Review

Enhancing Barrier and Antioxidant Properties of Nanocellulose Films for Coatings and Active Packaging: A Review

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ABSTRACT: Cellulose, a natural biopolymer, offers strong potential for sustainable packaging due to its impressive mechanical, thermal, and barrier properties. However, its high hydrophilicity remains a key challenge for industrial applications. This review delves into both chemical and physical methods to enhance nanocellulose's hydrophobicity while also exploring the incorporation of reinforcing fillers like antioxidants, antibacterial agents (e.g., tannins, lignin), and nanoclays to improve functionality in active packaging. Additionally, advanced surface modifications using compounds, such as stearic acid, silanes, and treatments, such as cold plasma, are discussed. By providing detailed insights into these techniques and materials, this review serves as a practical guide for researchers, especially in laboratory settings, to assess the feasibility of applying these innovations in their own work. Ultimately, it aims to advance the development of nanocellulose-based packaging solutions, offering a balance among sustainability, enhanced performance, and practical scientific guidance.

Multifunctional modifications to improve the performance of nanocellulose films
- **Hydrophobicity** Chemical and physical methods
- **Reinforcing fillers** antioxidants, antibacterial agents and nanoclay
- **Surface modification** stearic acid, silanes and cold plasma
- Film
- **Strong potential** for sustainable packaging

KEYWORDS: *Nanotechnology, Sustainable packaging, Antioxidant biomaterials, Biopolymer Composites, multilayered systems*

1. INTRODUCTION

Although cellulose is the easiest biopolymer that can be obtained in nature, about 150 years earlier, it was first utilized as a raw product. It is primarily utilized for producing cardboard and paper, but efforts are being made to find alternative applications. The packaging industry is in increasing demand for new biodegradable materials to replace plastics produced using fossil fuel resources. In addition to the obvious ecological benefits, cellulose is a great alternative, as the desired properties for each application in this main area can be achieved by modifying the cellulose by chemical or physical methods. Integrated fibrillated cellulose manufacturing facilities are designed to accommodate large-scale applications, including paper, packaging, and coatings. Notably, several international companies, including Kruger and Sappi, have successfully showcased the production of fibrillated cellulose products within these integrated plants.[1]

Nanocellulose is used to synthesize different packaging materials. Because of its strong mechanical properties, it can be made using bacterial cellulose[2] or mainly from microfibrillated cellulose (MFC), nanofibrillated cellulose, or cellulose nanocrystal (CNC) formulations.[3] Within these, nanocellulose stands out from kraft paper processed by mechanical defibrillation. This material is easily and inexpensively produced, and it is possible to mix components before or after defibrillation that presents quite diverse reactions so that the association is further enhanced when blending materials

concomitant with physical disintegration, such as tannins,[4] and other biopolymers and macromolecules.[5] If these compounds are incorporated during cellulose defibrillation, the contact angle, antioxidant power, and film transparency are severely modified.

Many natural polymers and extracts have been reported for food packaging applications.[6] For instance, CNCs, which are typically produced via acid hydrolysis, are elongated, rigid, rodlike nanoparticles that range in length from 100−6,000 nm and width from 4−70 nm, exhibiting a crystallinity index of 54% to 88%.[7] CNCs offer a range of desirable properties, including unique optical characteristics, excellent stability, a large surface area, enhanced tensile capacity (10 GPa), and an impressive Young's modulus (140−150 GPa).[8] CNFs are typically produced industrially from cellulose pulp through mechanical processes that facilitate their extraction.[9] This extraction can involve rotary milling or freezing followed by grinding.[10] CNFs are characterized by a network of flexible, interwoven nanofibers that are both longer and wider, whose widths vary

Table 1. Available Economic Studies on Nanocellulose Production

raw material	production technology	research scenarios	capacity[a] (ton/year)	product type	cost/price[a] (USD/kg)	start year	country	reference
Dissolving pulp	Size reduction and acid hydrolysis	Acid recovery and colocation or not	17,500	NCC	3.6−4.4[b]	2019	USA	15
Bleached long-fiber Kraft pulp	Mechanical grinding and acid hydrolysis	Independent or integrated with existing	30,000	MFC	1.8[b]	2014	Finland	19
Bleached eucalyptus Kraft pulp	Acid and enzymatic hydrolysis	Alternative hydrolysis processes	4,250	NCC	7.8−50[b]	2017	Brazil	16
Wood chips	Mechanical treatment and bleaching	Various biorefinery scenarios	42,000	NCC and NFC	1.7- 2.5[c]	2021	Canada	20
Sugar cane bagasse	Thermochemical pretreatment and alkaline/acidic hydrolysis	Various pretreatments and extractions	400,000−460,000	Nonspecific NC	0.7−3.1[b]	2022	Colombia	21
Sugar cane bagasse	Pretreatment, enzymatic and acid hydrolysis	Organic and inorganic acid catalysts	1,500−2,400	NCC and NFC	6.9−10.9[c]	2021	Brazil	18, 22
Oil palm fronds	Thermochemical pretreatment and acid hydrolysis	Basic, best-, and worst-case scenarios	25,000	NCC	1.2−1.5[c]	2020	Malaysia	23
Miscanthus	Alkaline treatment and bleaching	Biorefinery with various products	18,000−91,000	MFC	1.5−3[b]	2019	Korea	24
Reed canary grass (*Phalaris aquatica*)	Chemical and mechanical protocols	Different scenarios and types of NC	2,000−2,800	NCC; NFC; MFC	3.4−3.7; 4.0−4.4; 3.1−3.4[b]	2023	Greece	17

[a]Approximate value. [b]Production cost (PC). [c]Minimum selling price of the product.
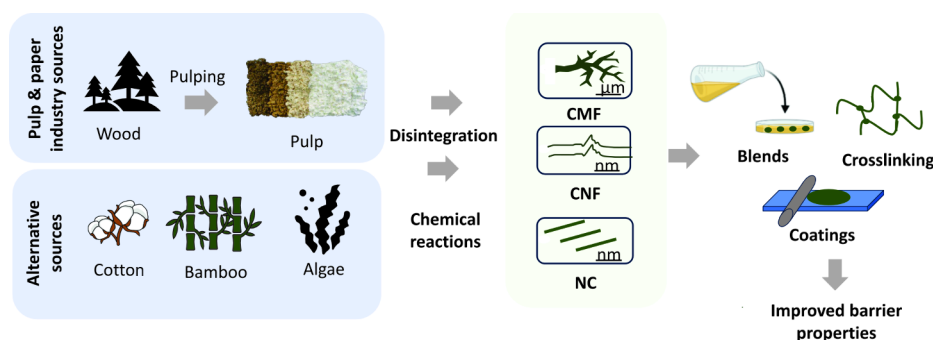

Figure 1. Schematic overview of biomass modification strategies for enhanced barrier properties explored in this review.

between 20−100 nm and lengths surpassing 10,000 nm. Compared to CNCs, CNFs exhibit lower crystallinity.[11] However, several processes are required for its extraction and synthesis in order get a pure raw material, which may raise the total cost.[12] Industrial scale nanocellulose extraction faces major challenges, such as the necessity for affordable raw resources and environmentally friendly production techniques, high expenses for operations, and efficient, cost-effective extraction techniques.[13] The choice of cellulose feedstock significantly influences both the performance and the manufacturing cost of fibrillated cellulose, as described in Table 1. Wood, the primary feedstock for the industry of pulp and paper, is anticipated to remain a dominant commercial source of fibrillated cellulose production.[1] But other commercial sources can be highlighted, such as the sugar cane bagasse. It is a significant and inexpensive feedstock that may be used to produce fibrillated cellulose, providing possibilities for integration of processes in biorefineries based on sugar.[14] Producing nanocellulose involves balancing economic costs with environmental considerations. The cost of CNC production typically ranges from 3.6 to 4.4 USD/kg[15] to 7.8 to 50 USD/kg[16] with a capital expenditure (CAPEX) further elevated by the costs associated with acid recovery, neutralization, and effluent treatment. The CNF production costs range between 4 and 10.9 USD/kg.[17,18]

Alternatively, MFC has been reported as a potential alternative, as it is very cheap to produce[25,26] and very

resistant.[27] The MFC, commonly obtained by defibrillation of cellulosic pulp from different sources, bleached or unbleached, allows one to obtain a homogeneous, transparent, and highly resistant film. An ultrafine component mill's mechanical defibrillation process makes it possible to incorporate various substances during the defibrillation process.[4,28] The interaction between the added substances and nanofibrils is significantly impacted by this process. As a result, it offers many opportunities that have not been explored in the film synthesis yet. The nanocellulose, whether MFC, NFC, or CNC, exhibits a high oxygen barrier because their polarity differences result in a reduced oxygen diffusion. In addition, there is a high cohesive energy density formed by hydrogen bonds between the nanofibrils. This force is strong enough to narrow the distance between the nanofibrils, and thereby blocking molecular gases.[29] Moreover, the gaseous molecules necessary pass through a tortuous path created by the nanofibrils, and their ordering is parallel to the surface of the films themselves, which greatly contributes to their extraordinary oxygen barrier values.

However, moisture and water vapor have a negative impact on the barrier properties. Water molecules disassociate hydrogen bonds, acting as plasticizers, which results in a reduction in cohesive energy density along with a rise in porosity.[30] As a result, moisture promotes the development of passages between nanofibrils, and molecules can then permeate through these passages. The decline of the oxygen barrier

property at high humidity has contributed to research progress to solve these problems. Developed techniques includes surface modification of nanofibrils,[31] enzymatic pretreatments,[32] mixing of nanofibrils with other materials[33] like lignin nanoparticles,[34] cross-linking,[35] hydrophobic coatings and adding nanofibril films to plastic films.[36] For plastic packaging, nanocellulose exhibits excellent barrier properties at low to medium relative humidity levels (<50% RH).[37] However, in certain formulations a high barrier property can be achieved at 80% RH.[38]

The major subject of our review lies in the nuanced modifications employed to fortify these materials for improved barrier performance in producing coatings or active packaging. We investigate blends incorporating tannins, lignin, crude tall oil, nanoclay, starch, and PLA, strategically integrated to bolster barrier attributes. Furthermore, our analysis encompasses cross-linking methodologies, specifically acetylation and silanization, as well as coating strategies such as polypropylene laminated coatings and cold-plasma treatment. Figure 1 serves as a schematic representation, encapsulating the essence of our exploration into the intricate realm of biomass modification for advanced barrier functionalities.

Smart packaging, a broad term that includes both active and intelligent packaging, transcends traditional packaging functions by integrating technologies that interact with the product or the environment. Active packaging changes the internal conditions of the package to enhance product quality, safety, or shelf life, while intelligent packaging monitors the product's status and provides real time data without altering the product or packaging environment. These innovations allow packaging not only to protect but also to improve product longevity and quality through advanced materials, sensors, and electronics.[39−42]

Controlled release packaging is designed to release active ingredients onto various surfaces, such as food, in a controlled manner. By managing the release of these compounds, packaging can enhance the degradation process of specific substances, like essential oils, to deliver antioxidant and antimicrobial benefits effectively. In the literature, terms like controlled release packaging often overlap with smart and active packaging, as they share similar goals. Controlled release packaging works by protecting the product within mechanisms such as sensors, UV irradiation, polymer degradation, and nanocomposite fillers, which trigger the release of active ingredients as needed.

In particular, nanocellulose-based active packaging, functionalized with antimicrobial agents or essential oil, helps prevent bacterial growth, extending the freshness of food products like produce, meat, and dairy.[43−51] Additionally, nanocellulose coatings control moisture and act as carriers for preservatives for UV-blocking, and antioxidants, gradually releasing them to protect against spoilage.[4,52,53−55]

It is possible to produce edible coatings, related to thin, edible layers applied directly to the food surfaces to extend shelf life, improve safety, and provide added functionality.[56−58] These coatings can alter the food's environment and can be combined with active ingredients or sensors.[59−61]

Nanocellulose, being nontoxic and plant-based, is ideal for creating food-grade edible coatings that act as natural barriers against moisture loss and contamination, replacing traditional wax coatings.[62−64] Applications of nanocellulose-based edible coatings include protecting fruits from environmental damage,

slowing spoilage in meats and fish, and preventing oxidation while improving texture.[65−73]

Nanocellulose is being explored as a coating for textiles to enhance strength, flexibility, and durability while maintaining lightness.[74,75] Functionalized with antimicrobial or water-repellent properties, it enhances hygiene, reduces odor, and improves the fabric's moisture resistance, while also being used in textile dyes, UV-resistance, self-cleaning, and flame retardancy. Additionally, these coatings are ecofriendly alternatives to traditional synthetic finishes, offering biodegradability.[76−80]

Intelligent packaging integrates nanocellulose with responsive materials to create systems that actively respond to environmental changes.[81] For instance, while biosensor-based nanocellulose films monitor pathogens or chemical changes, providing real-time data on food safety.[82,83] Examples include time−temperature indicators (TTIs), gas sensors, and freshness indicators that help consumers track product quality.[84−89,49] For example, nanocellulose-based packaging is being developed to change color as food begins to spoil, alerting consumers early.[90−93]

In the automotive industry, nanocellulose is being applied to develop corrosion resistance for metal parts and lightweight, ecofriendly coatings for vehicle interiors. These innovations offer a unique balance of strength, reduced weight, and sustainability, making nanocellulose a versatile and valuable material across industries from food packaging to automotive manufacturing.[94−98]

Nanocellulose's versatility in packaging and coating, whether smart, active, edible, or environmentally sustainable, makes it a key material in future developments across industries. These diverse uses highlight its potential for revolutionizing packaging, particularly with its green credentials and high performance. This packaging will be at the forefront of the packaging industry evolution, combining sustainability with cutting edge technology to improve product longevity, safety, and consumer interaction.

The future of nanocellulose holds exciting possibilities and challenges, as research focuses on improving manufacturing processes and specialized variants of properties for cellulose nanocrystals and nanofibrils. Tailoring characteristics such as mechanical resistance, thermal stability, and conductivity of electricity will enable nanocellulose to meet the demands of various industries. Precision control over these characteristics will be made possible by developments in surface functionalization and composite formulations, expanding the potential of nanocellulose across numerous industries. As this field expands, it is possible to foresee important advances, such as nanocellulose with graphene, leading to multifunctional materials with self-healing capabilities. Among the common fields using for packaging, it may also be used for further fields, like additionally, nanocellulose's potential in nanomedicine includes targeted drug delivery and tissue engineering.[99,100] By further exploring its structure, researchers can develop innovative applications positioning nanocellulose as a versatile material for future technologies such as

1. Electrochemical Sensors: Nanocellulose's conductive properties can be combined with nanosensors to create "intelligent" packaging. This packaging would detect gases released from food spoilage, humidity levels, or other chemical changes, providing real-time quality monitoring that goes beyond current "smart labels".

Such sensors could alert consumers via color changes or even wireless signals connected to mobile apps.[101−104]

2. Thermal Insulation and Energy Harvesting: Nanocellulose can be integrated with thermoelectric materials to produce packaging that both insulates and uses temperature gradients to generate small amounts of power. This could be useful for keeping perishable items at optimal temperatures while also powering embedded sensors or displays. For instance, packages with such technology could regulate internal temperatures by adjusting their properties based on external conditions, without the need for active power sources.[105−108]

3. Self-Healing and Damage Repair: Inspired by natural materials, self-healing nanocellulose composites could be used in packaging that repairs minor tears or punctures, extending the package's integrity and shelf life without requiring manual intervention. This would be especially beneficial for food storage in logistics, as even small breaches in packaging can result in significant waste.[106,109,110]

4. Ecofriendly Nanocoatings with Enhanced Degradability: Future packaging could use nanocellulose-based coatings engineered to degrade rapidly after disposal. Unlike standard bioplastics, these coatings can be precisely programmed to break down only under specific environmental conditions, such as high humidity or composting, making disposal and recycling processes more efficient.[111,103,112]

5. Nanocellulose-Based Bioactive Films for Nutrient Release: Research is exploring packaging that not only preserves food but also enriches it. Such films could release nutrients or probiotics into the food over time, enhancing the product's nutritional value while maintaining freshness. For example, fortified packaging for certain foods could help address nutrient deficiencies in regions where food quality and nutrition are a concern.[102,113,114]

Beyond summarizing recent developments in nanocellulose-based packaging, this Review aims to provide practical insights into the production methods that enable these innovations. By detailing the techniques and modifications that enhance the performance of these materials, we offer a valuable guide for researchers looking to implement these strategies in their own work. This review not only highlights advancements in material properties but also emphasizes the feasibility of scaling these solutions for industrial use, encouraging researchers to actively explore and apply these methodologies to advance sustainable packaging solutions.

