexibility of the film. Goudarzi and Shahabi-Ghahfarrokhi [49] developed a photo-producible starch/kefiran–TiO_2 composite as a potential alternative for food packaging applications. They reported that enhanced physicochemical, water-related, and thermal properties of starch/kefiran by the presence of TiO_2 could be improved by the UV-radiation (345 nm) during a defined time (1 h).

Arezoo et al. [50] informed that sago starch film combined with cinnamon essential oil and TiO_2 showed antimicrobial activity against *E. coli*, *Salmonella* Typhimurium, and *S. aureus*. Also, their incorporation of sago starch-based film improved its mechanical, optical, and water-related properties. On the other hand, Fei et al. [32] evaluated the effects on the physicochemical properties and structure of a starch–poly(ε-caprolactone (PCL)) composite by nano-TiO_2 incorporation and reported that mechanical properties and water resistance were improved by TiO_2 addition compared with non-reinforced material, but these effects were dose-dependent with an optimum TiO_2 concentration of 6 wt%. According to the authors, the formation of intramolecular hydrogen bonds and covalent interaction (C–O–Ti bond) between starch and nano-TiO_2 promotes a decrease in the rigidity of the starch–PCL structure.

Furthermore, the functionality of starch–TiO_2 hybrid films could be enhanced by the surface modification of TiO_2 with the presence of other inorganic compounds in its network. Chueangchayaphan et al. [51] evaluated the influence of Al_2O_3 on the properties of the starch–TiO_2–Al_2O_3 hybrid composite and found that physicochemical (water contact angle, hardness, and thermal stability) properties of the ternary hybrid film improved in a Al_2O_3-dependent concentration. Similarly, Hajizadeh et al. [52] informed that the incorporation of TiO_2:Ag-doped nanoparticles into the starch matrix increased the water resistance of the hybrid film and significantly inhibited the growth of *E. coli* and *S. aureus*, associated with the antibacterial effect of TiO_2.

According to the results, the incorporation of TiO_2 into starch-based materials can improve the physicochemical, thermal, mechanical, optical, and water-related properties through covalent and noncovalent interactions with the potential to develop food and non-food packaging.

3.1.2. Other Applications of Starch–TiO_2 Hybrid Material

Other potential applications of starch–TiO_2, such as environmental remediation, biomedical, and dye-sensitized solar cells, have been investigated (Table 1). Yun et al. [53] prepared a starch/PVA film reinforced with TiO_2 and found that tensile strength, degree of swelling, solubility, and water vapor absorption were enhanced up to 1.14–1.52 times compared with films without nano-TiO_2, whereas the elongation at break was negatively affected (decreased 1.60 times). Moreover, the authors reported that the starch/PVA/TiO_2 film exhibited photocatalytic activity (under UV and visible light) against bisphenol A (degree of decomposition of 0.825 and 0.534, respectively) and 2,4-dichlorophenoxyacetic acid (decomposition degree of 0.597 and 0.396, respectively) in aqueous solution (10 ppm) after 4 h of exposure. Furthermore, starch/PVA/TiO_2 has a photocatalytic degradation efficiency of 37% against methylene blue dye (10 mg/L) after 90 min of UV-light irradiation [54]. Similarly, Yun et al. [55] developed a starch/PVA film reinforced with TiO_2 and poly(methyl methacrylate-co-acrylamide) for photocatalytic purposes. They reported that hybrid films showed photocatalytic properties against methylene blue and acetaldehyde under UVA and visible light irradiation. The photocatalytic efficiency of starch–TiO_2 hybrid materials is directly proportional to the TiO_2 concentration [61]. However, it should consider that the enhanced functional properties of starch by the addition of TiO_2 could be negatively affected by a long UVA exposure time because a rupture of polysaccharide structure may occur [35].

Additionally, Ahmed et al. [56] evaluated in vivo the wound-dressing properties of a PVA–starch–g–C_3–N_4–Ag–TiO_2 hydrogel membrane in an open excision-type wound-healing study in adult female Albino mice. They found that hybrid membranes had better-wound healing (reduction wound area of 97%) efficiency than cotton gauze (reduction wound area of 19.5%) or untreated (reduction wound area of 7.4%) groups after seven days of evolution. Nonetheless, animals treated with the hybrid hydrogel membrane showed better re-epithelization with good anti-inflammatory response than control groups, which are parameters related to the wound-healing activity. Ujcic et al. [57] developed a biodegradable wheat starch–TiO_2 composite with a controlled drug (vancomycin) release profile and bacteriostatic properties against *S. aureus* without TiO_2 release from the hybrid matrix to the medium.

Khanmirzaei and Ramesh [24] fabricated a dye-sensitized solar cell using a nanocomposite polymer electrolyte formed with a rice starch–TiO_2 hybrid material. They reported that, during solar cell development, the ionic conductivity of rice starch/ionic liquid composite was enhanced by incorporating TiO_2 with an efficiency of 0.17 at 1000 W/m^2 light intensity.

In summary, the starch–TiO_2 hybrid material exhibited photocatalytic and antimicrobial activities and good ionic conductivity for potential environmental, biomedical, and dye-sensitized solar cell applications.

3.2. Sodium Alginate–TiO_2 Hybrid Material

Sodium alginate (SA) is a degradable, nontoxic, functional, and compatible biopolymer with a wide range of applications [31,62]. Recently, several authors have combined SA with TiO_2 nanoparticles aimed to enhance the technological and functional properties of alginate-based materials (Table 2).

Table 2. Effect of TiO_2 incorporation on sodium alginate matrix properties.