2. MULTILAYER SYSTEMS IN BIOPOLYMER PACKAGING

An alternative to address the constraints of the properties of biobased materials and address the drawbacks of single-layer biopolymer films is the adoption of multilayer systems. In these systems, a single layered structure is formed by combining two or more materials that possess distinct and complementary properties, resulting in improved efficiency of biopolymers.[115] Single-layer systems have a faster decomposition time compared to multilayer systems, but they fall short of meeting the expectations for use as packaging materials. Multilayered systems enhance some properties like water solubility, mechanical strength, and as a gas barrier.[116] Currently, there

is a notable advancement in the field of biopolymers focused on the production of multilayer films.[117]

The bond between these layers is a crucial factor for assembling. Adhesion, which refers to the tendency of different surfaces to adhere through physical and chemical intermolecular forces at their interfaces, can be significantly influenced by plasma treatments. By modifying the free surface energy of polymers, these treatments can enhance adhesion or facilitate antiadhesion properties, tailored to suit specific applications.[118,119]

2.1. Nanocellulose-Based Laminated Coatings. NFC films are hygroscopic; that is, they have a high transmission rate and water vapor permeability; however, it is reduced if NFC films are laminated onto polymers. Furthermore, increasing the thickness of cellulosic nanomaterials (CNM) films further decreases its oxygen transmission rate values, attributed to a longer diffusion path.

In response to the growing demand for sustainable materials, poly(butylene succinate) (PBS) has been identified as a highly promising biobased and biodegradable polymer, demonstrating excellent suitability for applications in film blowing and lamination processes.[120] Researchers examined the formation of multilayer laminate structures (composed of 1, 5, 10, or 20 layers) by using nanofibrillated cellulose (NFC) as a coating agent. Notably, a single NFC layer reduced the transmission rate of water vapor (WVTR) by as much as 5.5 times. However, adding more than 10 NFC layers compromised the laminate adhesion and introduced structural defects. Additionally, optical transparency decreased significantly—from 65% to 25%, as the number of NFC layers increased. Despite these challenges, NFC provided effective barrier properties without requiring chemical modification, positioning these laminates as a promising sustainable solution for food packaging. However, as a hydrophilic polymer, NFC tends to swell upon moisture absorption, which decreases the layer density and contributes to structural imperfections.

A proposed method is to obtain a film by solvent-casting and then laminating with a biaxially oriented polypropylene (BOPP) film in a hot roll laminator. Polyurethane films can also be inserted between NFC and BOPP films to give adhesion and present different interfaces. However, the performance of nanocellulose laminates at high relative humidity is still not sufficient due to moisture-induced plasticization and swelling.[121]

An adhesive layer can be applied to reduce the region that is susceptible to vaporized water penetration, thereby restricting water-vapor-induced swelling and maintaining the ability of CNM films to act as barriers to oxygen, especially under conditions of high relative humidity (RH) (Figure 2). Lamination of NFC films with polypropylene improves oxygen resistance capabilities at 80% RH. Moreover, the oxygen transmission rate of layered materials with NFC is decreased by as much as 3 times. This mechanism is based on the critical influence of an adhesive layer for the integration of all layers into a robust composite structure without pores, and thick adhesive layers (50 μm) are employed during lamination. In the absence of a sealing adhesive layer, water vapor can compromise the adhesion at the PP/CNM interface, facilitating its penetration into the CNM films. The addition of an adhesive layer minimizes the permeable area for water vapor, thereby reducing the swelling caused by water vapor and maintaining the films of CNM effectiveness as oxygen barriers under high relative humidity (RH) conditions.[121]
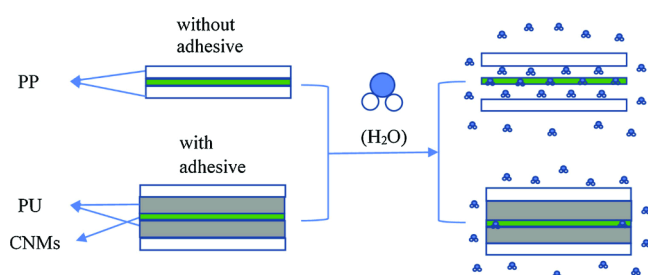
Figure 2. A schematic elucidating the protective mechanism of an adhesive layer against moisture-induced swelling in cellulose nanomaterial films. Adapted with permission from ref 121. Copyright 2024 Elsevier, approved License Number 5732211197037.

Thinner plastic and adhesive layers (10 μm) can significantly improve the barrier properties (<4 cm^3·μm/(m^2·day·kPa)) of CNM laminates, making them suitable for food packaging applications such as potato chips, peanuts, coffee, and meat.[38]

In the same context, cellulose nanocrystal (CNC) coatings with fully compostable laminates (LAMCNC) structured in "cellophane (19 μm)/aluminum (<1 μm)/Tie (2 μm)/CNC (1 μm)/Tie (3 μm)/PLA (55 μm)" can potentially be applied to be oxidation-sensitive for food products as packaging. In addition, they can be used to replace conventional synthetic laminates (LAMEVOH), composed of "PET (28 μm)/Tie (1.2 μm)/EVOH (3.3 μm)/Tie (1.2 μm) PET (25 μm)/Tie (1.2 μm)/PE (12.25 μm)". CNC-based compostable laminates less than 1 μm thick exhibited better gas barrier properties (oxygen permeability at 0% relative humidity is 0.06 cm^3·24h^{-1}·m^{-2}·bar^{-1} at 0% RH) compared to that of EVOH 3−4 μm thick. Thus, the production of sustainable coatings with significant barrier properties is made possible by laminating CNC coatings over two layers through insulation, a structure that repels water, such as metallized cellophane, and a polymer that can be sealed, like PLA.[36]

Through successive lamination processes, epoxy resin, glycerol, and nanofibers of 2,2,6,6-tetramethylpiperidine-1-oxy-oxidized cellulose (TEMPO-CNF) have been developed to replace transparent synthetic polymers and glass materials.[122] By adjustment of the thickness and quantity of TEMPO-CNF layers, the study indicated that it is easy to control the thickness of TEMPO-CNF/epoxy laminates up to 2.4 mm. At 600 nm, the laminates displayed excellent optical transparency (66% to 85%) and mechanical strength (bending modulus: 11.6 to 17 GPa, flexural strength: 209 to 272 MPa). Thus, these laminates can be potential sustainable alternatives with millimeter thicknesses for various applications.

2.2. Nanocellulose Multilayers with Cold Plasma Treatment.
Polymeric materials can be surface activated and functionalized by using cold plasma, which involves changing the outer layer of polymers structurally or chemically. It is produced at normal atmospheric pressures or under a vacuum and requires less energy for activation. Within plasma surface treatments, surface functionalization is one method, involving the introduction of specific functional groups to the material surfaces. Additionally, these treatments are employed for cleaning or etching polymeric surfaces, removing unwanted impurities, and for depositing thin coatings and sterilization purposes.[123] Enhancing the adhesion of polymeric surfaces is one of the most significant applications of atmospheric pressure plasma treatment. Additional polar groups including amino, hydroxyl, amide, and carboxyl are generated when species formed during plasma discharge react with chemical groups on the polymer surface. These transformations alter polymer properties, converting them from hydrophobic to hydrophilic, resulting in improved adhesion, wettability, and biocompatibility. These effects are challenging to achieve through conventional activation methods, and therefore, cold plasma enhances the adhesion of biopolymers, creating novel packaging materials with enhanced properties like physical, structural, mechanical, barrier, and thermal characteristics as well as antimicrobial action.[118]

This enhancement is due to the increased diffusion rate of functional components on surfaces, facilitating polymer adhesion and intensifying the antimicrobial efficacy. Effectiveness is influenced by the plasma gas composition, biopolymer composition, and processing parameters (voltage and treatment duration). A sustainable method that produces no waste from chemicals is cold plasma. Furthermore, plasma treatment contributes to increasing the biodegradation capacity of packaging films.[124,125] To elucidate these potentials, Table 2 summarizes the advancements made in the production of multilayer systems using renewable resources, particularly those that comprise nanocellulose. Only two previous studies[126,127] have employed plasma with positive outcomes regarding multilayer systems, highlighting a scarcity of information in understanding the benefits of this surface treatment and underscoring the need for new scientific advances when considering nanomaterials for sustainable packaging.

Among these studies using plasma to improve the properties of CNF-based systems, we highlight the single-layer bionanocomposite containing CNF and chitosan produced by casting. The authors showed that cold plasma treatment can improve water vapor permeability by 31%, oxygen transmission rate by 34%, moisture content by 3%, and the water contact angle by 28%, as well as mechanical properties such as tensile strength and elongation at break, by up to 69% (Figure 3). The primary mechanisms explaining this outcome relate to the treatment process, which likely replaced weaker C−N interactions with stronger ones, thereby reinforcing the network structure. Moreover, the application of cold plasma enhanced interfiber hydrogen bonding, potentially increasing chitosan adsorption.[127]

The researchers noted enhanced results in the chemical attributes of the packed strawberries with a 15 min plasma treatment on the films. However, it is crucial to consider energy consumption for industrial-scale production. Furthermore, the effectiveness of modified atmosphere systems and cold plasma relies on the surrounding environment.[127]

The layering of nanocellulose significantly influences the water-vapor transmission rate (WVTR) values observed in the literature (Figure 4a). Among the studies reviewed, the CNC bilayer consistently exhibits the highest WVTR and oxygen transmission rate (OTR) across the evaluated samples. However, despite its cellulose origin, the CNC bilayer has yet to reach the performance levels of conventional polymers such as polystyrene (PS) or polypropylene (PP).

In terms of tensile strength, the values presented in the standard references indicate average performance metrics (Figure 4b). Nevertheless, the overall mechanical properties of films derived from nanocellulose suggest characteristics similar to many common polymers. It is important to note, however, that their tensile strength does not match the durability of polyethylene terephthalate (PET). Detailed data

Table 2. Summary of the Novel Multilayered System Described in the Literature with Renewable Sources and Cold Plasma Treatment

raw materials	product	process	key characteristics	results	ref
CNF, wax, lignin, nanochitin	Multilayer	Vacuum filtration	Sandwich film (CNF + Carnauba wax + CNF); Multilayer film (CNF + Carnauba wax + nanochitin/Lignin)	WVTR sandwich film: 5 ± 1 g/m²·day; oxygen barrier multilayer film: 3 ± 1 cm³/m²·day at 50% RH; strength of CNF: 204 ± 24 MPa; complete UV shielding protection with 4% of lignin	128
CNC, Nanochitin, PLA	Multilayer	Spray coating	Layer-by-layer film; up to 5 layers intercalated	Oxygen barrier: neat PLA 70 and multilayered ~20 cm³·μm/m²/day/kPa at 50 RH. WVTR 75 for neat PLA and multilayered ~150 g·water/m²/day	129
CNF, CNC, paper	Multilayer	Coating	Bilayers of CNF and CNC with different formulations intercalated	Bilayer, with CNC on top, yielded the best results. Air resistance ~9000 Gurley seconds, oxygen barrier ~3 ($\times 10^4$) g/m²/day, and WVTR: 90 g/m²/day.	130
Cellulose, tannin	Bilayer films	Dip coating	Regenerated cellulose films; various amounts of tannin covalently bound to the film surface	TCF-3 increased antioxidant (80–90%), improved hydrophobicity (~75°), WVTR: ~400 g^{-2} day^{-1} and wet tensile strength 26.8 MPa	131
CNF, tannin	Biohybrid films	Vacuum filtration	Mixtures of CNF and tannins with different mass ratios	5% (w/w) of tannin extract resulted in good antioxidants (28 ± 2 and) and absorbed 92% of UV light - below 320 nm, tensile strength of 160 ± 9 MPa	54
CNF, CNC, BNC, chitosan, alginate	Multilayer	Vacuum filtration and casting	25 different formulations and 7 biopolymer films	The best films for packing are polysaccharide-based ones with additional CNC, chitosan with 3% CNC increased hydrophobicity, with CA of 108 ± 2, and WVTR of 63 ± 2 g·cm^{-1}·day^{-1}, and alginate +5% CNC exhibited a tensile strength 42.6 ± 3.6 MPa.	132
CMNF, plasma - DBD (N2)	Single-layer micro/nanocellulose films	Sheet Former (ISSO Standard S269-1)	Films produced from refined pulp with different enzymatic pretreatment times; plasma treatment for 0 s, 30 s, and 60 s	Increase of E-modulus to 10.03 GPa for micro-/nanofibrillated cellulose films after 360 min of enzymatic treatment time. Surface free energy reached around 65 mJ m^{-2} after plasma treatment.	126
Chitosan, CNF, plasma - DBD	Single-layer films	Casting	Chitosan 1.25%, CNF (1.5% per chitosan); Plasma treatment for 5, 10, and 15 min	Plasma treatment of 10–15 min improved tensile strength to ~20 MPa, WVTR ~6.4 × 10^{-10} GPa^{-1}·s^{-1}·m^{-1}, OTR ~ 1500 cm³·mm^{-2}·day^{-1}·atm^{-1}, and CA ~65°.	127

from these figures are included in the Supporting Information (Table S1).

3. NANOCELLULOSE IN STARCH AND CHITOSAN BLENDS

Starch is a great alternative as a blend because it is widely available and relatively low in price and is used in the paper industry. Cationic starch creates an electrostatic interaction due to the positive charges incorporated into its molecular chain, which bind to negatively charged areas on other materials such as the cellulose surface. However, its tensile strength is inadequate, and its water vapor permeability is high due to its hydrophilic character, resulting in difficulty controlling its sensitivity to the moisture content. Thus, loading nanofibrils with starch increases the mechanical strength, gas permeability resistance, and thermal characteristics. This can be attributed to nanofibrils dispersing well in the starch matrix.

The auto bar coater technique was used to coat kraftliner paper with nanocrystalline cellulose (NCC) gel added with cationic starch at different concentrations. With constant weights of 10 mL, the layers of NCC and cationic starch (3, 5, and 7% by weight) were filtered and applied to the base paper surface at a speed of 5 cm/s^{-1}. After coating, they were placed firmly between blotters and dried using a contact drying technique for 72 h at 23 °C, 4 bar of pressure, and 50% relative humidity. The 5% concentration of NCC showed better properties than the NCC/cationic starch film. The results indicated a reduction in water absorption, air resistance, and tensile strength when using the NCC coating with starch.[133] The coating material's continuous layer development, which shows fewer pores than the control sample, may be the cause of this decrease in water absorption. Consequently, the amount of water that can penetrate the surface is significantly reduced. Oil permeability was also reduced compared with the uncoated film, achieving a 60% decrease. In most cases, significant fiber beating contributes to the enhanced barrier properties. The decreased surface porosity attained using nanocomposites and chitosan (CS) is directly correlated with enhanced barrier properties. When coating nanocomposites are present at increased concentrations, greater amounts of nanoparticles bond to CS and paper fibers, covering the pores in the paper and preventing oil absorption.[133] However, more studies need to be carried out, as the large-scale application requires broad barrier conditions to oxygen and water vapor in addition to improved mechanical properties for packaging.