Application	Method/Presentation	* Composition	Relevant Results	Ref.
Photocatalyst	Evaporative casting/Hydrogel	SA (0.5 g 50 mL^{-1}), TiO_2 (150 mg)	The hydrogel showed good adsorption and removal efficiency of methyl violet dye.	[63]
Photocatalyst	Evaporative casting/Film	SA (2 g 17 mL^{-1}), TiO_2 (0.15 g)	The hybrid film showed good photocatalytic properties against Congo red dye.	[64]
Photocatalyst	Evaporative casting/Film	SA (1 g 100 mL^{-1}), TiO_2 (10% *w/w*)	The hybrid film exhibited excellent oil/water separation efficiency and methyl orange degradation.	[37]
Photocatalyst	Freeze-drying/Composite	SA (2% *w/w*), CMC (3% *w/w*), TiO_2 (20% *w/w*), GO (0.05 g)	The SA–CMC–TiO_2:GO composite showed good photocatalytic degradation (98%) against Congo red dye.	[65]
Biomedical	Freeze-drying/Hydrogel	SA (2% *w/v*), gelatin (0.5% *w/v*), TiO_2 (0.1% *w/v*), β-tP (1% *w/v*)	The hybrid hydrogel had adequate porosity and mechanical resistance for biomedical applications.	[5]
Biomedical	Freeze-drying/Scaffolds	SA (2 g 100 mL^{-1}), TiO_2:HAp (1% *w/v*),	Hybrid scaffolds are biocompatible with the human MG-63 cell line and showed controlled drug release.	[66]
Biomedical	Evaporative casting/Patches	SA (2 g 100 mL^{-1}), PVA (16 g 100 mL^{-1}), TiO_2 (0.1 g), curcumin (0.5 g)	Hybrid biocomposite showed antimicrobial activity against *B. subtilis* and *K. pneumoniae*.	[67]
Food and non-food packaging	Evaporative casting/Film	SA (10% *w/v*), TiO_2:Au (2.5% *w/w*), glycerol (10% *w/w*)	SA–TiO_2:Au showed higher antimicrobial activity against *S. aureus* and *E. coli* than SA–TiO_2 films.	[31]
Food and non-food packaging	Evaporative casting/ Film	Zein:SA (90:10), TiO_2 (0.5%), betanin (1%)	The hybrid film showed antimicrobial activity against *E. coli* and *S. aureus*.	[68]
Dye-sensitized solar cell	Evaporative casting/Film	SA (2.5 g 100 mL^{-1}), TiO_2 (8% *w/w*)	Ionic conductivity of the SA-based film was enhanced by adding TiO_2 in a temperature-dependent response.	[69]
Molecular electronics	Evaporative casting/Membrane	Sodium alginate (4 g/90 mL), TiO_2 (5% in total solid content)	TiO_2 improved dielectric and ac-electrical conductivity properties of an SA solution.	[70]
Separation processes	Evaporative casting/Membrane	SA (4 g 100 mL^{-1}), TiO_2 (40% *w/w*), poly(styrene sulfonic acid-co-maleic acid) (0.5% *w/w*)	The hybrid membrane showed good separation of isopropanol in an alcohol–water mixture solution.	[30]

* Material composition was based on the best-reported results. NI: no information; SA: sodium alginate; β-tP: β-tricalcium phosphate; CMC: carboxymethyl cellulose; GO: Graphene oxide.

3.2.1. Environmental Applications of Sodium Alginate–TiO_2 Hybrid Material

The use of SA–TiO_2 hybrid material as a photocatalyst as an alternative to conventional catalysts has been explored [63] (Table 2). Thakur and Arobita [63], using a cross-linked SA–TiO_2 hydrogel, reported a maximum adsorption capacity of methyl violet of 1156.1 mg g^{-1} with an adsorption efficiency of 99.6% in comparison with SA-based film (85%), attributed to the presence of TiO_2 in the hybrid hydrogel, which acts as an anionic center that participates in the electrostatic attraction with methyl violet dye. Similarly, Reveendran and Ong [64] informed that an SA–TiO_2 hybrid film was effective for the degradation of Congo red (5 mg L^{-1} at pH 8) under UV-radiation (6 h) without significant losses of catalytic activity after two cycles of reuse. In general, TiO_2 favored the surface adsorption and photocatalytic degradation of dyes; however, a high dye concentration could inhibit the photocatalytic properties of TiO_2 (surface saturation) because dye molecules tend to absorb energy (light and photons), thereby reducing the generation of reactive oxygen species and hydroxyl radicals.

Dai et al. [37] developed an SA–TiO_2 hybrid aerosol as a novel oil/water separation and wastewater treatment. The hybrid aerogel showed oil/water separation efficiency of 99.7% after 60 cycles of reuse compared with sodium alginate aerogel. Furthermore, the hybrid aerogel exhibited excellent photocatalytic degradation after six repeated uses against methyl orange (>85% in 2.5 h) dye under simulated sunlight irradiation (150 min). Furthermore, Thomas et al. [65] synthesized a cross-linked SA/carboxymethyl cellulose (CMC) with nano-TiO_2 and graphene oxide (GO) composite for Congo red (30 mg L^{-1}) dye degradation under direct sunlight irradiation (240 min). They reported that

SA–CMC–TiO_2–GO (1.2 g L^{-1}) showed higher dye degradation (98%) compared to SA–CMC–TiO_2 (70%) or SA–CMC–GO (60%); nonetheless, the SA–CMC–TiO_2–GO retained its degradation efficiency up to seven consecutive cycles. The enhanced photocatalytic properties of the hybrid material were attributed to the reduction of electro-hole pair recombination by the presence of TiO_2 and GO in the polymeric matrix, generating a higher concentration of hydroxyl radical.

The addition of TiO_2 into the polymeric matrix-like sodium alginate provides a major stabilization of TiO_2, enhancing its photocatalytic and dye-removal properties.

3.2.2. Biomedical Applications of Sodium Alginate–TiO_2 Hybrid Material

The potential biomedical applications of the SA–TiO_2 hybrid material as a scaffold for tissue engineering, as a drug delivery system, and as a wound-healing material have been investigated [66]. Naik et al. [66] evaluated the application of TiO_2–Hap–SA composite scaffolds as a bone implant material. In general, the hybrid material showed controlled swelling, acceptable degradation rate, excellent bio-mineralization, and biocompatibility with high cell viability in the human MG-63 cell line. Moreover, the hybrid material exhibited a controlled drug release profile of the methotrexate drug, which are suitable characteristics for biomedical applications. Furthermore, Selvi et al. [63] fabricated sodium SA–PVA–TiO_2–curcumin patches as a wound-healing material. They found that the hybrid material reinforced with 100 μg mL^{-1} of TiO_2 promoted antibacterial activity (by agar test diffusion assay) against *Bacillus subtilis* (inhibition of 11 mm) and *Klebsiella pneumonia* (inhibition of 8 mm), attributed to the ability of TiO_2 to interact with the cell membrane, to increase its permeability, and to lead to cell death. Urruela-Barrios et al. [5] mentioned that an SA/gelatin hydrogel 3D printing reinforced with TiO_2 and β-tricalcium phosphate exhibited a potential use for tissue engineering application. The fabricated hybrid material by the micro-extrusion process exhibits adequate porosity and mechanical resistance. However, the authors mentioned that further studies are needed to prove the material's safety and biocompatibility. According to the evidence, incorporation of TiO_2 into sodium alginate is a viable strategy to enhance its biological properties.