An innovative and sustainable method for producing films composed of regenerated starch (RS)/MFC was developed by Chen et al.[134] This innovative approach will help to create materials based on RS that have potential mechanical and biodegradable qualities and can be used as substitutes for petrochemical plastics. Dialysis and solution casting were used to create the films, which were made from starch dissolved in a 14% urea/4% NaOH solution. The results showed that RS/MFC films showed about 1.4 times greater tensile strength when compared to traditional gelatinized starch (GS) films mostly due to hydrogen bonds between MFC and RS. In comparison to GS film, the tensile strength and elongation at break improved by 44.8 and 82.4%, respectively. The optimum distribution of the materials provided lower viscosity, crystal size, and higher amylose content, exhibiting significantly improved mechanical properties.
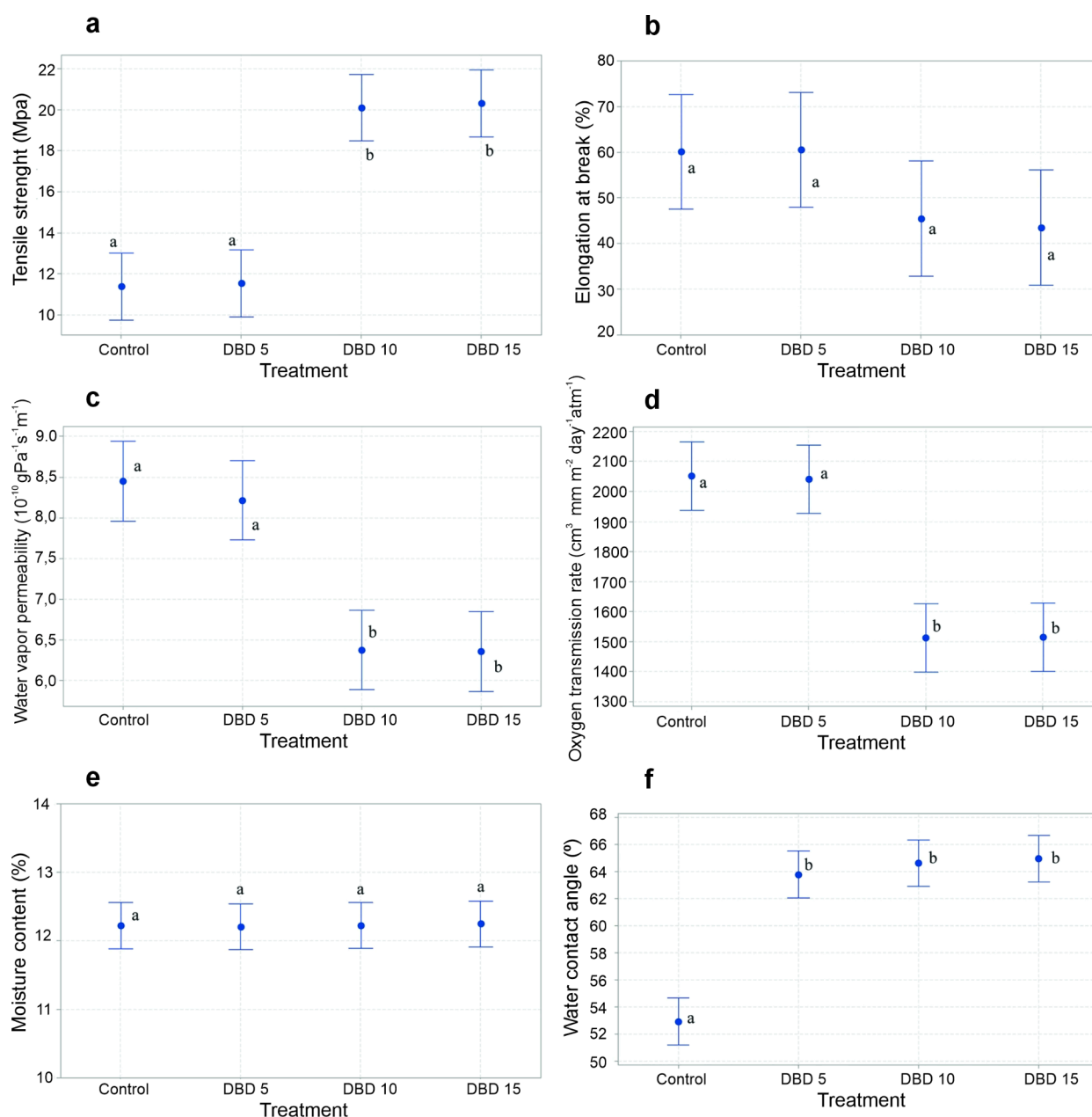
Figure 3. Tensile strength (a), elongation at break (b), water vapor permeability (c), oxygen transmission rate (d), moisture content (e), and water contact angle parameters (f) of the bio-nanocomposite films were evaluated under various plasma treatment conditions. Reproduced from ref 127. Available under a CC-BY Springer Nature license.

A naturally occurring linear polysaccharide is chitosan comprises 1,4-linked 2-amino-deoxy-D-glucan, which is the second most prevalent natural polysaccharide after cellulose and a partly deacetylated derivative of chitin. Chitosan is biodegradable, nontoxic, biocompatible, and biofunctional. Numerous researchers have found that it possesses potent antibacterial and antifungal properties.[135,136] Chitosan films have proven to be an effective packaging material for preserving and improving the quality of food.[4]

Crystalline nanocellulose was observed to act as an effective chitosan reinforcement agent, and just 3−5% of loading already presents good values for tensile strength. Strong blend-matrix interaction and the development of a percolation network were responsible for an enhancement in the mechanical properties. The nanocomposite films' surface

morphology showed a uniform structure, suggesting that the nanocellulose was sufficiently dispersed throughout the chitosan matrix.[137] A specialized laminator was used to apply the chitosan solution to the paper's surface. The coated samples were dried at 105 °C in a laboratory oven with air circulation. Each of the two coating layers was applied to one or both sides of the paper, and each layer was set aside to dry for 1 min. The speed of the coating bar was 2 m/min. Prior to testing, the dried samples were conditioned and kept for a minimum of 1 week at 23 °C and 50% relative humidity in an acclimatized environment. The kraft paper sheets were coated by using microcrystalline cellulose (MCC) and chitosan. The varying chitosan and MCC concentrations were measured. When 1% chitosan (4.7 g/m^2) was applied, the porosity doubled, the water absorption capacity (Cobb test) decreased
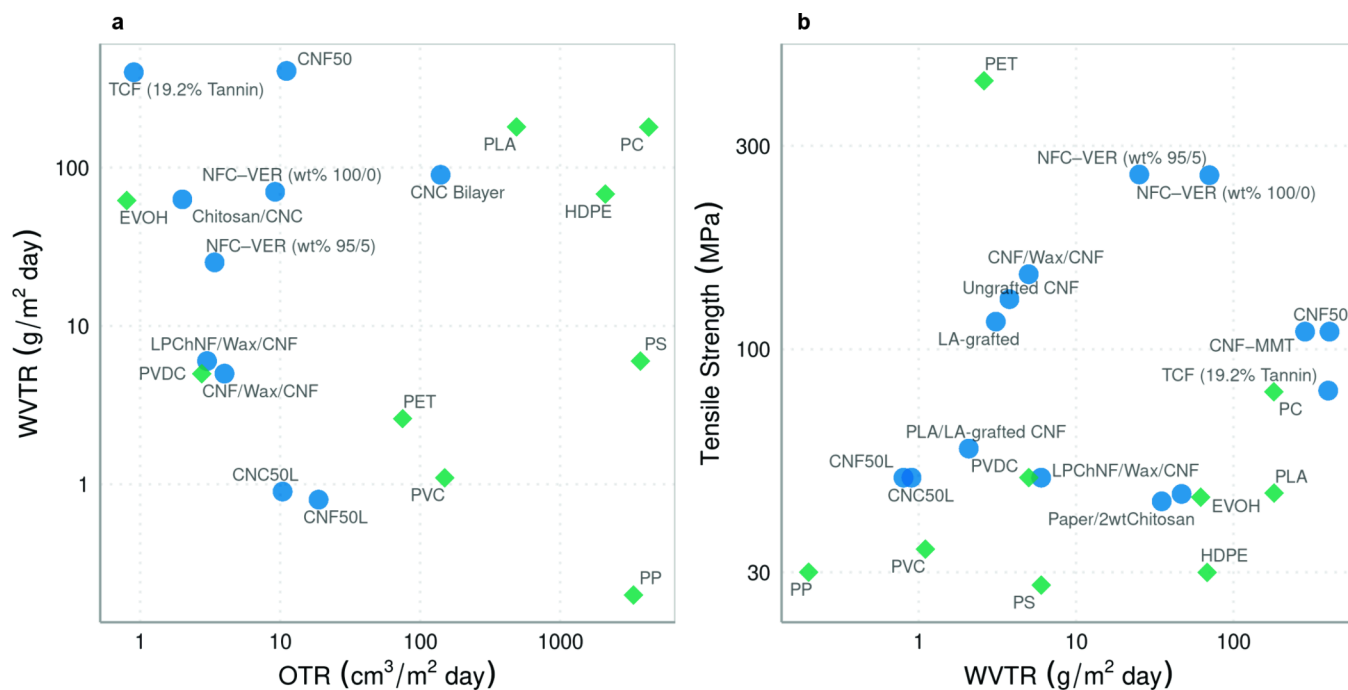
Figure 4. a) Log−log scale comparison of water vapor transmission rate (WVTR) vs oxygen transmission rate (OTR) for various nanocellulose films and standard polymers, highlighting the superior performance of the CNC bilayer relative to traditional materials. b) Log−log scale comparison of tensile strength versus WVTR, illustrating the mechanical properties of nanocellulose films compared to various polymer standards in terms of their moisture barrier performance. The standard polymer values are normalized to their mean values.
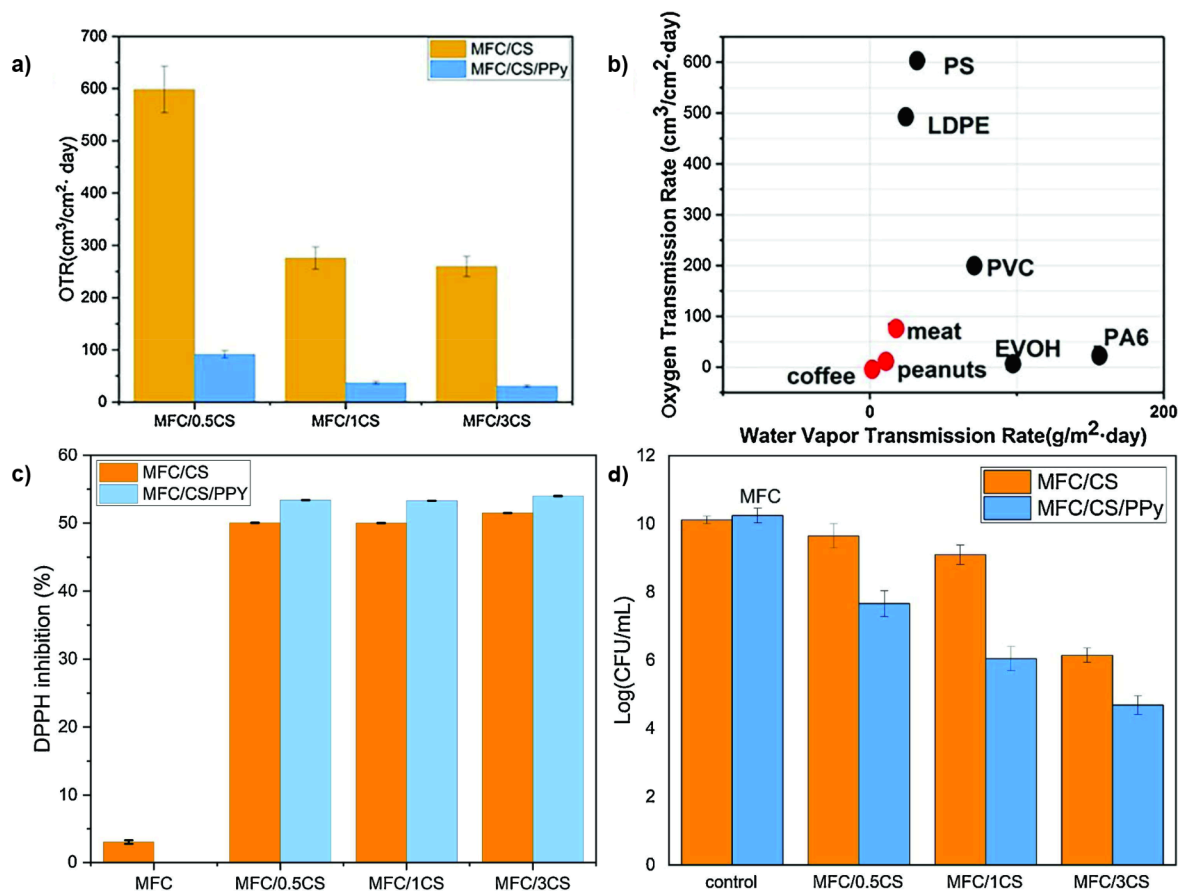

Figure 5. MFC, MFC/CS, and MFC/CS/PPy films with increasing loadings of chitosan solution in which a) oxygen transmission rate and b) packaging requirements of food products, c) DPPH activity inhibition, and d) antimicrobial activity. Adapted with permission from ref 138. Copyright 2024 Elsevier, under approved license number: 5732241082436.

by 54.9%, and the water vapor permeability rate (WVTR) decreased by 41.1%. Since the positively charged chitosan utilized to coat the substrates interacted intensely with the negatively charged cellulosic fibers, an increase in chitosan content greatly enhanced these properties. When MCC was added to the chitosan coating, the coated paper's gloss value improved.[137]

A film composed of MFC incorporated with chitosan (CS) and polypyrrole (PPy) produced by the coating method was effectively applied as an active packaging for fresh cherry tomatoes, extending shelf life by up to 10 days.[138] Thus, the MFC/CS/PPy film has potential for application in the packaging of different fresh fruits and vegetables. A coating of nanoparticles was created on the MFC/CS composite film's surface by the polymerization chemistry of PPy, causing water resistance (contact angle >122°) and decreasing the transmission of oxygen (32.38 cm^3·m^{-2}·day^{-1}) (Figure 5a,b). Additionally, the DPPH (2,2-diphenyl-1-picrylhydrazyl) method showed strong antioxidant activity and enhanced antibacterial efficiency against *Escherichia coli* (5.43 log CFU mL^{-1} reduction) due to the synergistic action of CS and PPy (Figure 5c). The antibacterial properties of the composite film are primarily due to its concentration of amino groups (Figure 5d). A protective inhibitory zone is formed by the amino groups that are positively charged and that compose chitosan (CS) molecules. These positive charges attract the negatively charged cell walls of microorganisms, leading to cell wall rupture and effectively preventing microbial growth.

4. NANOCELLULOSE-BASED FILMS WITH ANTIOXIDANT AND ANTIMICROBIAL PROPERTIES

The addition of plants or plant extracts while producing cellulose nanosuspension by mechanical defibrillation using any solvent can provide an alternative approach to incorporating antioxidants and antimicrobial compounds into NFC films. This technique usually produces a better interaction between the compounds and nanocellulose than simply mixing the ingredients after the synthesis of the MFC suspension, according to recent articles.[4,5] Among the various challenges of incorporating these extracts into cellulose films are the development of the nanosuspension and the potential depletion or degradation of bioactive compounds during subsequent film formation.[139] These chemicals can be protected by mixing during defibrillation, which improves the efficiency in any appropriate application.

Mechanical cogrinding offers a promising approach to enhancing the interactions between CNF and tannins, particularly when a nonionic surfactant is present. This process not only improves the antioxidant properties of the resulting films but also increases their water contact angles, indicating enhanced hydrophobicity. The findings suggest the potential for tailoring the properties of biobased packaging materials, advancing the pursuit of sustainable alternatives to conventional plastics.[140]

4.1. Tannins. Many plants generate tannins, which are phenolic compounds that are currently being researched because of their phenolic hydroxyl groups and high molecular weight that can cross-link with macromolecules and form hydrogen bonds with a donor polymer.[141] For tannins, the following patents have already been evidenced of the effect of tannin addition onto fibrillated cellulose composites. In one, a hydrogel with nanocellulose and tannin is obtained by

dispersing the material before ultrasonic drying[142] CN104262650B.

Another work shows a route for preparing different sizes of cellulose nanofibrils with the incorporation of tannin, and the process involves a series of acids and solvents for a good protective film[143] CN105536727B. In another work, there is nanocellulose and tannin biomass for the preparation of an adsorbent micro gel.[144]

Document[145] CN106189270 discloses a method of preparing a high-performance biodegradable film. In the patent application in question, collagen, sodium alginate, and carboxymethylcellulose were used to produce the film. However,[4] they used only raw material of plant origin, more precisely from plantations of fast-growing forests, which were nanocellulose, from eucalyptus plantations, and tannin, an extractive from the bark of the black wattle tree. The inclusion of the second material led the package to be "active", that is, it adds one more characteristic than a traditional packaging, with antioxidant capacity.

From the interaction between cellulose and tannin, both from natural sources, renewable and sustainable resources that are biodegradable and nontoxic to the environment are used. These can be replaced with high efficiency plastic packaging from oil refineries that degrade over a relatively long time.

The preparation of the nanocellulose and tannin suspension was initially tested with a simple mixture of nanocellulose and tannin powder. However, there is no interaction between the materials, and the tannin remains soluble in the aqueous solution, which was totally lost during the filtration process. From the mechanical defibrillation method with cellulose and tannin, an intimate interface between the materials is verified; that is, the tannin covers the cellulose nanofibrils. Thus, the only way to efficiently unite these two raw materials of forest origin, polar and without the use of chemical products, is by using the mechanical defibrillation process.[140] Other alternatives of interaction between tannin and nanocellulose with other directions, such as adsorption of heavy metals and pollutants, still depend on the chemical functionalization of nanocellulose or tannin so that there is an adequate interaction and high performance when applied in practice.[146−149]

4.2. Tannic Acid. Tannins are a class of phenolic compounds synthesized by various plants, drawing significant research interest due to their high molecular weight and the presence of phenolic hydroxyl groups. These characteristics enable them to interact with macromolecules through cross-linking mechanisms, particularly by forming hydrogen bonds with donor polymers.[141] Being water-soluble and frequently utilized as a food additive with antibacterial and antioxidant properties, tannic acid is a potential tannin.[150] It is regarded as one of the polyphenols with the highest in vitro antioxidant activity.[151] Also due to their cross-linking ability, tannins can protect epithelial tissues and can be used in antimutagenic, anticarcinogenic, anti-inflammatory, and antiviral applications.[152] Since the 1920s, tannic acid has been used to treat burns, and this has significantly decreased mortality rates.[153] Tannic acid has been reported to have antibacterial properties against a wide range of microorganisms, and it has also been shown to spontaneously cross-link chitosan and cellulose.[154,155] In a prior study, tannic acid and nanocrystalline cellulose were combined to create chitosan films, altering their mechanical properties when treated with heat.[155]

Another natural material with antibacterial properties and a strong ability for regeneration is chitosan.[136] Because of its
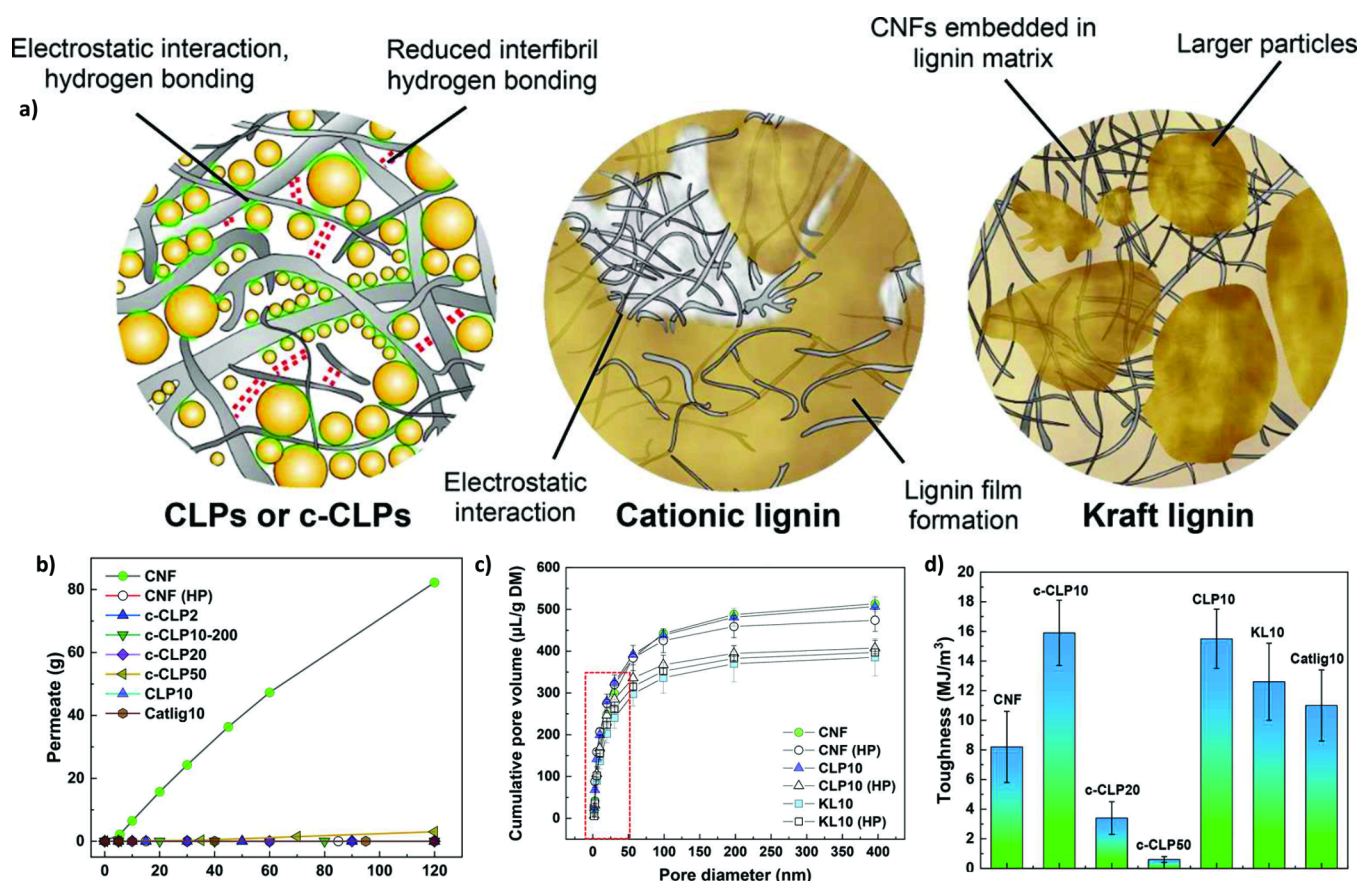
Figure 6. a) Representation of the potential interactions between CNF and distinct lignin structures where cationic, noncationic colloidal lignin particles (c-CLP and CLP) and kraft lignin (KL) were used, b) water permeation, and c) porosity, as well as d) film toughness. Adapted with permission from ref 171 under a CC-BY license.

extremely reactive amine groups, which can integrate active chemicals or produce nanoparticles, this material's functionality can be modified.[156] Therefore, its application when combined with other materials, like films, has been documented in numerous works;[135] even though chitosan films are already extremely delicate, they can be strengthened by adding tannic acid, which acts as a plasticizer.[154]

Tannic acid's antibacterial efficacy was demonstrated a century ago, although improper target doses may lead to adverse side effects. Notably, the polyphenols of tannic acid that are cross-linked with polymeric materials make a powerful compound that possesses the tannin's advantageous properties.[28] In addition, surface modifications in nanocellulose films have also been reported and patented showing effects similar to those already made with pure films on a large scale.[157,158]

The cross-linking of tannic acid polyphenols, nanocellulose obtained through mechanical defibrillation, and chitosan enabled the development of films with antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*, as well as the ability to reduce cell metabolism and inhibit NF-κB activity, characteristics associated with tannic acid. In addition, MFC films showed greater thermal stability, due to a more rigid lamellar structure (stronger hydrogen bonding) when incorporated with tannic acid.[28]

4.2.1. Potential Application and Manufacturing Method. MFC films have proven to be very useful for food packaging applications. However, it is feasible to incorporate certain natural substances to improve the lack of useful features found in pure films containing nanofibrils. Therefore, the use of

tannic acid provides antibacterial activities and improves the structure of these films using solvent casting.

Other methodologies have also been addressed in the literature to obtain resistant hydrophobic nanocellulose particles that can be incorporated into any organic solvent, such as using tannic acid to a nanocellulose suspension with NaOH, adjust the pH to 8, and toluene to form a two-phase system with decylamine. Cellulose nanofibrils were obtained by centrifugation and vacuum filtration and dried in a conventional oven or lyophilized. The dried nanocellulose can be dispersed in different organic solvents.[157]

Coating by spray deposition using an airbrush has also been proposed. Compressed nitrogen was used to atomize the nanocellulose suspension in order to accomplish spray deposition. A distance from the spray tip to the substrate led to spraying in a very dilute regime. Thus, several layers were made by spraying for 0.5 s, with an interval of 2 s, followed by repeated cycles 20×, obtaining a thickness of approximately 200 nm. The thickness increases linearly with the amount of spray pulses applied when intermittent drying. This procedure presents an easy route to prepare nanostructured cellulose-based thin films on a large scale with a low surface roughness.[159]

During spraying, tiny CNF suspension droplets are sprayed onto the heated substrate, where they solidify and dry. As a result, the final thin layer consisted of numerous fused droplets. In contrast to conventional spray-deposited thin films, the enhanced surface charge seems to facilitate the assembly of nanofibers, leading to a uniform, homogeneous, and densely

packed film with exceptionally low roughness. This highlights how modifying the surface charge density of the building blocks can modify the surface roughness of spray-deposited thin films. The higher surface charge density of nanofibrillated cellulose suspensions enhances the system's electrostatic stabilization, promoting nonagglomerating self-assembly in the films. According to the article, the smoothing of spray-deposited thin films is driven by the rapid increase in the CNF suspension concentration due to water evaporation, which also causes an ionic surge, leading to gel formation and instant lock in.[159,160]

The deposition or coating of substrates with CNF by the spraying method is considered an ideal technique for large-scale industrial production due to its properties of flexibility, continuity, and speed. In addition, spray-obtained CNF coatings showed excellent mechanical and oxygen barrier properties. However, moisture barrier properties are limited, requiring techniques that improve this function.[161]

4.3. Incorporation of Lignin into Nanocellulose.

Lignin's functional groups, such as phenolic units, ketones, and other chromophores, enable it to act as a natural UV blocker. Due to its phenolic groups, lignin exhibits exceptional antioxidant properties. Its aromatic structure enhances the resilience of polymer blends to oxidation and temperature variations, while also improving their ability to scavenge free radicals.[162] Currently, many ultraviolet (UV) protective applications rely on a combination of organic and inorganic UV blockers.[163] Organic UV blocking compounds degrade when exposed to sunlight and are often hazardous.[164] Nanoparticles are the most common form in which inorganic UV blockers, such as ZnO and TiO_2, are applied.[165] However, achieving complete UV blocking requires high doses, which frequently cause particle aggregation and reduce the transparency of nanocomposite films.

High lignin content films show a slight improvement in the water vapor barrier while creating a highly hydrophobic surface with exceptionally high water contact angle values. Lignin reduces the formation of hydrogen bonds while facilitating the development of hydrophobic pores.[166] A limitation of the production of lignin-based nanocellulose materials is the mismatch between hydrophobic lignin and hydrophilic cellulose. Furthermore, both crystalline nanocellulose and lignin are negatively charged, causing them to repel each other electrostatically at normal pH levels in the absence of chemical additives.[167]

4.3.1. Synthesis Method Using Lignin. Studies have demonstrated that ionic liquids can be used to produce cellulose films containing lignin; however, this approach is not cost-effective due to the high cost of the solvent.[168] Certain methods that involve hazardous organic solvents, including dimethyl sulfoxide/water and dioxane/water, lead to the formation of nonuniform films.[169] To make lignin and cellulose films compatible, diverse approaches have been made via covalent bonding.[170] Although these films are uniform, the process requires organic solvents and long preparation times.

Other alternatives, such as heat treatments, could be useful to allow the activation of lignin and facilitate binding with nanocellulose. However, the study by Farooq et al.[171] reports that high temperature treatment (above 90 °C) of nanofibrillated cellulose and lignin films (10% in bond) greatly reduced the tensile strength of the materials. Alternatively, intense changes in the morphology were identified. Hot pressing decreased the porosity and increased the amount of

interfibrillar bonds between nanofibrillated cellulose and lignin, playing a role as a plasticizer (Figure 6a). The strong interfibrillar interaction results in an overall reduction in cumulative pore volume with a decrease in water permeability (Figure 6b,c). Furthermore, Herrera et al.[172] reported that the formation of hydrophobic surfaces when the nanocellulose/lignin film is treated at 93 °C allows for low oxygen permeability values in contrast to commercial polymers such as polyethylene terephthalate (PET) and polystyrene.

The literature highlights the use of Fenton's reagent as an initiator to facilitate the formation of covalent bonds between lignin and cellulose nanocrystals.[173] By strengthening both covalent and noncovalent interactions between the two polymers, this technique improved the water resistance of the coated films. Using nanocrystalline cellulose and organosolv lignin, coatings with natural UV-absorbing properties were developed through the simple evaporation of a combined colloidal mixture.[169] Thin, transparent films with tunable antireflective and UV-blocking properties were formed, where lignin and CNC interacted through electrostatic and non-covalent forces.[174,175] Lignin-based transparent films have been produced using water-soluble polymers such as poly(vinyl alcohol);[176] however, the nanocomposite films obtained are not entirely biodegradable.

Polymers based on MFC acetylated with lignin (Ac-MFCL) and polylactic acid (PLA) were developed by Yetis et al. (2020).[177] The hydrogen bonds between Ac-MFCL and PLA provided better mechanical and thermal properties of the biocomposite. The Ac-MFCL compound acted as an effective reinforcing and nucleating agent. The Ac-MFCL-PLA biocomposite can be considered to be efficient for applications in packaging and biomedical products. Also using PLA, nanocomposites based on lignocellulosic nanofibers (LCNFs) and polyethylene glycol (PEG), with nanocellulose contents between 2 and 10%, were prepared by a fusion process.[178] Increases of 250% in tensile strength and 1100% in Young's modulus were observed. The wide dispersion of LCNFs in the application of PEG as a carrier within the PLA matrix allows LCNFs to be incorporated into other matrices to produce composites with improved mechanical properties.

Homogeneous and transparent films of CNC and lignin can be processed without using organic solvents, as shown in a recent study. Using an aqueous alkaline solvent with NaOH, this study outlines an innovative, yet simple, method for CNC/lignin nanocomposite film preparation. CNC is blended with alkaline lignin (AL) or kraft lignin (softwood-SKL) in an alkaline suspension. Films of CNC/AL and CNC/SKL were produced by using the solvent casting method. By the addition of NaOH, CNC aqueous suspensions, with or without lignin, can be adjusted to create transparent and homogeneous films. With 3−4% NaOH, maximum transparency was obtained, while the homogeneity of the films improved due to the uniform dispersion of lignin. Furthermore, kraft lignin with a 10 wt % concentration ensured complete UV blocking. These films exhibited consistent UV protection when exposed to UV radiation, and lignin acetylation lessened its coloration, with only a minor reduction in the extinction coefficient. The visible light transmittance at 550 nm increased by 67% with the addition of 10 wt % kraft lignin to CNC films, without notably altering the UV radiation blocking capability. The presence of lignin also provided thermal stability and surface wettability, which were observed by the contact angle technique. Owing to lignin's higher hydrophobicity compared to CNC, CNC/lignin

films maintained a more stable contact angle over time than CNC films alone. Additional enhancements could focus on reducing lignin coloration and improving the alignment of CNC.[179] Similar results have been reported for a patent using this procedure.[179]

Luo et al. (2021)[180] studied the effect of pretreatments of free laccase, alkaline sulfite, and alkaline hydrogen peroxide on lignin-incorporated cellulose micro/nanofibrils and the formation of films for application in packaging. The pretreatments provided better barrier properties for the films based on cellulose micro/nanofibrils incorporated with lignin, including decreased permeability to oxygen (OP) and water vapor (WVP). In particular, the pretreatment with alkaline sulfite showed lower values; at 23 °C and 0% RH, the oxygen permeability (OP) was 0.85 cm·μm/(m^2·24 h·kPa), while at 23 °C and 50% RH, the water vapor permeability (WVP) was 1.72 g·mm/(m^2·day·kPa). Lignin on cellulose fibrils aids water vapor resistance, but oxygen can still diffuse through structural voids. Removing xylose can increase these defects, though pretreatments that reduce lignin improve the lignin-cellulose compatibility and lower the oxygen permeability (OP). Consequently, pretreated lignin-cellulose films (LCMNF) show a lower OP than untreated films.

Furthermore, leveraging their nanoscale features and morphologies, CNF, CNC, and lignin nanoparticles demonstrate intrinsic compatibility and stability when combined in aqueous dispersions.[34] The authors observed that this compatibility resulted in coatings that maintain the conservation of cultural heritage object properties and their properties including surface roughness and vapor permeability while improving hydrophobic characteristics.