3.2.3. Food and Non-Food Packaging Applications of Sodium Alginate–TiO_2 Hybrid Material

Table 2 lists reports on the use of the sodium alginate–TiO_2 hybrid film for food and non-food applications. Tang et al. [31] developed a degradable SA film reinforced with TiO_2:Au for food packaging applications with advanced UV- and water-barrier properties and antimicrobial capacity. The incorporation of TiO_2:Au nanoparticles into the SA matrix improved its water resistance, mainly attributed to the increase in the surface hydrophobicity of the hybrid film. Furthermore, it showed higher antibacterial activity against *S. aureus* and *E. coli* (95 and 90%, respectively) in UV-light presence compared with the SA–TiO_2 film (90 and 80%, respectively), which was associated with an enhanced TiO_2:Au electron-hole recombination, improving the photocatalytic ability of the SA–TiO_2:Au hybrid film. Additionally, the zein/sodium alginate (90:10) film functionalized with TiO_2 (0.5%) and betanin (1%) showed interesting antioxidant properties 2,2-diphenyl-1-picryl-hydrazyl-hydrate (DPPH, radical scavenging of 64%) without toxicity effects on endothelial cells and high antimicrobial activity (by agar test diffusion assay) against *E. coli* (inhibition zone of 15.4 mm) and *S. aureus* (inhibition zone of 16.9 mm), which exhibited potential to be used for the preservation of fresh foods [68].

In general, the SA–TiO_2 hybrid material can overcome the disadvantages of conventional nano-photocatalysts, which are hard to recycle. Furthermore, the obtained hybrid composite could be a low-cost and eco-friendly alternative for the removal and degradation of dyes from aqueous solutions.

3.2.4. Other Applications of Sodium Alginate–TiO_2 Hybrid Material

Other investigated applications of the sodium alginate–TiO_2 hybrid composite include the separation process, dye-sensitized solar cell, and molecular electronics [30,69,70]. Premakshi et al. [30] used a cross-linked SA-based membrane with TiO_2 for dehydration of isopropanol by pervaporation. They reported that the hybrid membrane showed improved separation ability for the water–isopropanol system and suggested that the membrane exhibited high selectivity toward water molecules even with higher water concentrations in the feed (flux of 25×10^2 kg/m^2 h), associated with the ability of TiO_2 to form hydrogen-bonding interactions with the sodium alginate and water molecules. Furthermore, the SA–TiO_2 membrane showed enhanced mechanical and thermal properties in a dose-dependent response with an optimum concentration of TiO_2 of 10% *w/w*.

Uddin et al. [69] developed an SA–TiO_2 film for dye-sensitized solar cell applications to increase the ionic conductivity and to reduce the fragility of electrodes. They reported that the highest conductivity was achieved with 8% of TiO_2 (0.0472 S/m) at room temperature, which increased by 38% with an increase of the temperature (25 to 64 °C) due to nano-TiO_2 creating overlapping paths in the hybrid network which allowed the charge carriers to pass through the less resistant routes. However, at high TiO_2 concentration (>8%), electrodes were fragile and unstable. According to Peining et al. [16], the conductivity efficiency of the hybrid electrodes was improved because TiO_2 may act as a scattering center, reflecting the photons into the electrode. Furthermore, the hybrid composite showed improved mechanical and optical properties compared to a pure sodium alginate film in a dose-dependent manner, which was associated with the hydrogen-bond formation between both components and the increase in the π-conjugated system. Likewise, Padma et al. [70] prepared an SA-based membrane reinforced with TiO_2 nanoparticles for molecular electronics applications and found that the membrane-forming solution showed improved dielectric properties and ac-electrical conductivity with better thermal stability (250 °C) than the sodium alginate membrane (180 °C).

According to these data, the SA–TiO_2 hybrid material showed potential separation processes, sensitized solar cells, and molecular electronics applications.

3.3. *Cellulose–TiO_2 Hybrid Material*

Cellulose is an organic compound that can form intra- and intermolecular interactions with inorganic compounds [71,72]. For this reason, it is an excellent candidate for supporting nano-TiO_2 (Table 3).

Table 3. Effect of TiO_2 incorporation on cellulose-based materials properties.

Application	Method/Presentation	* Composition	Relevant Results	Ref.
Food and non-food packaging	Sol-gel/Coating	MFC–TiO_2 (0.74:1)	The sol-gel method is a viable strategy for cellulose–TiO_2 hybrid materials development.	[11]
Food and non-food packaging	Evaporative casting/ Film	CMC (2g 50 mL^{-1}), TiO_2 (2% *w/w*), glycerol (50% *w/v*)	TiO_2 improved the mechanical, thermal, and antimicrobial properties of CMC-based film.	[21]
Food and non-food packaging	Evaporative casting/ Film	HMC (NI), TiO_2 (0.001 g 100 mL^{-1})	The hybrid film exhibited significant antimicrobial activity against *S. aureus* and *E. coli*.	[36]
Food and non-food packaging	Evaporative casting/ Film	Wheat gluten (9 g 100 mL^{-1}), cellulose (7.5% in gluten content), TiO_2 (0.6% in gluten content), glycerol (2% *w/v*)	The hybrid film showed improved antimicrobial activity against *S. cerevisiae*, *E. coli*, and *S. aureus*.	[73]
Food and non-food packaging	Evaporative casting/ Film	CMC (1.5 g 100 mL^{-1}), Na-MMT (5%), TiO_2 (1%)	The hybrid film exhibited remarkable UV-light blocking properties.	[74]
Food and non-food packaging	Casting/Film	WPI (10% *w/v*), cellulose (1% *w/v*), glycerol (6% *w/v*), TiO_2 (1% *w/v*), REO (2% *w/v*)	Coated meat treated showed acceptable microbial quality without changes in sensory attributes for 6 days at 4 °C.	[75]
Food and non-food packaging	Casting/Film	WPI (10% *w/v*), cellulose (1% *w/v*), glycerol (6% *w/v*), TiO_2 (1% *w/v*), REO (2% *w/v*)	Meat treated with the hybrid film showed reduced lipid peroxidation during cold storage.	[76]
Food and non-food packaging	Evaporative casting/Film	WPI (10% *w/v*), cellulose (1% *w/v*), glycerol (6% *w/v*), TiO_2 (1% *w/v*), REO (2% *w/v*)	The hybrid film exhibited antimicrobial and antioxidant activities.	[77]
Food and non-food packaging	Mixing/Film	Cellulose (0.3% *w/v*), TiO_2 (0.15% *w/v*), PVA (3% *w/v*), glycerol (1% *w/v*)	Hybrid composite did not show toxicity in normal cells and did not affect the typical intestinal bacteria profile.	[78]
Photocatalyst	Phase inversion technique/Film	Cellulose:TiO_2:water (81:12:7)	The hybrid film showed high methylene blue degradation under UVA and visible light.	[71]
Photocatalyst	Casting/Film	Hydroxypropyl methylcellulose (4 g 100 mL^{-1}), TiO_2 (1 *wt*%), glycerol 25 (*wt*%)	The hybrid composite showed barrier, thermal, mechanical, physicochemical, and structural properties appropriate to degrade ethylene or other substrates	[79]