5. FILMS INCORPORATED WITH CLAY NANOSTRUCTURES (NANOCLAY)

Xu (2016)[181] used "tempo" oxidized nanofibrillated cellulose in addition to calcium carbonate, clay, and latex for paper coating. The coated paper demonstrated a more resistant and smoother surface, as shown by the results. However, due to the hydrophobicity of the nanofibrils, there was an increase in the permeability of moisture.

5.1. Introduction to Nanoclays.
Nanoclay are very unique due to its unique oxygen barrier properties in blends from nanocellulose films, which are very competitive, and superior compared synthetic polymers used in industries.[182] However, the water vapor barrier property is still very low, which is due to the strong hydrophilic characteristic of cellulose nanofibrils. However, such a property is still positively much lower in MFC films than pure bleached kraft paper.[183] These values decay rapidly when using certain types of nanoclay, such as sodium montmorillonite.[184,185] Reinforcement fillers of bentonite or organic derivatives are great for improving the properties of nanocomposites, especially the barrier properties. The improvement of barrier properties, especially to gas molecules, is related to the presence of layers of silicate layers dispersed in the polymer matrix, which have a high aspect ratio and are arranged in an orderly manner,[186] so this material is an excellent and attractive additive in nanocomposites aiming at applications for food packaging.[185,187]

Clay structure is closely related to the final applications of MFC. The literature provides that 10% is already sufficient to massively change the structure, such as increasing the mechanical strength in stress−strain tests, thermal properties,

and surface hydrophobicity. However, the mixture must be good so that material aggregation does not occur, and the film properties can decrease due to this factor. In this aspect, it is noteworthy that the exposure of these materials to high shear forces or ultrasonication is necessary to prevent this agglomeration, allow exfoliation, and, consequently, increase the surface area.[188]

5.2. Bentonite Nanoclay.
Bentonite has a high cation exchange capacity, high expansion power, low hydraulic conductivity, and high specific surface. Furthermore, the physical properties of bentonite can be modified through interaction when in contact with some fluid.[189]

In addition to having an abundant reserve worldwide, bentonite is already used in the industrial sector for various purposes, such as plasticizer in the ceramic industry, preventing paint runoff after application, filtration of olive oils and wines in the food industry, absorption, and elimination of odors in sanitary bin granules and soil waterproofing. Bentonite properties such as high cation exchange capacity can help reduce possible leaching of compounds present in the structure, and its plasticizing effect can be useful to increase mechanical strength. The high expansion capacity can be controlled through the pH of the liquid medium since the highest degrees of expansion occur at a pH close to 8.

Montmorillonite-type clay mineral particles, such as bentonite, can be used advantageously in the form of films in favor of reducing the permeation of gases. Specifically, the flat and broad morphology of these clay minerals hinders, or prevents, the gas molecules' migration inside the matrix.[185,187,190]

The interaction of hemicellulose with bentonite nanostructures is already evidenced in some works, exhibiting that 10% results in a layered structure and with a nacre structure appearance for the addition of bentonite at 30−70%, showing good mechanical properties. As bentonite is impermeable to all gases, it is normally incorporated into packaging that requires barrier properties. In addition, the permeability to oxygen and water vapor shows excellent values; that is, bentonite acts as a physical obstacle and hinders the absorption of various gases.[191]

Likewise, the interaction between previously exfoliated bentonite nanostructures and NFC was recently observed during film formation under different loads of inorganic material (15, 30, and 45%).[192] Two types of bentonites were used, PGN and PGV, in which they differ by aspect ratio, a platelet aspect ratio of 300−500 for PGN and 150−200 for PGV. It was observed that 15% PGN bentonite filler decreased the permeability of water vapor from 425 to 375 g/m^2/day and improved oxygen permeability (OTR), an important property for application in food packaging. The incorporation of PGN type bentonite in NFC films can provide a reduction of up to 3 times in this rate, reaching 5.95 (cm^3/m^2/day) for 0% RH. However, loads higher than those tested tend to impair the waterproofing of the surface, since the high hydrophilicity of PGN compared to PGV possibly explains this tendency toward greater water absorption. Other pertinent aspects were that the lower cation exchange capacity of the PGN bentonite may hinder the movement of water in the nanobentonite and NFC films. In addition, PGV-type bentonite tends to produce a more brittle surface, unlike PGN, which provides a more ductile NFC film.

Overall, bentonite's unique properties allow it to interact effectively with liquids, gases, and other substances, making it a

highly valuable material for various packaging applications, including moisture control, enhancing gas barriers, and providing antimicrobial activity. While bentonite provides exciting possibilities for advanced packaging applications, ensuring safety remains a top priority.[193]

5.3. Halloysite. Halloysite nanotubes as reinforcing fillers are very promising, since these nanotubes have little interaction with each other due to their geometry, which results in easier formation of hydrogen bonds with polymers. This is attributed to hydroxyl groups located on the tube's exterior surface, which can disperse very well in the polymer matrix without additional chemical modifications.

Due to the greater strength and greater length/diameter ratio of haloysite nanotubes, compared to bentonite, the polymer matrix exhibits an enhanced degree of reinforcement. Acid treatment on these nanotubes helps improve interfacial bonding with the nanofibrillated cellulose by expanding the surface area and porosity, and numerous functional groups are formed (15% sulfuric acid, temperature 85 °C between 1.5 and 2 h dissolves outer and inner layers, and the inner part becomes amorphous silica). Additionally, the acid treatment results in films with improved mechanical and thermal properties.[194]

Tests with bentonite, however, show that the interaction of nanofibrils with overlying bentonite layers is limited due to the van der Waals forces between the layers. The nanofibrils form a fibrous network that encases the bentonites as their interaction with the bentonite is insufficient. The mechanical properties of NFC decreased with the higher concentration of bentonite, while for haloysite nanotubes, the mechanical properties were increased. The targeted and porous structure of halloysite nanotubes exhibits superior mechanical properties, potentially offering better performance in nanocellulose biocomposites compared to bentonite.[194]

5.3.1. Production Method of Nanocellulose Films Containing Haloysite Nanotubes. The simple homogenization method, which uses a homogenizer or just mixing with a magnetic stirrer, with subsequent vacuum filtration for maximum water removal is commonly reported in the literature. After filtering, the film is removed and sandwiched between two metal plates that are also in contact with a paper filter. Soon after, these metallic plates are pressed by a constant force and vacuum-dried at 70 °C for 2 h after being dried at 40 °C for 24 h. Another approach is not to use a constant force in the drying process but, after going through the drying process, use a hot press using a pressure of 100 MPa at 160 °C for 5 min. This method also allows for a homogeneous film with a high concentration of nanocellulose.[195,196]

Another study showed that multifunctional hybrid CNF/haloisite nanotubes (HNTs)-zinc oxide (ZnO) films were manufactured using a vacuum-assisted filtering technique and subsequent hydrophobic changes.[197] The films were immersed in a trichlorosilane and isopropanol solution for 2 h at 65 °C to accomplish the hydrophobic modification, which enhanced the UV shielding performance. This improvement occurs because ZnO nanoparticles are anchored to the surface of HNTs through Zn–O–Si covalent bonds. Consequently, the CNFs/HNTs-ZnO films demonstrated excellent blocking efficiencies, achieving 95.7% for UVA, 98.7% for UVB, and 99.8% for UVC radiation. In addition, the membrane for filtration presented a rough architecture, contributing to the superhydrophobicity (contact angle >155°). Simultaneous self-cleaning function and excellent thermal stability were also observed. The results

indicate that CNFs/HNTs-ZnO films can be potential materials for the development of sustainable UV protection techniques with important applications in packaging, smart windows, and other materials sensitive to UV radiation.

5.4. Sodium Montmorillonite Nanoclay. Films containing sodium montmorillonite nanoclay (Na+ -MMT) and MFC have already been patented, where this mixture forms a lamellar pattern[198,199] and is oriented parallel to the paper surface. There is also the addition of a water-soluble cross-linking agent, such as chitosan or hyaluronic acid, and this suspension can be incorporated onto cardboard as a coating.

Positively charged chitosan as a cross-linking agent in these structures can result in a good flocculating or ionic cross-linking effect on both MFC and MMT via electrostatic interactions and hydrogen bonding. Thus, the filtration time during processing is reduced to about a tenth of that without it. The incorporation of a small amount of chitosan (10% by weight) results in a layered structure, which in the biometrics area relates it to a nacre structure and increased the nanocellulose film's mechanical strength and oxygen resistance properties at 50% RH. The cross-linker can also be any water-soluble polymer, such as hyaluronic acid, or polysaccharides, or combinations thereof, which preferably contain positive charges when in an aqueous solution.

The MFC and clay syntheses produce layers that are parallel to the film surface and interpenetrate each other. The explanation of the layered structure is due to the numerous hydroxyl groups and negative charges on the MFC surface. The hydroxyl groups lead to the MFC being more hydrophilic, and the negative charges induce the microfibrils to repel each other, resulting in more separate nanofibers when the nanoclay is incorporated. High oxygen and water vapor barriers are highlighted in the film. The suspensions formed by mixing MFC and Na+ MMT remain stable, even after 10 h. In addition, the film is excellent against flames.

5.4.1. Production Method of Nanocellulose Films Containing Sodium Montmorillonite. In a patent by Berglund & Liu (2014),[198] the suspension of the MFC and clay mixture in water was prepared by magnetic stirring and ultrasonic dispersion for 30 min. Then the mixture was vacuum filtered by *Rapid Kothen*, a paper making machine. Finally, the films were carefully stacked between metal grids, placed between two filter papers and vacuum-dried for 10−15 min at 93 °C. The entire manufacturing time to obtain a film varies between 30−90 min, based on the amount of nanoclay and the ultimate film thickness. The film can be used as a coating applied to other paper, board, cardboard, or packaging material. The coating can be applied to the surface by a variety of techniques, including dip coating, spray coating, painted or laminated.[183]

A sustainable system based on CNF, incorporated with colloidal montmorillonite nanoclay (MMT), epichlorohydrin polyamidoamine (PAE), and Acrodur thermoset acrylic resin (ACR) was proposed by Tayeb and Tajvidi (2019).[33] MMT was exfoliated, induced by 5 min of sonication, and cross-linked with 1% CNF in a centrifugal mixer at 2000 rpm for 5 min. A Petri dish was filled with the mixture, and the internal cross-linkers PAE and ACR were added (about 1.5% each) and dried at 140 °C for 10 min. To create the matrices, colloidal components were evaporatively induced, and then a thermal curing procedure was applied to enable cross-linking. The incorporation of MMT into CNF reduced the WVTR of the film by 60%, in addition to contributing to a denser structure and resistance to oily substances. The study suggests that

CNF/MMT/PAE/ACR-based films can be a sustainable, low-cost form with good barrier properties (low moisture permeability) applied in food and drug packaging.

5.5. Gibbsite. Recent works have investigated the use of gibbsite, which has a similar structure to nanoclays and is characterized as one of the mineral forms of aluminum hydroxide. It is evident that the properties of this component prevent the diffusion and permeation of gas molecules.[200,201] Positively charged gibbsite nanoplates exhibit very similar results to MFC with nanoclays, and it is possible to alter the film's characteristics by changing the ionic strength of both the MFC suspension and the film while it is drying.

A hydrothermal method that treats 0.08 M aluminum isopropoxide and 0.08 M aluminum *sec*-butoxide in 0.09 M hydrochloric acid can produce gibbsite nanoplates. This step takes 10 days to dissolve, and then suspension is then exposed to heat in an oven at 84 °C for 72 h.

After this process, deionized water is used to dialyze the suspension, and ultrafiltration is used to concentrate it using 10 000 Da membranes (Milipore) at approximately 5% by weight. The pH was fixed at 5.9 using 0.1 M hydrochloric acid.[201]

5.5.1. Production Method of Nanocellulose Films Containing Gibbsite Nanoplates. Before depositing the first layer of gibbsite nanoplates, a multilayer "primer" consisting of successive layers of polyanions and polycations is applied to a cardboard substrate. This is achieved by immersing the polyanions and polycations in their respective solutions for 20 and 15 min, respectively, with 5 min water rinses in between. Following this procedure, a negatively charged cardboard material is immersed for 5 min into the positively charged gibbsite nanoplate suspension, rinsed for 5 min with distilled water, and then submerged for 5 min in the negatively charged microfibrillated cellulose suspension. These rinsing processes are necessary to ensure that only strongly interacting particles are adsorbed while eliminating weakly attached nanoparticles.

The effect on the oxygen barrier properties of thin films coated on cardboard shows that with more layers deposited on the cardboard the oxygen transmission rate (OTR) value drops between 20 and 36% when coated with 4 nanogibbsite/MFC bilayers compared to the pure cardboard substrate (Figure 7a,b). This effect is intensified by using 7 bilayers and allowed for a 75% decrease in the level of the OTR in smart paper coating and 59% in the level of the OTR in PE coated board (Figure 7). This finding shows that the main factors controlling the oxygen barrier properties at 50% relative humidity are film thickness and tortuosity, which are linked to particle morphologies and the film structure[201] (Figure 6).

6. MODIFICATION OF NANOCELLULOSE WITH STEARIC ACID

The main drawbacks limiting the overall performance of nanocelluloses are their poor dispersion in nonpolar solvents and with nonpolar synthetic polymers.[38] Nanocelluloses are typically modified on their surface with functional groups, such as alkyl groups, and synthetic polymer chains through grafting techniques to address these issues.[202]

Through esterification reactions, modification on cellulose polymeric chains occurs in order to obtain cellulose esters. It is possible to use both homogeneous and heterogeneous esterification in the synthesis of cellulose esters. However, such a synthesis can be adjusted to only occur on the surface of
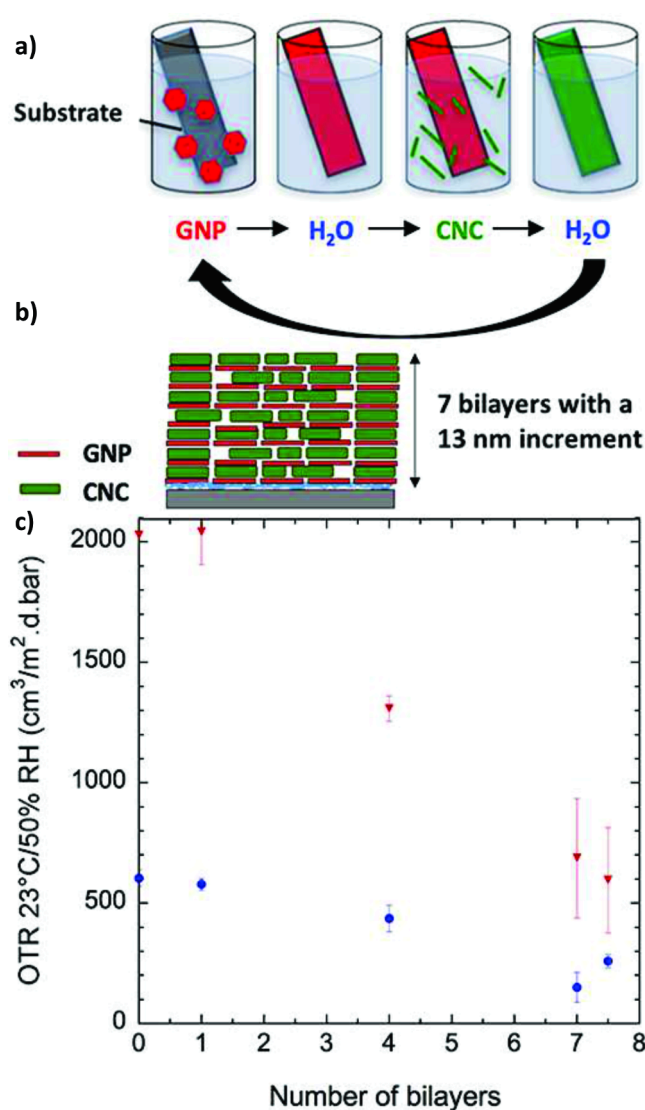

Figure 7. A schematic illustration of the a) layer by layer technique, b) likely structure of 7 bilayers, and c) oxygen transmission rate of films. Adapted with permission from ref 201 under a CC-BY license.

the nanofibrils, leaving the internal cellulose structure as crystalline.[203] Additionally, surface modification of native cellulose is predominantly achieved through reactions under heterogeneous conditions, which is a key strategy for both isolating and chemically changing nanocelluloses.[38] Because of its simplicity, esterification of the hydroxyl groups on the nanocellulose surface is a commonly used modification technique. Nanocellulose produced by hydrolysis of hydrochloric acid can also be sulfated using sulfuric acid to introduce sulfate fractions in a controlled manner. The primary difficulty lies in conducting the reaction in a manner that preserves the integrity of the internal crystalline arrangement while focusing on esterifying the hydroxyl groups on the surface of the nanocelluloses.[204]

6.1. Synthesis Method for Esterification. Acetic anhydride can be used to acetylate nanocelluloses when sulfuric and perchloric acids are present as catalysts. Acetylated nanocelluloses were created using these techniques on the surface of a suspension of microfibrillated cellulose.[205] Additionally, a novel direct method for esterifying the surface of nanocellulose has been introduced, using citric acid as a

catalyst.[203] Only acetic anhydride was the sole solvent applied in a sufficient amount to ensure the dispersion of the nanofibrils with proper stirring of the suspension; no additional solvent was needed. Under mild conditions at 120 °C and using a magnetic stirrer for 3 h, acetylated crystalline nanocelluloses with varying degrees of substitution (DS = 0.18 and 0.34) were produced on the surface by adjusting the amount of catalyst. Throughout the chemical treatment, the core, or internal crystalline arrangement, of the nanocellulose stayed intact; only the surface underwent esterification.

Modified on the surface with alkyl chains, nanocelluloses show good compatibility with other synthetic polymers and are employed as reinforcements in materials like films and foams.[206,207] Typically, postesterification of hydroxyl groups on the surface of nanocelluloses has been used to immobilize alkyl groups on the surface. Specifically, it is possible to do esterification after producing the cellulose nanosuspension. The acetylation of nanocellulose is the most widely studied method among various postesterification reactions for introducing alkyl groups.

Esterification can be used to graft polymeric chains onto the surface of the nanocellulose. In a comparative study, Pang et al. (2016) examined various surface esterification methods for nanocellulose, including acid chlorides, acid anhydrides, acid-catalyzed carboxylic acids, and in situ activated carboxylic acids, to introduce hexanoyl-, acetyl-, oleoyl-, dodecanoyl-, and methacryloyl-functional groups. The graft efficiency of acid anhydrides was found to be superior to those of the other methods.

6.2. Synthesis Method Using Stearic Acid. The use of stearic acid to promote postsuspension nanocellulose surface enhancement has been previously reported and patented.[208,209] For these works, a nanocellulose suspension with 60 mL of anhydrous ethanol was mixed and ultrasonicated for 30 min. Stearic acid in an amount equal to the solids content of the MFC was added and again taken to ultrasound for 30 min. For 8 h, the reaction was conducted at 80 °C. and mixed using magnetic stirring. Anhydrous ethanol helps drive the reaction to the correct esterification path. Soon after, this suspension was filtered and dried for 24 h at 50 °C after being washed with anhydrous ethanol. Cassava starch in 3.5% by weight solution was plasticized, and nanocellulose particles were added; such particles were first dissolved for a few minutes at 80 °C in ethanol and added at various concentrations to the cassava starch to form films with different concentrations of micro-crystalline cellulose. This material has shown promise for the development of films with hydrophobic moisture barrier properties, and it does not retain moisture and is also biodegradable with applications in food packaging. To obtain the hydrophobic property, stearic acid is used, which modifies the surface of the microfibrillated cellulose suspension. In addition, films with this compound increase their mechanical and hydrophobic properties. Despite modification with stearic acid, the material preserved key aspects of its fundamental crystalline form, which was classified as cellulose II.

Chen et al. (2020)[204] developed cassava starch films with the incorporation of MFC and NFC modified with stearic acid (Figure 8a). MFC and NFC were first treated by acid hydrolysis, with 90% phosphoric acid for MFC and 65% sulfuric acid for NFC. After adding anhydrous ethanol and mixing for 30 min, stearic acid was added to an amount equivalent to the solid content of the cellulose and sonicated for 30 min. The incorporation of MFC and NFC esterified
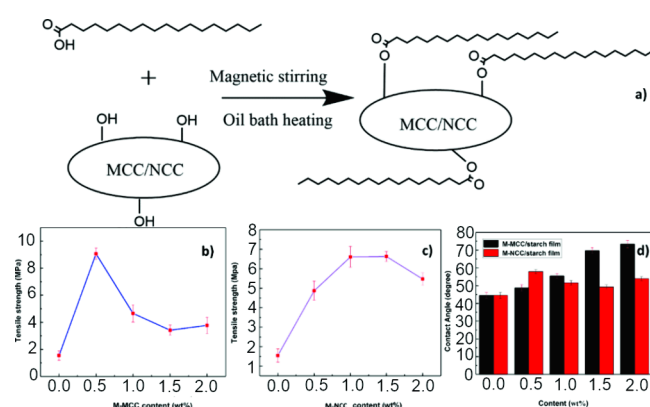

Figure 8. a) MCC/NCC's chemical interaction with stearic acid, b) M-MCC/starch films' tensile strength, c) M-NCC/starch films, and d) the contact angles. Adapted with permission from ref 204. Copyright 2024 Elsevier, under license number 5732321157537.

with stearic acid provided good mechanical, thermal and barrier properties (greater hydrophobicity) for the cassava film (Figure 8b−d).

The degree of esterification of 2.99 was achieved in cellulose stearate ester, synthesized through the reaction of stearic acid, trifluoroacetic anhydride, and microcrystalline cellulose.[210] However, cellulose ester can be obtained through a reaction with carboxylic acids, like anhydrides, in uniform solutions such as N,N-dimethylacetamide/LiCl or N_2O_4/DMF.[211] Due to the toxicity of the reagents and the difficulty in removing them, this reaction has limitations. Therefore, enzymatic esterification could serve as a more advantageous alternative method. A method for the enzymatic esterification of stearic acid with bacterial cellulose, utilizing immobilized lipase, has been described. In this procedure, bacterial cellulose powders are combined with 0.1 g of stearic acid, 5 mL of n-butanol, and 0.1 g of immobilized lipase. The mixture is kept at 50 °C, with incubation times ranging from 6 to 30 h in intervals of 6 h. Afterward, the solid was collected by filtration. After the solid (ester) was washed with ethanol, it was dried in an oven at 80 °C. The filtrate underwent titration using a 0.1 M aqueous solution of NaOH. The degree of esterification was calculated by separating the mass of reacted stearic acid from the total mass of bacterial cellulose.

The ideal esterification conditions occurred in 18 h with a ratio of 1:5 (cellulose:stearic acid mass ratio). The changes in the properties of esterified cellulose were confirmed by the appearance and change in bands in the FTIR spectrum. Cellulose stearate esters were confirmed with a degree of substitution of 0.35. Esterification led to a reduction in the hydrophilic properties and an improvement in the crystallinity of bacterial cellulose.[212]

7. MFC AND CNC MODIFICATION WITH CRUDE TALL OIL

Derived from conifer trees, tall oil fatty acid (TOFA) is a secondary product generated in the pulp and paper industry. It is an ecological option to be used as a hydrophobicity-inducing component, where this oil is made by distilling crude tall oil, which is a blend of mostly unsaturated, nonconjugated fatty acids, including oleic, linoleic, and pinolenic acids. Every year, the pulp and paper sector recovers about 450,000 tons of crude tall oil from pulp mills of resinous species.

TOFA is a low-cost, sustainable, and nonedible product, in addition to being a sustainable natural resource utilized in various applications, including cleaning, surfactants, and diverse chemical derivatives. However, a variety of fatty acids are combined to create TOFA, which is used to make kraft pulp. Trienoic acids, like pinolenic acid, undergo isomerization, forming conjugated compounds that are susceptible to "Diels—Alder" reactions. Consequently, the material may cross-link and produce cyclized byproducts, which could cause issues with solubility. Additionally, unmodified TOFA is susceptible to autoxidation, which makes TOFA-based products unstable. These processes may contribute to the synthesized compounds' "aging". However, it is easy to transform unsaturated structures into less reactive saturated forms.

In addition to the previously mentioned points, to synthesize materials with TOFA and be able to use as films, a high degree of substitution (GS) is required, because low values prevent cellulose-based polymers from being plastic and reduce their solubility. Therefore, an elevated value of GS can be achieved with homogeneous or heterogeneous reactions, as explained above.

It has been reported that hydrophobic cellulose derivatives, such as palmitic acid or decanoid esters of cellulose, can produce films that could be utilized as biodegradable coating materials.

7.1. Synthesis Method Using Crude Tall Oil.
Cellulose was acylated with unsaturated, saturated, and branched TOFA fatty acids to create hydrophobic cellulose-based composites.[213] This method involved immersing the films for 30 min in 100 mL of pyridine. Prior to adding fatty acid chlorides, the pyridine solution's temperature was increased to 110 °C. After 90 min, the surface reaction was removed and allowed to dry overnight at ambient temperature. After drying, the films were Soxhlet-extracted for 24 h using ethanol to eliminate any nonbonded fatty acids.

In another study, only the surface of the film was modified. After the film was presoaked in a pyridine solution kept at 110 °C, it was hot striped, and a thin coating of fatty acid chloride was promptly brushed over the surface. The films remained at ambient temperature overnight and were then subjected to Soxhlet extraction, as described in the bulk modification, to remove residual fatty acids.

Another route that can be considered for surface modification of nanocellulose films, specifically CNC, is the addition of the films in 250 mL of pyridine and 4-toluenesulfonyl chloride (TsCl) under constant stirring and nitrogen gas purge, followed by the slow addition of the carboxylic acids in a 1:1 TsCl/acid molar ratio. For 1 to 4 h, the reaction temperature was kept at 50 °C. Following this step, ethanol and methanol were used to wash the films. After this step, the films were washed with methanol and ethanol, followed by Soxhlet extraction using methanol for 18 h. At last, a final step of filtration and washing with methanol, ethanol, acetone and water, followed by vacuum drying.[214] For this route, there is a reduction in the films' thermal stability, in which the temperature and degradation are dependent on the type of fatty acid used and the DS (degree of substitution) on the nanocellulose's surface. It was observed by the CNC that a change in the temperature of T_g, this referring to water bound to the cellulose structure, of the pure cellulose from 81 to 85 °C occurs after functionalization with fatty acids from the tall oil. The present water acts as a softener in the cellulose's amorphous domains, making it possible to observe the T_g.

Addition of TOFA showed similar behavior to other fatty acids regarding the modification of reactions on the cellulose surface.

Hosseinpourpia et al. (2020)[215] used four products from the distillation of tall oil, with different concentrations of fatty acids, to develop formulations with furfuryl alcohol. The formulations were used for applications on cellulosic paper sheets. Under standard and humid climatic conditions, tall oil distillation products with higher concentrations of fatty acids (3−5%) and a lower resin concentration of melamine-urea-formaldehyde (10−12%) showed better performance in terms of strength tensile, thermal and hydrophobic.

8. MODIFICATION OF NANOCELLULOSE WITH SILANES

Functionalization of materials with silanes is a technique well-known in the literature for improving surface characteristics, such as hydrophobicity, antimicrobial activity, and compatibilization with synthetic polymers.[216]

The impact of amine-functionalized silanes on nanocellulose properties is indeed multifaceted, making them valuable in enhancing the compatibility between nanocellulose and various polymer matrices. This compatibility is essential, as it directly affects the thermal, mechanical, and barrier characteristics of the composite, all of which are essential for a range of uses.

Silanes significantly enhance the mechanical properties of nanocellulose composites. This enhancement is mainly attributed to the strong interaction between the amine groups of the silane and the polymer matrix facilitated by the silane agent that eliminates a significant number of hydroxyl groups. For example, observed by the dramatic decrease of the hydroxyl group absorption peak on FTIR (OH ~ 3330 cm^{-1}) in biopolymeric packaging films, films made of natural red seaweed and kenaf cellulose nanofiber (CNF) were used in biopolymeric packaging films, which were then treated on their surface with silane.[217] Amine groups create covalent or hydrogen bonds with the cellulose and polymer chains, improving the adhesion between the nanocellulose and the surrounding polymer as well as the interaction between water and the film. This stronger bond at the interface allows for better stress transfer between nanocellulose and the matrix of polymers, leading to a composite that can withstand higher mechanical loads.

For example, a study by Anlovar et al. (2020) demonstrates how to increase interaction with linear low-density polyethylene (LLDPE) in nanocomposites by using cellulose nanocrystals (CNCs) treated with 3-isocyanatopropyl triethoxysilane (ICPTS). This modification led to enhanced mechanical properties when processed with LLDPE, particularly in Young's modulus. At a molding temperature of 120 °C, the nanocomposites exhibited up to a 20% increase in Young's modulus compared to unreinforced LLDPE. In contrast to the silane side chains of ICPTS, which function as a plasticizer and thus reduce the LLDPE crystallinity degree, CNCs are used as crystallization seeds, enhancing the LLDPE crystallinity.[218]

Silane modification generally tends to remain stable in terms of thermal stability, as shown by previous works, which usually tends to remain stable due to interaction between the nanocellulose and silane, while the property from the composite film remains relatively similar.[218] However, when studying single nanocellulose film silane-modified, the stability temperature decomposition can increase from 333 to 358 °C. This is because the silane modification protects the cellulose

fibers from thermal decomposition and reinforces the matrix, allowing it to withstand higher temperatures without breaking down.[219]

Silanes with amine groups also enhance the nanocellulose composites' barrier qualities, increasing their resistance to moisture and gas absorption. Silane treatment reduces the hydrophilicity of nanocellulose, making it less likely to absorb moisture. The silane-modified nanocellulose aligns better with hydrophobic polymer matrices, creating a denser composite structure with fewer voids or microchannels where gases and moisture could penetrate. The reduced water uptake and minimized voids mean that oxygen and moisture find it more challenging to diffuse through the composite, enhancing its suitability for packaging applications that require strict moisture and oxygen barriers. The work by Poothanari et al. (2024) investigates the effects of hydrophobic silane treatment, clay addition, and thermal annealing on the oxygen and water vapor barriers in MFC films at an elevated relative humidity. Results show that adding clay decreases the OTR by 30% at 80% relative humidity (RH) partly as a result of exfoliation and by 50% when silylation is added. Silylation enhances surface hydrophobicity, achieving a WCA of 146.5°. The combination of these treatments significantly reduces the OTR to 8 cm^3/m^2/day/bar at 80% RH and reduces the WVTR for MFC at 23 °C and 50% relative humidity from 49 to 22 g/m^2/day. These reductions in OTR and WVTR are correlated with increased hydrophobicity, which limits water molecule access within the MFC network, indicating that these modifications effectively improve the films' barrier properties.[220]

Nanocellulose, known for its slow degradation, supports long-term stability in applications requiring durability such as composite films. When modified with silane, nanocellulose exhibits enhanced compatibility and structural reinforcement, which are crucial for long-term performance films. For instance, Liu et al. achieved a TEMPO-oxidized CNF/Ti_3C_2TX composite film with high mechanical stability, sustaining over 10,000 cycles, and sensitivity suitable for various applications.[221] NFC-reinforced starch can exhibit low reactivity due to NFC agglomeration and starch retrogradation. To address this, ball-milling enhances material reactivity by reducing energy activation and promoting starch plasticization and modification. When combined with metal ions like Ca^{2+}, which interact with starch molecules to prevent recrystallization, ball-milling improves the dispersion and bonding of surface-modified NFC within starch.[222]

While nanocellulose is naturally biodegradable, the addition of silane groups can alter the rate and extent of degradation. The effect on biodegradability is largely dependent on the type and concentration of silane used. Researchers are exploring ecofriendly silanes that maintain nanocellulose's biodegradability without compromising performance. For instance, using silanes that can break down under specific environmental conditions, such as exposure to moisture and microbes, would allow these composites to biodegrade more readily, aligning with sustainability goals. According to Surya et al. (2022), biodegradation revealed that films modified with silane degraded more slowly than films that were not, suggesting increased stability. During the last phases of soil burial, weight loss for modified films was 52.6% compared to 75.1% for unmodified films, representing a 22.5% improvement in stability. Adding CNF further reduced the biodegradation rate; after 1 week, unmodified films showed 44.9% weight loss, while films with 1% CNF had decreased losses to 35.2% for unmodified and 24.5% for modified films. This highlights that CNF and silane treatments significantly improve the durability of biocomposite films.[217]

Several challenges must be addressed for broader industrial adoption of silane-modified nanocellulose. Cost remains a major barrier, as silane coupling agents can be expensive. Additionally, for consistent material performance, manufacturing concerns, like guaranteeing that nanocellulose is uniformly dispersed in the polymer matrix, are essential. Uniform dispersion is challenging due to the tendency of nanocellulose to aggregate, especially in high concentrations, which can limit its effectiveness in reinforcing the polymer.