Table 3. *Cont.*

Application	Method/Presentation	* Composition	Relevant Results	Ref.
Photocatalyst	Sol-gel/Composite	The TiO_2–cellulose mass ration of 0.5	The TiO_2–cellulose composite showed a photocatalytic reduction of Ag(I) to Ag and Au(III) to Au.	[80]
Photocatalyst	Sol-gel/Fibers	Cellulose fiber (NI), TiO_2 (0.02 mol 50 mL^{-1} of isopropanol)	The hybrid film showed high adsorptive and photocatalytic properties against methylene blue dye under simulated sunlight.	[81]
Photocatalyst	Sol-gel/Coating	Cellulose (NI), TiO_2 (NI)	TiO_2 coated in cellulose showed photocatalytic degradation against phenol dye.	[82]
Photocatalyst	Dip coating/Film	Cellulose (NI), TiO_2 (NI)	The hybrid composite showed Rhodamine B degradation.	[83]
Photocatalyst	Evaporative casting/Hydrogel	Cellulose (7% *w/w*), TiO_2 (0.7% *w/w*), carrageenan (5.6% *w/w*)	Ternary hydrogel exhibited enhanced adsorptive and photocatalytic properties against methylene blue dye.	[84]
Photocatalyst	Casting/Film	Paper stock (0.1 g) TiO_2: Ag (40% *w/w*)	The hybrid composite showed stable degradation rates of methyl orange dye up to six catalytic cycles.	[85]
Textile	Sol-gel/Coating	Cotton pulp (NI), TiO_2 (NI)	The hybrid coating exhibited UV-barrier properties.	[86]
Textile	Sol gel/Coating	Cellulose (10% *w/v*), TiO_2 (5% *w/v*)	Hybrid material showed self-cleaning properties without affecting the comfort properties of cotton fabrics.	[87]
Textile	Sol-gel/Coating	Cellulose (5 g L^{-1}), TiO_2:SiO_2 (NI)	The hybrid coating showed stain degradation under sunlight conditions.	[88]
Ammonia gas sensor	Electrospinning and immersion/Nanofibers	Cellulose nanofibers (NI), TiO_2 (NI), polyaniline (NI)	Cellulose/TiO_2–polyaniline showed higher gas–ammonia sensitivity performance than cellulose–polyaniline.	[89]

* Material composition was based on the best-reported results. NI: no information; MFC: micro-fibrillated cellulose; CM; CMC: carboxymethyl cellulose; HCM: hydroxypropyl methylcellulose; Na-MMT: sodium montmorillonite; WPI: whey protein isolate; REO: rosemary essential oil.

3.3.1. Food and Non-Food Applications of Cellulose–TiO_2 Hybrid Material

Table 3 lists the work on cellulose-based materials functionalized with TiO_2 for food and non-food packaging development with beneficial properties. The sol-gel method is a viable strategy to developed cellulose–TiO_2 hybrid materials [11]. In general, the incorporation of TiO_2 into the cellulose matrix improved mechanical, thermal, UV-light blocking, and water-related properties in a dose-dependent manner, attributed to the strong interactions between TiO_2 and –OH functional groups of carboxymethyl cellulose (CMM) structure. However, a high amount of TiO_2 and an inhomogeneous dispersion through films negatively affects its physicochemical (thermal, mechanical, and water-barrier) properties. Furthermore, the CMC–TiO_2 showed antimicrobial activity against *E. coli* and *S. aureus*, associated with the reactive oxygen species (ROS) generation ability of TiO_2 with cell growth inhibition properties [21,36,79].

El-Wakil et al. [73] informed that the wheat gluten–nanocellulose–TiO_2 hybrid film could be a viable alternative for the development of food active packaging materials. The hybrid film showed antimicrobial activity (reduction of viable cells of 98.5%) against *Saccharomyces cerevisiae*, *E. coli*, and *S. aureus* through oxidation of bacteria cell membranes. Fathi-Achacholouei and Zahedi [74] reported that a carboxymethyl cellulose–sodium montmorillonite (5%)–TiO_2 (1%) hybrid composite showed enhanced UV-light blocking (removing more than 98% of visible light), mechanical (an increase of tensile strength and elongation at break), thermal (glass transition increased from 72 to 80.3 °C), and water-related (moisture uptake reduction in 40%) properties compared with a carboxymethyl cellulose-based film.

Alizadeh-Sani et al. [75] evaluated the efficacy of a whey protein isolate–cellulose nanofiber functionalized with TiO_2 (1% *w/w*) and rosemary essential oil (REO, 2% *w/w*) in the preserving quality (microbial deterioration and sensory attributes) parameters of refrigerated meat during storage (4 °C). They reported that the lamb meat treated with the hybrid film showed acceptable microbial quality (total viable count of 4.1 log colony-forming unit (CFU) g^{-1}) after six days of storage without changes in color, odor, texture, and overall acceptability. Moreover, the treated meat showed reduced lipid oxidation during storage, associated with the presence of antioxidant compounds (80% of radical scavenging by DPPH assay) into the film [76]. Additionally, the TiO_2 and REO incorporation in a whey protein isolate/cellulose nanofiber film improve mechanical and water-related properties with a decrease in its transparency. Also, the hybrid film showed remarkable antimicrobial activity against pathogenic bacteria (*L. monocytogenes, E. coli* O157:H7, *S. enteritidis*, and *P. fluorescens*) in a dose-dependent response, attributed to the presence of TiO_2 and bioactive compounds (polyphenol) in the REO, altering the cell membrane and finally cell death [74]. Furthermore, the authors informed that a low content of TiO_2 migrated from the polymeric matrix to the meat product but was under Food Drug Administration (FDA) limit recommendations [76].

Yu et al. [78] used a cellulose nanofibril–TiO2 hybrid composite as a reinforcement agent for the development of PVA-based packaging. The mechanical and UV-barrier properties improved in the presence of the cellulose–TiO_2 hybrid composite. Furthermore, the PVA–cellulose–TiO_2 composite did not show toxicity against cancerous (Caco-2 cell) and normal colon cells in a concentration of one mg mL^{-1}, whereas the cells showed epithelial integrity and viability (membranes, mitochondria, and nuclei were normal and without the presence of TiO_2 nanoparticles within the cells), associated with the strong interaction between cellulose and TiO_2 avoiding the nanoparticle release from the hybrid material to the medium. Furthermore, the hybrid material did not affect the typical intestinal bacteria (*E. coli, Lactobacillus acidophilus*, and *Bifidobacterium animalis* Bif-g cells). On the other hand, the addition of the carboxymethyl cellulose–TiO_2 hybrid composite into the PVA system could negatively affect the mechanical and barrier properties as a result of a saturation of the polymeric matrix [90].

To summarize, research-based reports support that incorporation of TiO_2 into the cellulosic matrix improved the technological (mechanical, thermal, UV-protective, and water-related) properties of cellulose-based materials with potential food and non-food packaging applications.

3.3.2. Environment Applications of Cellulose–TiO_2 Hybrid Material

Usage of cellulose as a supporting material of TiO_2 for removal and degradation of diverse organic and inorganic pollutants from aqueous media have been explored [70]. Miao et al. [74] fabricated a cellulose–TiO_2 mesoporous hybrid material capable of reducing Ag(I) into Ag and Au(III) to Au through photocatalytic reactions. Uddin et al. [81] prepared photoactive fibers combining cellulose and TiO_2 nanoparticles for photocatalytic purposes. They found that hybrid materials showed adsorptive and photocatalytic activities against methylene blue (0.05% *w/v*) and heptane-extracted bitumen fraction (0.2 *w/v*% of a mixture of heavy aromatic hydrocarbons) under simulated sunlight with catalytic properties even after 20 reaction cycles and without cellulose-support degradation.

Zeng et al. [82] reported that TiO_2 immobilization in a cellulose matrix is a viable alternative for removal and photocatalytic degradation of water-dye pullulans, which is low-cost and easy to be applied. They found that a macroporous hybrid structure formed among cellulose and TiO_2 (through electrostatic and hydrogen-bonding interactions) showed efficient adsorptive and photocatalytic properties against phenol dye. Furthermore, immobilized TiO_2 nanoparticles on cellulose supports have been used for Rhodamine B degradation under UV-radiation (120 min) through the de-ethylation process promoted by •OH radicals adsorbed onto the surface of hybrid material and associated with the hydrophobicity/hydrophilicity of TiO_2-coated samples, which is pH-dependent (decreased while increased pH from 1.5 to 6) [83].

Additionally, ternary cellulose-based hybrid materials have been developed to improve the photocatalytic properties of cellulose–TiO_2. Jo et al. [84] fabricated a cellulose/carrageenan–TiO_2 hybrid hydrogel with enhanced adsorptive and photocatalytic (removal of 115.3 mg g^{-1} with 85% of degradation) properties against methylene blue (60 mg L^{-1}) compared with cellulose–TiO_2 (removal of 0.8 mg g^{-1} with 33% of degradation) and cellulose (without effect) materials under UV-radiation (254 nm) after 3 h of exposure in a carrageenan dose-dependent and its adsorptive properties.

Wang et al. [85] investigated the photocatalytic and antimicrobial activity of a cellulose fiber-based paper filled with TiO_2:Ag (40% *w/w*) nanoparticles. They reported that the cellulose–TiO_2:Ag hybrid film exhibited stable degradation rates (0.95) against methylene orange (0.02 g L^{-1}) in an aqueous solution under UV-radiation (254 nm) after four hours of exposure in comparison with a cellulose–TiO_2 (0.90) film with good efficiency after three photocatalytic cycles (degradation rate of 0.95 and 0.85, respectively), but the effects were in a TiO_2:Ag nanoparticles dose-dependent response. Furthermore, the hybrid material showed antibacterial activity against *E. coli*, where photocatalytic and antimicrobial activities were attributable to silver ion release.

Mohamed et al. [71] informed that a cellulose–TiO_2:N-doped hybrid film showed remarkable photocatalytic activity under UVA (30 W at 312 nm) and visible (30 W at >420 nm) light for methylene blue (40 mg L^{-1}) degradation (96 and 78%, respectively) after 360 min of exposure. They mentioned that the presence of nitrogen atoms into the TiO_2 network through hydrogen-bonding interactions (Ti–O–C) enhances the absorption energy of the hybrid film, promoting high catalytic activity.

In general, immobilization of TiO_2 onto a cellulose matrix is a feasible way to improve the adsorptive, photocatalytic, and antimicrobial properties of cellulose-based materials, which are suitable for removal of pollutants from aqueous media.

3.3.3. Other Applications of Cellulose–TiO_2 Hybrid Material

Other investigated applications of the cellulose–TiO_2 hybrid composite include textile (UV-protective and self-cleaning properties) and ammonia gas sensors. The introduction of TiO_2 nanoparticles in a cellulose matrix improved the UV-protective properties, associated with the optical and light scattering capability of TiO_2 [86]. Kale et al. [87] developed cotton fabric self-cleaning by coating cellulose–TiO_2 on its surface with stable properties after ten washing cycles in a dose-dependent manner. On the other hand, the self-cleaning properties of a cellulose–TiO_2 coating could be negatively affected by the surface modification of TiO_2 with SiO_2 (cellulose–TiO_2:SiO_2) [88].

Pang et al. [89] developed a cellulose/TiO_2–polyaniline (PANI) hybrid composite through P–N heterojunctions to improve ammonia-sending properties in a homemade test system at room temperature and reported that cellulose–TiO_2–PANI showed higher gas sensitivity performance than the cellulose–PANI sensor, associated with the P–N heterojunction at the interface of PANI and TiO_2 nanoparticles.

According to the evidence, the cellulose–TiO_2 hybrid material could be used for the development of fabric cotton and biosensors with advanced properties.

3.4. Chitosan–TiO_2 Hybrid Material

Chitosan is a deacetylated form of chitin with a poly-cationic character and is nontoxic, biodegradable, and biocompatible with organic and inorganic compounds [91]. Recently, a detailed review of the chitosan–TiO_2 hybrid composite has been published [1]. It is a versatile hybrid material with enhanced physicochemical, mechanical, and barrier properties with diversified applications that include antimicrobial, environmental, biomedical, and food and non-food packaging applications [1]. Nonetheless, further studies on the chitosan–TiO_2 applications have emerged (Table 4).

Table 4. Effect of TiO_2 incorporation on chitosan-based materials properties.