Scalability is another significant challenge. Producing silane-modified nanocellulose composites on an industrial scale requires processes that are not only efficient but also maintain the quality and properties of the material. The precise control over silane concentration and its even application across nanocellulose particles are crucial for consistent performance in large-scale manufacturing.

Nonetheless, the use of silane-modified nanosuspension has already been evidenced in the literature, where it was prepared by adding hydrolyzed alkoxysilane to a nanocellulose suspension koxysilane MTMS (methyltrimethoxysilane) was prehydrolyzed under acidic aqueous conditions at pH 4, and then the prehydrolyzed MTMS was added to the NFC suspension. The modified suspensions were used as a coating on "Linerboard" papers by means of an automatic film applicator at a coating speed of 70 mm/s.[223] The modified suspension consistency was adjusted to 2%. Coating weights were controlled by a four-sided applicator with different gap sizes. The coated paper was dried in a hot air dryer at 120 °C.

The silane coating acted as a reinforcing agent within the nanocellulose, forming a hydrophobic surface, which increased the water vapor barrier. Thermal stability, static and dynamic mechanical properties of the nanofibrils were improved after the silylation process.[224] However, a low coating density cannot provide sufficient barrier properties due to inefficient covered area and thickness, with 10 g/m^2 being the adequate coating weight for significant barrier performance against air, liquid water, water vapor, and oil. In addition, a smaller fibril diameter is advantageous to increase hydrophobization and reduce permeation of substances, such as water vapor and oxygen. Air resistance, oxygen barrier properties, and oil resistance were mainly related to the average fibril diameter; small values are ideal, but there is still no consensus on the optimal value.[223]

Silanes containing amine groups (gamma-aminopropyltrimethoxysilane) in their chain result in better adhesion performance compared to silanes containing epoxy (gamma-glycidoxypropyltrimethoxysilane) and/or methacryloxy (gammamethacryloxypropyltrimethoxysilane) groups on aluminum and glass surfaces, in addition to increasing hardness, elastic modulus, tear strength, optical properties, and surface hydrophobicity of the NFC film. Higher proportions of aminosilanes tended to increase adhesion performance.[216] Using this approach, the silanes were prepared and prehydrolyzed in a water:ethanol solution (10:100 by weight) and subsequently added to the 1.5% NFC suspensions (20−50 nm in diameter and degree of polymerization in around 1636) under constant agitation for 2 h at room temperature, followed by resting for 24 h before being used as a surface coating element. The coated film was dried for 2 h at 120 °C.

Similarly, NFC films were functionalized with aminosilanes (3-aminopropyl)-trimethoxysilan with permeability below 1 mL mm m^{-2} day^{-1} atm^{-1} for a 95% RH environment, showing better results if compared to silyl groups (HDMS). This very low permeability to O$_2$ was related to the self-condemnation reactions that occurred during the binding of aminosilane groups on the surface of NFC films. In addition, the hydrophobic surface was observed with a contact angle of around 60°, and was stable over time for NFC functionalized with APTES, and around 70° for HDMS.[225]

CNF aerogels were modified with 6% N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane at 90 °C, 4 h, and under 900 rpm stirring in butanol.[226] Through silane treatment, amino groups were maximally loaded, achieving a CO$_2$ adsorption capability of 1 mmol/g at 25 °C and 15 kPa, in addition to a physisorption capability of 0.35 mmol/g. Effective chemisorption occurred under low-pressure conditions, making this approach suitable for capturing CO$_2$ from flue gas emissions.

8.1. Modification of Nanocellulose with Fluorinated Silane and Free-Fluorinated Silane Approaches.

To create greater stability in aqueous dispersions, stable electrostatic forces are introduced onto the surface of nanocelluloses through sulphation. In addition to in situ sulfation during NFC isolation through sulfuric acid-catalyzed hydrolysis, NFC can also be prepared by hydrolyzing cellulose with postsulfated hydrochloric acid in the presence of sulfuric acid, allowing controlled introduction of sulfate groups.[38]

Apparently, Li et al. 2010 were the first to introduce a self-healing superhydrophobic coating.[227] The polymer coating, which is fluorine-modified and micro/nanostructured with porous features, holds onto the curing agents from the reacted fluoroalkylsilane. Once the original fluoroalkylsilane layer is broken down through oxygen plasma treatment, these preserved curing agents move to the surface of the coating and undergo chemical cross-linking. However, there is currently an absence of artificial superhydrophobic surfaces that can heal physical damage in the same manner as natural superhydrophobic surfaces. The low durability of artificial superhydrophobic coatings negatively interferes with practical applications. As a result, natural superhydrophobic coatings are more viable.[228]

Traditional hydrophobic surface modifications often rely on costly and environmentally hazardous methods such as silane-mediated or fluorocompound techniques. The use of perfluorinated alkyl substances (PFAS) in these methods poses serious health risks due to their persistence within the human body. To address these problems, recent advancements have focused on more sustainable alternatives. One promising method involves modifying nanocellulose, specifically dialdehyde cellulose (DAC), with octadecylamine (ODA). This process enhances the hydrophobic properties of various substrates, such as filter paper and cotton fabric, by significantly increasing their water contact angle. The DAC-ODA coating proves resilient across diverse pH levels and saline environments, making it suitable for various applications.[229]

In a related study, DAC-ODA-coated paper was developed as a superhydrophobic material. DAC, synthesized through periodate oxidation, reacts with the ODA to create a hydrophobic coating. The use of only water and ethanol in this process avoids toxic solvents, while the addition of hydrophilic nanosilica results in a durable superhydrophobic surface. This coated paper achieves a contact angle exceeding 155°, demonstrating excellent resistance to high temperatures, corrosive liquids, and mechanical abrasion. Additionally, it is recyclable and biodegradable, making it a sustainable choice for applications like packaging. This approach offers a significant improvement over traditional methods, addressing environmental and health concerns while providing effective hydrophobic properties.[230]

The nanocellulose-based multifunctional superhydrophobic coatings (NMSC) represent a significant advancement in sustainable surface modification. Created using a simple silylation method with ethyl orthosilicate and cetyl trimethoxysilane, NMSC coatings achieve a remarkable water contact angle of 169° and exhibit excellent durability against high temperatures (up to 495.5 °C), corrosive liquids, and mechanical abrasion. The coatings maintain their superhydrophobicity even after exposure to pollutants and heavy scratching. Additionally, NMSC shows strong antimicrobial efficacy toward both Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*. These properties make NMSC a versatile and ecofriendly solution for applications such as oil−water separation and food packaging, offering a cost-effective and green alternative to traditional hydrophobic treatments.[231]

9. CONCLUSIONS

In conclusion, this review highlights nanocellulose as a promising biodegradable material for various industrial applications, including coatings and active packaging. While its natural properties, such as hydrophilicity, require improvement for broader use, methods such as cold plasma surface treatment and the incorporation of composites offer effective solutions. By integration of compounds such as tannin, kraft lignin, and stearic acid, nanocellulose can be enhanced to achieve improved hydrophobicity, mechanical strength, thermal resistance, and antioxidant activity. These modifications make nanocellulose-based materials suitable for diverse applications, including the biomedical, cosmetic, chemical, and food industries.

However, challenges remain, particularly in food packaging, where sensory and toxicological interactions must be carefully evaluated when incorporating composites. This Review broadens the understanding of both new modification methods and the potential of various composites, providing a practical guide for researchers to improve nanocellulose properties. As we move toward more sustainable materials, further research into scaling these innovations and ensuring their safety in sensitive applications is essential for the development of next-generation biodegradable packaging.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.4c04805.

> A table listing data for multilayered nanocellulose films alongside various common polymers. This table provides columns for film, tensile strength, water vapor transmission rate (WVTR), water vapor permeability (WVP), oxygen transmission rate (OTR), references, and DOI, allowing for a comprehensive comparison of these materials' properties (PDF)

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Notes

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■ REFERENCES

(1) Li, T.; Chen, C.; Brozena, A. H.; Zhu, J. Y.; Xu, L.; Driemeier, C.; Dai, J.; Rojas, O. J.; Isogai, A.; Wågberg, L.; Hu, L. Developing Fibrillated Cellulose as a Sustainable Technological Material. *Nature* **2021**, *590*, 47−56.

(2) Abdelraof, M.; Hasanin, M. S.; Farag, M. M.; Ahmed, H. Y. Green Synthesis of Bacterial Cellulose/Bioactive Glass Nanocomposites: Effect of Glass Nanoparticles on Cellulose Yield, Biocompatibility and Antimicrobial Activity. *Int. J. Biol. Macromol.* **2019**, *138*, 975−985.

(3) Yang, R.-T.; Yu, H.-Y.; Song, M.-L.; Zhou, Y.-W.; Yao, J.-M. Flower-like Zinc Oxide Nanorod Clusters Grown on Spherical Cellulose Nanocrystals via Simple Chemical Precipitation Method. *Cellulose* **2016**, *23* (3), 1871−1884.

(4) Missio, A. L.; Mattos, B. D.; Ferreira, D. de F.; Magalhães, W. L. E.; Bertuol, D. A.; Gatto, D. A.; Petutschnigg, A.; Tondi, G. Nanocellulose-Tannin Films: From Trees to Sustainable Active Packaging. *J. Clean. Prod.* **2018**, *184*, 143−151.

(5) Aliabadi, M.; Chee, B. S.; Matos, M.; Cortese, Y. J.; Nugent, M. J. D.; de Lima, T. A. M.; Magalhães, W. L. E.; de Lima, G. G. Yerba Mate Extract in Microfibrillated Cellulose and Corn Starch Films as a Potential Wound Healing Bandage. *Polymers (Basel).* **2020**, *12* (12), 2807.

(6) Lengowski, E. C.; de Muñiz, G. I. B.; de Andrade, A. S.; Simon, L. C.; Nisgoski, S. Morphological, Physical and Thermal Characterization of Microfibrillated Cellulose. *Rev. Arvore* **2018**, *42* (1). DOI: 10.1590/1806-90882018000100013.

(7) Naz, S.; Ali, J. S.; Zia, M. Nanocellulose Isolation Characterization and Applications: A Journey from Non-Remedial to Biomedical Claims. *Bio-Design Manuf.* **2019**, *2* (3), 187−212.

(8) Fornari, A.; Rossi, M.; Rocco, D.; Mattiello, L. A Review of Applications of Nanocellulose to Preserve and Protect Cultural Heritage Wood, Paintings, and Historical Papers. *Appl. Sci.* **2022**, *12* (24), 12846.

(9) Kim, J. H.; Shim, B. S.; Kim, H. S.; Lee, Y. J.; Min, S. K.; Jang, D.; Abas, Z.; Kim, J. Review of Nanocellulose for Sustainable Future Materials. *Int. J. Precis. Eng. Manuf. - Green Technol.* **2015**, *2* (2), 197−213.

(10) Kargarzadeh, H.; Ioelovich, M.; Ahmad, I.; Thomas, S.; Dufresne, A. Methods for Extraction of Nanocellulose from Various Sources. In *Handbook of Nanocellulose and Cellulose Nanocomposites*; Wiley, 2017; pp 1−49. .

(11) Nechyporchuk, O.; Belgacem, M. N.; Bras, J. Production of Cellulose Nanofibrils: A Review of Recent Advances. *Ind. Crops Prod.* **2016**, *93*, 2−25.

(12) de Queiroz Antonino, R.; Lia Fook, B.; de Oliveira Lima, V.; de Farias Rached, R.; Lima, E.; da Silva Lima, R.; Peniche Covas, C.; Lia Fook, M. Preparation and Characterization of Chitosan Obtained from Shells of Shrimp (Litopenaeus Vannamei Boone). *Mar. Drugs* **2017**, *15* (5), 141.

(13) Clauser, N. M.; Felissia, F. F.; Area, M. C.; Vallejos, M. E. Chapter 2 - Technological and Economic Barriers of Industrial-Scale Production of Nanocellulose. In *Micro and Nano Technologies*; Shanker, U., Hussain, C. M., Rani, M., Eds.; Elsevier, 2022; pp 21−39. DOI: 10.1016/B978-0-12-823296-5.00015-0.

(14) Klein, B. C.; de Mesquita Sampaio, I. L.; Mantelatto, P. E.; Filho, R. M.; Bonomi, A. Beyond Ethanol, Sugar, and Electricity: A Critical Review of Product Diversification in Brazilian Sugarcane Mills. *Biofuels, Bioprod. Biorefining* **2019**, *13* (3), 809−821.

(15) de Assis, C. A.; Houtman, C.; Phillips, R.; Bilek, E. M. T.; Rojas, O. J.; Pal, L.; Peresin, M. S.; Jameel, H.; Gonzalez, R. Conversion Economics of Forest Biomaterials: Risk and Financial Analysis of CNC Manufacturing. *Biofuels, Bioprod. Biorefining* **2017**, *11* (4), 682−700.

(16) Rosales-Calderon, O.; Pereira, B.; Arantes, V. Economic Assessment of the Conversion of Bleached Eucalyptus Kraft Pulp into Cellulose Nanocrystals in a Stand-Alone Facility via Acid and Enzymatic Hydrolysis. *Biofuels, Bioprod. Biorefining* **2021**, *15* (6), 1775−1788.

(17) Penloglou, G.; Basna, A.; Pavlou, A.; Kiparissides, C. Techno-Economic Considerations on Nanocellulose's Future Progress: A Short Review. *Processes* **2023**, *11* (8), 2312.

(18) Bondancia, T. J.; De Aguiar, J.; Batista, G.; Cruz, A. J. G.; Marconcini, J. M.; Mattoso, L. H. C.; Farinas, C. S. Production of Nanocellulose Using Citric Acid in a Biorefinery Concept: Effect of the Hydrolysis Reaction Time and Techno-Economic Analysis. *Ind. Eng. Chem. Res.* **2020**, *59* (25), 11505−11516.

(19) Vanhatalo, K. M.; Parviainen, K. E.; Dahl, O. P. Techno-Economic Analysis of Simplified Microcrystalline Cellulose Process. *BioResources* **2014**, *9* (3), 4741−4755.

(20) Blair, M. J.; Mabee, W. E. Techno-Economic and Market Analysis of Two Emerging Forest Biorefining Technologies. *Biofuels, Bioprod. Biorefining* **2021**, *15* (5), 1301−1317.

(21) Ospina-Varón, R. A.; López-Suárez, F. E.; Aristizábal-Marulanda, V. Prefeasibility Study for the Nanocellulose Production from Biomass in the Colombian Context. *Biomass Convers. Biorefinery* **2022**, *12* (10), 4245−4256.

(22) Bondancia, T. J.; Batista, G.; de Aguiar, J.; Lorevice, M. V.; Cruz, A. J. G.; Marconcini, J. M.; Mattoso, L. H. C.; Farinas, C. S. Cellulose Nanocrystals from Sugar Cane Bagasse Using Organic and/or Inorganic Acids: Techno-Economic Analysis and Life Cycle Assessment. *ACS Sustain. Chem. Eng.* **2022**, *10*, 4660.

(23) Boo Chen Qing, E.; Kirzner Chong Kai Wen, J.; Seh Liang, L.; Qian Ying, L.; Quan Jie, L.; Mubarak, N. M. Pilot Study of Synthesis of Nanocrystalline Cellulose Using Waste Biomass via ASPEN plus Simulation. *Mater. Sci. Energy Technol.* **2020**, *3*, 364−370.

(24) Lan, K.; Xu, Y.; Kim, H.; Ham, C.; Kelley, S. S.; Park, S. Techno-Economic Analysis of Producing Xylo-Oligosaccharides and Cellulose Microfibers from Lignocellulosic Biomass. *Bioresour. Technol.* **2021**, *340*, No. 125726.

(25) Claro, F. C.; Jordão, C.; de Viveiros, B. M.; Isaka, L. J. E.; Villanova Junior, J. A.; Magalhães, W. L. E. Low Cost Membrane of Wood Nanocellulose Obtained by Mechanical Defibrillation for Potential Applications as Wound Dressing. *Cellulose* **2020**, *27*, 10765.

(26) Naomi, R.; Bt Hj Idrus, R.; Fauzi, M. B. Plant- vs. Bacterial-Derived Cellulose for Wound Healing: A Review. *Int. J. Environ. Res. Public Health* **2020**, *17* (18), 6803.