Application	Method/ Presentation	* Composition	Relevant Results	Ref.
Photocatalysts	γ-radiation-induced copolymerization/Hydrogel	CS (NI), AA (NI), TiO_2 (1 wt.%)	CS–AA–TiO_2 hydrogels showed a major removal percentage of MB compared to CS-AA hydrogel.	[92]
Photocatalysts	Evaporative casting/Film	CS (0.64% *w/v*), PVDC (20 mL), TiO_2:Au (20 mg)	The hybrid film showed 70 to 90% of EtBr dye removal with 60% of it photodegraded in the first 60 min under sunlight.	[93]
Photocatalyst	Evaporative casting/Film	CS (NI), TiO_2 (NI)	Tetracycline degradation using the chitosan–TiO_2 hybrid composite is multifactorial-dependent.	[94]
Photocatalyst	NI/Disks	CDF (0.04g), CS (0.2 g), TiO_2 (0.05g)	CDF–CS–TiO_2 showed enhanced antibacterial activity against *E. coli* (99%) compared with CDF (93%).	[95]
Photocatalyst	Evaporative casting/Film	CS (1 g 100 mL^{-1}), TiO_2 (2 g 100 mL^{-1})	The hybrid composite showed good removal of turbidity efficiency from wastewater.	[96]
Food and non-food packaging	Microwave-assisted/Film	CS (0.5 g 50 mL^{-1}), TiO_2 (0.5 g)	Chemical synthesis of CS–TiO_2 films enhanced thermal stability compared to physical synthesis.	[97]
Food and non-food packaging	Evaporative casting/Film	PVA–CS (80:20), TiO_2 (NI)	The swelling properties of PVA–CS–TiO_2 were pH-dependent.	[98]
Food and non-food packaging	Evaporative casting/Film	CS (0.5 g 50 mL^{-1}), TiO_2:Ag (10% *w/v*)	The elasticity of CS-based films could be affected by high amounts of TiO_2:Ag nanoparticles.	[99]
Food and non-food packaging	Evaporative casting/Film	CS (2 g 100 mL^{-1}), TiO_2 (1% *w/v*), CCEO (1.5%), glycerol (0.75 mL g^{-1} chitosan)	Hybrid film is effective in extending the shelf life of minced meat in 10 days at cold storage.	[100]
Biomedical	Evaporative casting/Film	CS (0.5 g 100 mL^{-1}), TiO_2 (10% *w/v*)	The hybrid film showed better wound-healing properties than chitosan-based film.	[101]
Biomedical	Coating/Foam	NI	Mattress coated with CS–TiO_2 showed antimicrobial activity against *S. aureus*.	[102]
Cosmetic	Wet impregnation/Hydrogel	CS (NI), TiO_2 (10%), CMC (NI)	The CS–CMC–TiO_2 hydrogel showed a low–moderate solar protection factor with an antibacterial effect against *E. coli*.	[103]
Cosmetic	NI/Hydrogel	CS (0.2 g 100 mL^{-1}), TiO_2 (0.05g), H_2O_2 (6%)	Hydrogel showed good bleaching effects on the tooth surface	[104]

* Material composition was based on the best-reported results. NI: no information; CS: chitosan; PVA: polyvinyl alcohol; AA: acrylic acid; PVDC: polyvinylidene chloride; CDF: ceramic disk functionalized; CCEO: *Cymbopogon citratus* essential oil.

3.4.1. Environmental Applications of Chitosan–TiO_2 Hybrid Material

The Chitosan–TiO_2 hybrid composite has been used for the removal and degradation of diverse organic compounds from aqueous media under UV-light irradiation. Mahmoud et al. [92] prepared a chitosan–acrylic acid (CS–AA) hydrogel reinforced with nano-TiO_2 with enhanced swelling and adsorptive properties for methylene blue dye removal from aqueous solution (20 mg L^{-1}). They informed of a remarkable change in the adsorption rate of MB (90%) using the CS–AA–TiO_2 hybrid hydrogel (0.20 g) compared with CS-AA (60%) in pH-dependent response with an optimum pH value of 10, mainly associated with the porosity and large surface area of the hybrid hydrogel. El-Ella et al. [93] investigated the carcinogenic ethidium bromide (EtBr) efficiency degradation (in aqueous media at pH 12 and aeration condition) using a chitosan–polyvinylidene–TiO_2:Au hybrid composite under sunlight conditions (400–600 W/m^2). They found that the hybrid film removes 70 to 90% of the EtBr dye, where 60% of it was photodegraded in the first 60 min. According to the authors, the pH of the medium and aeration promotes •OH formation, facilitating dye adsorption and photodegradation. Additionally, Ikhlef-Taguelmimt et al. [94] immobilized TiO_2 nanoparticles into chitosan support for tetracycline (TC) degradation under UV-irradiation (360 nm at 30 W). The efficiency removal (87%) was dependent on agitation speed in the batch system and TiO_2 concentration; moreover, the efficiency was TC concentration-dependent with a decrease when increased from 30 to 40 mg L^{-1}

after 60 min of reaction, associated with the saturation of active sites by agglomeration on the catalyst surface, decreasing light absorption capacity, and leading photocatalytic properties.

Xu et al. [95] functionalized a ceramic disk filter (CDF) with the chitosan–TiO_2 hybrid composite for bacterial removal from drinking water. They reported that CDF–chitosan–TiO_2 showed enhanced *E. coli* removal (99%) from contaminated water (1×10^6 CFU mL^{-1}) compared with CDF (93%), mainly attributed to the direct interaction of bacteria (negative charge) with the chitosan–TiO_2 (positive charge) composite and the oxidative stress in cell membrane from ROS generated by TiO_2. Moreover, they explain that the ROS generation of TiO_2 is enhanced by the presence of chitosan due to the prevention of radical recombination, inhibiting oxygen reduction and water oxidation. Furthermore, Marey [96] reported that the chitosan–TiO_2 composite is a viable strategy for removing turbidity (total solid soluble (TSS)) from wastewater because the hybrid composite showed adsorption (efficiency TSS removal of 18% nephelometric turbidity unit (NTU)) and photocatalytic (under visible light) properties in pH-dependent response, associated with the poly-cationic properties of chitosan.

In summary, chitosan-based materials functionalized with TiO_2 nanoparticles could be a viable, low-cost, and efficient alternative for water treatment.

3.4.2. Food and Non-Food Applications of Chitosan–TiO_2 Hybrid Material

In general, the physicochemical properties of chitosan have been improved by the incorporation of TiO_2 nanoparticles. Hussein et al. [97] reported that chitosan–TiO_2 composites via the chemical route (291 °C) showed enhanced thermal stability compared to the physically prepared (273 °C) and chitosan-based (240 °C) material. Nugraheni et al. [98] informed that the PVA–chitosan–TiO_2 hybrid membrane showed enhanced swelling properties in alkaline conditions (pH 10) compared with the acidic conditions (pH 4), associated with the protonation of an amine group from chitosan in acidic conditions. On the other hand, the physical interaction of TiO_2:Ag with chitosan influences the properties of the hybrid film, and high amounts of TiO_2:Ag nanoparticles could affect the plasticizing or elasticity of chitosan-based films due to the agglomeration of particles into the polymeric matrix [99]. Additionally, the chitosan–TiO_2 composite has been used for food preservation. Hosseinzadeh et al. [100] evaluated the chitosan-based film reinforced with TiO_2 (1% *w/v*) and *Cymbopogon citratus* essential oil (1.5% *w/v*) for preserving quality (microbial, physicochemical, and sensory) parameters of minced meat at cold storage (4 °C). They reported that minced meat treated with the hybrid film showed acceptable microbial quality (total viable count of <7 log CFU g^{-1}) after 10 days of storage without significant changes in pH values (5.94 to 6.83) and organoleptic (color, odor, and taste) properties.

Evidence indicates that chitosan functionalized with TiO_2 showed enhanced physicochemical, antimicrobial, and barrier-protective properties for the development of diverse packaging materials.

3.4.3. Biomedical and Cosmetic Applications of Chitosan–TiO_2 Hybrid Material

The potential biomedical and cosmetic applications of the chitosan–TiO_2 hybrid composite have been explored. Hanafy et al. [101] informed that the hybrid composite formed by chitosan and TiO_2 exhibited inhibition growth against *Bacillus cereus* (85%), *S. aureus* (79%), *Candida albicans* (46%), *Aspergillus niger* (81%), and *E. coli* (60%). Furthermore, in an open excision-type wound-healing study in adult female rats, the hybrid film recovered faster (98% of closure after 14 days of surgery) than chitosan-based films (86% of closure after 14 days of surgery) and promoted cell growth and higher re-epithelization processes without scar formation. On the other hand, Cheng et al. [102] coated chitosan–TiO_2–Ag nano-powder on a bendable double mattress for antibacterial purposes. According to the authors, it showed an antibacterial effect against *S. aureus* (inhibition of 99%), which can reduce the incidence of bedsores in patients and can reduce the frequency of mattress disinfection, decreasing cleaning costs.

Petrick et al. [103] fabricated a chitosan–TiO_2 composite as an active ingredient for the development of a multifunctional sunscreen composed of water and carboxymethyl cellulose as an emulsifier.

They reported that hybrid cream (with 10% of TiO_2) showed a moderate UV-protection effect (solar protection factor of 21.4); moreover, it exhibited excellent antimicrobial disinfection against *E. coli* (99.7%) within two hours, mainly by the photocatalytic properties of TiO_2 in visible light. Moreover, Kolsuz-Ozcetin and Surmelioglu [101] informed that an experimental 6% hydrogen peroxide hydrogel combined with the chitosan–TiO_2 composite provided effective bleaching without adverse effects on the tooth surface, which can be potentially employed for preventing dental-related problems. They argue that TiO_2 accelerates the bleaching reaction under UV-light at 385 nm.

In summary, the chitosan–TiO_2 hybrid composite exhibited enhanced antimicrobial, wound-healing, and UV-protective properties for biomedical and cosmetic applications.

3.5. Other Polysaccharides Functionalized with TiO_2

Additionally, other nonconventional polysaccharides such as gellan gum, agar, gelatin, and pullulan among others have been functionalized with TiO_2 to enhance their technological and functional properties (Table 5).

Table 5. Effect of TiO_2 incorporation on nonconventional polysaccharide-based materials properties.

Application	Method/Presentation	* Composition	Relevant Results	Ref.
Food and non-food packaging	Evaporative casting/Film	k-Carrageenan (0.6 g), xanthan gum (0.1 g), gellan gum (0.2 g), TiO_2 (5% *w/w*), glycerol (2 g)	TiO_2 enhanced the physicochemical properties of the biopolymer mixture film.	[17]
Food and non-food packaging	Evaporative casting/Film	Pullulan (4 g 100 mL^{-1}), TiO_2 (0.04 g 100 mL^{-1}), glycerol (0.6 g 100 mL^{-1})	TiO_2 improved the mechanical and water-barrier properties of pullulan in a dose-dependent response.	[20]
Food and non-food packaging	Evaporative casting/Film	Gellan gum (1 g 100 mL^{-1}), TiO_2 (0.01 g 100 mL^{-1})	The hybrid film showed antimicrobial activity against *S. aureus*, *Streptococcus sp.*, *E. coli*, and *P. aeruginosa* without changes in the film transparency.	[33]
Food and non-food packaging	Wet spinning process/Fiber	Agar (13.6 g 100 mL^{-1}), TiO_2 (0.3 g 100 mL^{-1})	Hybrid fibers showed improved mechanical, water- and UV-barrier properties.	[105]
Food and non-food packaging	Evaporative casting/Film	Agar (1 g 100 mL^{-1}), carrageenan (1 g 100 mL^{-1}), TiO_2 (1% *w/w*), glycerol (30% *w/w*)	TiO_2 enhanced the mechanical, UV-barrier, and water-related properties of the agar–carrageenan film.	[34]
Food and non-food packaging	Evaporative casting/Film	Agar (1.5 g 100 mL^{-1}), gelatin (4 g 100 mL^{-1}), TiO_2 (0.5 g), glycerol (35% *w/v*)	The hybrid film showed marked UV-light scattering ability and improved water resistance.	[106]
Food and non-food packaging	Evaporative casting/Film	Agar (1.5 g 100 mL^{-1}), gelatin (4 g 100 mL^{-1}), TiO_2 (0.5 g), glycerol (35% *w/v*)	The hybrid film could retard fish oil oxidation.	[107]
Food and non-food packaging	Evaporative casting/Film	Guar gum (NI), TiO_2 (NI), glycerol (NI)	The coated fruits maintained quality parameters and increased the shelf life up to 8 weeks at 0 °C.	[108]
Food and non-food packaging	Evaporative casting/Film	BPSG (4% *w/w*), MPEO (4% *w/v*), TiO_2 (2% *w/w*), glycerol (2% *w/w*), PEG (4% *w/w*)	The hybrid film showed higher antimicrobial activity against gram-positive bacteria than gram-negative bacteria.	[109]
Food and non-food packaging	Solvent casting/Film	JFPS (10 g 100 mL^{-1}), TiO_2 (3% *w/w*), glycerol (3 g g^{-1} of JFP)	The hybrid film showed antimicrobial activity against *E. coli* and *S. aureus*.	[110]
Food and non-food packaging	Evaporative casting/Film	SSPS (2.4 g 40 mL^{-1}), TiO_2 (5% *w/w*)	The physicochemical properties of SSPS-based films were improved by adding TiO_2.	[111]
Biomedical	Evaporative casting/Biofilm	Gellan gum (1 g 100 mL^{-1}), TiO_2 (1% *w/w*)	Hybrid biofilm promoted cell proliferation and cell migration to accelerate the open-excision wound-healing process in an animal model.	[38]
Biomedical	Evaporative casting/Biofilm	Gellan gum (1 g 100 mL^{-1}), TiO_2 (1% *w/w*)	Hybrid biofilm is compatible with 3T3 mouse fibroblast cells and showed accelerated re-epithelialization without an inflammatory phenomenon in an animal model.	[112]

* Material composition was based on the best-reported results. NI: no information; BPSG: bean pod shell gum; MPEO: *Mentha pulegium* essential oil; PEG: polyethylene glycol; JFPS: jackfruit filum polysaccharide; SSPS: soluble soybean polysaccharide.

3.5.1. Food and Non-Food Applications of Nonconventional Polysaccharides Functionalized with TiO_2

Table 5 lists reports on the use of the chitosan–TiO_2 hybrid material for developing food and non-food packaging applications. Li et al. [105] developed hybrid agar–TiO_2 fibers through the wet spinning process with enhanced mechanical, and water- and UV-barrier properties, which were associated with the optical and hydrophilic properties of TiO_2 nanoparticles. Moreover, the mechanical, UV-barrier, and water-related properties in an agar–carrageenan film were enhanced by the addition of 1% *w/v* of nano-TiO_2 [34]. Similar trends were reported when TiO_2 was added in a film composed of a mixture of K-Carrageenan, xanthan gum, and gellan gum (mechanical, thermal, and water- and UV-barrier properties improved); moreover, it exhibited partial inhibition of *S. aureus* [17].

Vejdan et al. [106] studied the effect of TiO_2 incorporation in a fish gelatin/agar bilayer film. They found that the addition of TiO_2 at low levels (<0.5 g/100 mL) positively influenced the water-related, mechanical, and UV-barrier properties of the hybrid film. However, higher concentrations of TiO_2 (>0.5/100 mL) lead to a reduction of mechanical properties due to an inhomogeneous dispersion and agglomeration of inorganic particles in the polymeric matrix. Furthermore, the gelatin/agar–TiO_2 could be a viable alternative for preventing fish oil oxidation, mainly by its low light transmission through the hybrid film capability [107].

Abdel-Baky et al. [108] reported that edible guar gum-based films incorporated with nano-TiO_2 can maintain quality (soluble solids content, color, acidity, total phenol, and flavonoid compounds) attributes of some dates (Medjool and Barthy) during cold storage (for 8 weeks at 0 °C with 75% relative humidity) without microbial pollution (psychrophilic bacteria, mold, and yeast) growth. According to the authors, the hybrid film generates a low oxygen/high carbon dioxide microclimate, providing a physical barrier that decreases metabolic processes and prevents dehydration and microbial deterioration of the fruits.

Nasiri et al. [109] informed that bean pod shell gum combined with *Mentha pulegium* essential oil (4% *w/w*) and TiO_2 (2% *w/w*) showed antimicrobial activity against *S. aureus*, *B. cereus*, *E. coli*, *S. typhoid*, and *P. aureginosa*. Gram-positive bacteria were more susceptible than gram-negative bacteria, which was related to the type of bacteria (cell physiology–morphology) and attributed by the variation on their cell wall.

Jin et al. [110] prepared a hybrid film composed of jackfruit filum polysaccharides and nano-TiO2 (JFPT) using the solvent casting method for food and non-food packaging purposes. The addition of TiO_2 decreased the transparency, moisture uptake, and soluble matter of the hybrid film, and the mechanical and thermal properties were enhanced, which were ascribed to the formation of strong inter- and intramolecular interactions between the biopolymer and TiO_2 nanoparticles. Furthermore, the JFPT composite showed higher antimicrobial activity against *E. coli* (79%) than *S. aureus* (60%), which was associated with the inherent differences of each bacteria cell wall structure and the ability of TiO_2 to generate ROS to inactivate bacteria by causing cell lysis.

Salarbashi et al. [111] functionalized a soluble soybean polysaccharide with TiO_2 and found that swelling degree, water vapor permeability, and thermal and mechanical properties considerably improve in a dose-dependent response. Furthermore, the hybrid film showed antimicrobial activity against *Staphylococcus epidermis* (4 mg mL^{-1}) and *Penicillium expansum* (2.5 mg mL^{-1}), attributed to the catalytic properties of $TiO_{2,}$ affecting the viability of the cells.

Liu et al. [20] reported that mechanical, and water- and UV-barrier characteristics of pullulan-based films were improved by the presence of TiO_2 in a dose-dependent manner, associated with the formation of intermolecular hydrogen bonds during hybrid film preparation. On the other hand, the hybrid composite formed by pectin and TiO_2:Cu-doped nanoparticles showed methyl orange dye photodegradation from aqueous media [23].

The incorporation of TiO_2 into nonconventional polysaccharide-based materials significantly improved their physicochemical, mechanical, thermal, water-resistance, and UV-barrier properties, which are suitable characteristics for the development of food and non-food packaging materials.

3.5.2. Biomedical Applications of Nonconventional Polysaccharides Functionalized with TiO_2

The potential biomedical applications of nonconventional polysaccharide-based materials functionalized with TiO_2 have been investigated (Table 5). Razali et al. [33] informed that the addition of TiO_2 in gellan gum films improved their thermal stability and antimicrobial activity (by agar test diffusion assay) against *S. aureus* (inhibition of 10 mm), *Streptococcus sp.* (inhibition of 12 mm), *E. coli* (inhibition of 11 mm), and *Pseudomonas aeruginosa* (inhibition of 10 mm) without significant changes in transparency (transmittance of 94%) compared with the gellan gum-based film (without antimicrobial activity and transmittance of 100%). The improved physicochemical properties were attributed to the hydrogen-bond formation between the biopolymer and nano-TiO_2, while the antibacterial activity of the hybrid film was attributed to the presence of TiO_2 and its ability to ROS generation, promoting a malfunction of bacteria membrane, leading to cell death. Furthermore, the biocompatibility of the gellan gum–TiO_2 hybrid film has been tested in a mouse fibroblast cell line (3T3), indicating no cytotoxic effects. Moreover, in an open-excision-type wound-healing study in adult Sprague Dawley rat, the hybrid film promoted an accelerated re-epithelialization (more than 50% on day 3 of wound operation) without inflammatory phenomenon after 14 days of evaluation in comparison with a gellan gum-based film. This phenomenon could be related to the presence of nano-TiO_2 in the polymeric matrix, which was able to promote cell growth and cell migration to accelerate open-excision wound healing, mainly by TiO_2, which may affect protein interaction and subsequent cell adhesion and proliferation; nonetheless, the acceleration of the wound-healing process may be related to the antimicrobial properties of the hybrid film [38,112].

According to these data, nonconventional polysaccharides-based materials functionalized with TiO_2 showed interesting properties for biomedical applications. However, further studies are required to validate their safety and efficacy use.

4. Conclusions

Evidence indicates that the use of TiO_2 as a reinforcement agent in polysaccharide-based materials is a viable strategy that significantly enhanced their mechanical, thermal, and UV-barrier properties and water resistance. Biopolymer–TiO_2 hybrid composite is an active research area for environmental remediation and biomedical applications. Moreover, it is a low-cost and eco-friendly alternative for the development of packaging materials for food and non-food purposes based on its antimicrobial and photocatalytic properties. However, it is necessary to evaluate the possible structural changes promoted by the storage time and work temperature on the physicochemical properties of polysaccharide–TiO_2 hybrid composites to guarantee their stability and safe use during a determined time.

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