(27) de Lima, G. G.; Ferreira, B. D.; Matos, M.; Pereira, B. L.; Nugent, M. J. D.; Hansel, F. A.; Magalhães, W. L. E. Effect of Cellulose Size-Concentration on the Structure of Polyvinyl Alcohol Hydrogels. *Carbohydr. Polym.* **2020**, *245*, No. 116612.

(28) Aliabadi, M.; Chee, B. S.; Matos, M.; Cortese, Y. J.; Nugent, M. J. D.; de Lima, T. A. M.; Magalhães, W. L. E.; de Lima, G. G.; Firouzabadi, M. D. Microfibrillated Cellulose Films Containing Chitosan and Tannic Acid for Wound Healing Applications. *J. Mater. Sci. Mater. Med.* **2021**, *32* (6), 67.

(29) Ferrer, A.; Pal, L.; Hubbe, M. Nanocellulose in Packaging: Advances in Barrier Layer Technologies. *Ind. Crops Prod.* **2017**, *95*, 574−582.

(30) Hubbe, M. A.; Grigsby, W. From Nanocellulose to Wood Particles: A Review of Particle Size vs. the Properties of Plastic Composites Reinforced with Cellulose-Based Entities. *BioResources* **2020**, *15* (1), 2030−2081.

(31) Lafia-Araga, R. A.; Sabo, R.; Nabinejad, O.; Matuana, L.; Stark, N. Influence of Lactic Acid Surface Modification of Cellulose Nanofibrils on the Properties of Cellulose Nanofibril Films and Cellulose Nanofibril−Poly(Lactic Acid) Composites. *Biomolecules* **2021**, *11* (9), 1346.

(32) Koppolu, R.; Banvillet, G.; Ghimire, H.; Bras, J.; Toivakka, M. Enzymatically Pretreated High-Solid-Content Nanocellulose for a High-Throughput Coating Process. *ACS Appl. Nano Mater.* **2022**, *5* (8), 11302−11313.

(33) Tayeb, A. H.; Tajvidi, M. Sustainable Barrier System via Self-Assembly of Colloidal Montmorillonite and Cross-Linking Resins on Nanocellulose Interfaces. *ACS Appl. Mater. Interfaces* **2019**, *11* (1), 1604−1615.

(34) Camargos, C. H. M.; Poggi, G.; Chelazzi, D.; Baglioni, P.; Rezende, C. A. Protective Coatings Based on Cellulose Nanofibrils, Cellulose Nanocrystals, and Lignin Nanoparticles for the Conservation of Cellulosic Artifacts. *ACS Appl. Nano Mater.* **2022**, *5* (9), 13245−13259.

(35) Liu, Y.; Fan, Q.; Huo, Y.; Li, M.; Liu, H.; Li, B. Construction of Nanocellulose-Based Composite Hydrogel with a Double Packing Structure as an Intelligent Drug Carrier. *Cellulose* **2021**, *28* (11), 6953−6966.

(36) Fotie, G.; Gazzotti, S.; Ortenzi, M. A.; Piergiovanni, L. Implementation of High Gas Barrier Laminated Films Based on Cellulose Nanocrystals for Food Flexible Packaging. *Appl. Sci.* **2020**, *10* (9), 3201.

(37) Azeredo, H. M. C.; Rosa, M. F.; Mattoso, L. H. C. Nanocellulose in Bio-Based Food Packaging Applications. *Ind. Crops Prod.* **2017**, *97*, 664−671.

(38) Wang, J.; Gardner, D. J.; Stark, N. M.; Bousfield, D. W.; Tajvidi, M.; Cai, Z. Moisture and Oxygen Barrier Properties of Cellulose Nanomaterial-Based Films. *ACS Sustain. Chem. Eng.* **2018**, *6* (1), 49−70.

(39) Han, J. W.; Ruiz-Garcia, L.; Qian, J. P.; Yang, X. T. Food Packaging: A Comprehensive Review and Future Trends. *Compr. Rev. Food Sci. Food Saf.* **2018**, *17* (4), 860−877.

(40) Soltani Firouz, M.; Mohi-Alden, K.; Omid, M. A Critical Review on Intelligent and Active Packaging in the Food Industry: Research and Development. *Food Res. Int.* **2021**, *141*, No. 110113.

(41) Atta, O. M.; Manan, S.; Shahzad, A.; Ul-Islam, M.; Ullah, M. W.; Yang, G. Biobased Materials for Active Food Packaging: A Review. *Food Hydrocoll.* **2022**, *125*, No. 107419.

(42) Schaefer, D.; Cheung, W. M. Smart Packaging: Opportunities and Challenges. *Procedia CIRP* **2018**, *72* (March), 1022−1027.

(43) Zulfiana, D.; Karimah, A.; Anita, S. H.; Masruchin, N.; Wijaya, K.; Suryanegara, L.; Fatriasari, W.; Fudholi, A. Antimicrobial Imperata Cylindrica Paper Coated with Anionic Nanocellulose Crosslinked with Cationic Ions. *Int. J. Biol. Macromol.* **2020**, *164*, 892−901.

(44) Yang, Y.; Liu, H.; Wu, M.; Ma, J.; Lu, P. Bio-Based Antimicrobial Packaging from Sugarcane Bagasse Nanocellulose/Nisin Hybrid Films. *Int. J. Biol. Macromol.* **2020**, *161*, 627−635.

(45) Montero, Y.; Souza, A. G.; Oliveira, É. R.; dos Santos Rosa, D. Nanocellulose Functionalized with Cinnamon Essential Oil: A Potential Application in Active Biodegradable Packaging for Strawberry. *Sustain. Mater. Technol.* **2021**, *29*, e00289.

(46) Hasanin, M. S.; Youssef, A. M. Ecofriendly Bioactive Film Doped CuO Nanoparticles Based Biopolymers and Reinforced by Enzymatically Modified Nanocellulose Fibers for Active Packaging Applications. *Food Packag. Shelf Life* **2022**, *34*, No. 100979.

(47) Casalini, S.; Baschetti, M. G.; Cappelletti, M.; Guerreiro, A. C.; Gago, C. M.; Nici, S.; Antunes, M. D. Antimicrobial Activity of Different Nanocellulose Films Embedded with Thyme, Cinnamon, and Oregano Essential Oils for Active Packaging Application on Raspberries. *Front. Sustain. Food Syst.* **2023**, *7*. DOI: 10.3389/fsufs.2023.1190979.

(48) Zou, D.; Li, X.; Wu, M.; Yang, J.; Qin, W.; Zhou, Z.; Yang, J. Schiff Base Synergized with Protonation of PEI to Achieve Smart Antibacteria of Nanocellulose Packaging Films. *Carbohydr. Polym.* **2023**, *318* (April), No. 121136.

(49) Perera, K. Y.; Pradhan, D.; Rafferty, A.; Jaiswal, A. K.; Jaiswal, S. A Comprehensive Review on Metal Oxide-Nanocellulose Composites in Sustainable Active and Intelligent Food Packaging. *Food Chem. Adv.* **2023**, *3*, No. 100436.

(50) Casalini, S.; Giacinti Baschetti, M. The Use of Essential Oils in Chitosan or Cellulose-Based Materials for the Production of Active Food Packaging Solutions: A Review. *J. Sci. Food Agric.* **2023**, *103* (3), 1021−1041.

(51) Xu, Y.; Wu, Z.; Li, A.; Chen, N.; Rao, J.; Zeng, Q. Nanocellulose Composite Films in Food Packaging Materials: A Review. *Polymers (Basel).* **2024**, *16*, 423.

(52) Jiang, Y.; Song, Y.; Miao, M.; Cao, S.; Feng, X.; Fang, J.; Shi, L. Transparent Nanocellulose Hybrid Films Functionalized with ZnO Nanostructures for UV-Blocking. *J. Mater. Chem. C* **2015**, *3* (26), 6717−6724.

(53) Yang, W.; Wang, X.; Gogoi, P.; Bian, H.; Dai, H. Highly Transparent and Thermally Stable Cellulose Nanofibril Films Functionalized with Colored Metal Ions for Ultraviolet Blocking Activities. *Carbohydr. Polym.* **2019**, *213*, 10−16.

(54) Li, P.; Sirviö, J. A.; Haapala, A.; Khakalo, A.; Liimatainen, H. Anti-Oxidative and UV-Absorbing Biohybrid Film of Cellulose Nanofibrils and Tannin Extract. *Food Hydrocoll.* **2019**, *92*, 208−217.

(55) Abdalkarim, S. Y. H.; Chen, L. M.; Yu, H. Y.; Li, F.; Chen, X.; Zhou, Y.; Tam, K. C. Versatile Nanocellulose-Based Nanohybrids: A Promising-New Class for Active Packaging Applications. *Int. J. Biol. Macromol.* **2021**, *182*, 1915−1930.

(56) Hassan, B.; Chatha, S. A. S.; Hussain, A. I.; Zia, K. M.; Akhtar, N. Recent Advances on Polysaccharides, Lipids and Protein Based Edible Films and Coatings: A Review. *Int. J. Biol. Macromol.* **2018**, *109*, 1095−1107.

(57) Arnon-Rips, H.; Poverenov, E. Improving Food Products' Quality and Storability by Using Layer by Layer Edible Coatings. *Trends Food Sci. Technol.* **2018**, *75*, 81−92.

(58) Jeevahan, J.; Chandrasekaran, M. Nanoedible Films for Food Packaging: A Review. *J. Mater. Sci.* **2019**, *54* (19), 12290−12318.

(59) Yousuf, B.; Wu, S.; Siddiqui, M. W. Incorporating Essential Oils or Compounds Derived Thereof into Edible Coatings: Effect on Quality and Shelf Life of Fresh/Fresh-Cut Produce. *Trends Food Sci. Technol.* **2021**, *108*, 245−257.

(60) Perez-Vazquez, A.; Barciela, P.; Carpena, M.; Prieto, M. A. Edible Coatings as a Natural Packaging System to Improve Fruit and Vegetable Shelf Life and Quality. *Foods* **2023**, *12* (19), 3570.

(61) Nunes, C.; Silva, M.; Farinha, D.; Sales, H.; Pontes, R.; Nunes, J. Edible Coatings and Future Trends in Active Food Life Increasing. *Foods* **2023**, *12* (3308), 3308.

(62) Pirozzi, A.; Ferrari, G.; Donsì, F. The Use of Nanocellulose in Edible Coatings for the Preservation of Perishable Fruits and Vegetables. *Coatings* **2021**, *11* (8), 990.

(63) Zhang, W.; Zhang, Y.; Cao, J.; Jiang, W. Improving the Performance of Edible Food Packaging Films by Using Nanocellulose as an Additive. *Int. J. Biol. Macromol.* **2021**, *166*, 288−296.

(64) Palanisamy, S.; Selvaraju, G. D.; Selvakesavan, R. K.; Venkatachalam, S.; Bharathi, D.; Lee, J. Unlocking Sustainable Solutions: Nanocellulose Innovations for Enhancing the Shelf Life of Fruits and Vegetables − A Comprehensive Review. *Int. J. Biol. Macromol.* **2024**, *261* (P1), No. 129592.

(65) Silva-Vera, W.; Zamorano-Riquelme, M.; Rocco-Orellana, C.; Vega-Viveros, R.; Gimenez-Castillo, B.; Silva-Weiss, A.; Osorio-Lira, F. Study of Spray System Applications of Edible Coating Suspensions Based on Hydrocolloids Containing Cellulose Nanofibers on Grape Surface (Vitis Vinifera L.). *Food Bioprocess Technol.* **2018**, *11* (8), 1575−1585.

(66) Dehghani, S.; Hosseini, S. V.; Regenstein, J. M. Edible Films and Coatings in Seafood Preservation: A Review. *Food Chem.* **2018**, *240*, 505−513.

(67) Noori, S.; Zeynali, F.; Almasi, H. Antimicrobial and Antioxidant Efficiency of Nanoemulsion-Based Edible Coating Containing Ginger (Zingiber Officinale) Essential Oil and Its Effect on Safety and Quality Attributes of Chicken Breast Fillets. *Food Control* **2018**, *84*, 312−320.

(68) Khaledian, Y.; Pajohi-Alamoti, M.; Bazargani-Gilani, B. Development of Cellulose Nanofibers Coating Incorporated with Ginger Essential Oil and Citric Acid to Extend the Shelf Life of Ready-to-Cook Barbecue Chicken. *J. Food Process. Preserv.* **2019**, *43* (10), 1−13.

(69) Medina-Jaramillo, C.; Quintero-Pimiento, C.; Gómez-Hoyos, C.; Zuluaga-Gallego, R.; López-Córdoba, A. Alginate-Edible Coatings for Application on Wild Andean Blueberries (Vaccinium Meridionale Swartz): Effect of the Addition of Nanofibrils Isolated from Cocoa by-Products. *Polymers (Basel)* **2020**, *12* (4), 824.

(70) Umaraw, P.; Munekata, P. E. S.; Verma, A. K.; Barba, F. J.; Singh, V. P.; Kumar, P.; Lorenzo, J. M. Edible Films/Coating with Tailored Properties for Active Packaging of Meat, Fish and Derived Products. *Trends Food Sci. Technol.* **2020**, *98*, 10−24.

(71) Kwak, H.; Shin, S.; Kim, J.; Kim, J.; Lee, D.; Lee, H.; Lee, E. J.; Hyun, J. Protective Coating of Strawberries with Cellulose Nanofibers. *Carbohydr. Polym.* **2021**, *258*, No. 117688.

(72) Wang, M.; Miao, X.; Guo, F.; Deng, Z.; Bian, F.; Xiao, T.; Chen, C. Optimized Hybrid Edible Surface Coating Prepared with Gelatin and Cellulose Nanofiber for Cherry Tomato Preservation. *Int. J. Biol. Macromol.* **2024**, *279* (P1), No. 134822.

(73) Nascimento, D. R.; Mesquita, J.; da Silva, T.; Hernandes, T.; Lengowski, E. C.; Takeuchi, K. A Novel Approach to Protect Brazil Nuts from Lipid Oxidation: Efficacy of Nanocellulose−Tocopherol Edible Coatings. *Coatings* **2024**, *14* (9), 1182.

(74) Saremi, R.; Borodinov, N.; Laradji, A. M.; Sharma, S.; Luzinov, I.; Minko, S. Adhesion and Stability of Nanocellulose Coatings on Flat Polymer Films and Textiles. *Molecules* **2020**, *25* (14), 3238.

(75) Spagnuolo, L.; D'Orsi, R.; Operamolla, A. Nanocellulose for Paper and Textile Coating: The Importance of Surface Chemistry. *ChemPlusChem* **2022**, *87* (8). DOI: 10.1002/cplu.202200204.

(76) Ke, W. T.; Chiu, H. L.; Liao, Y. C. Multifunctionalized Cellulose Nanofiber for Water-Repellent and Wash-Sustainable Coatings on Fabrics. *Langmuir* **2020**, *36* (28), 8144−8151.

(77) Krause Bierhalz, A. C. Cellulose Nanomaterials in Textile Applications. *Cellul. Chem. Technol.* **2021**, *55* (7−8), 725−741.

(78) Hongrattanavichit, I.; Aht-Ong, D. Antibacterial and Water-Repellent Cotton Fabric Coated with Organosilane-Modified Cellulose Nanofibers. *Ind. Crops Prod.* **2021**, *171*, No. 113858.

(79) Tavakoli, M.; Ghasemian, A.; Dehghani-firouzabadi, M. R.; Mazela, B. Cellulose and Its Nano-Derivatives as a Water-Repellent And Fire-Resistant Surface: A Review. *Materials* **2022**, *15*, 82.

(80) Sayam. Nanocellulose in Textiles: A Potential Resource for Sustainable Textile Manufacturing. *ChemRxiv* **2023**, DOI: 10.26434/chemrxiv-2023-94r25-v2.

(81) Wang, Y.; Liu, K.; Zhang, M.; Xu, T.; Du, H.; Pang, B.; Si, C. Sustainable Polysaccharide-Based Materials for Intelligent Packaging. *Carbohydr. Polym.* **2023**, *313*, No. 120851.

(82) Golmohammadi, H.; Morales-Narváez, E.; Naghdi, T.; Merkoçi, A. Nanocellulose in Sensing and Biosensing. *Chem. Mater.* **2017**, *29* (13), 5426−5446.

(83) Guruprasath, N.; Sankarganesh, P.; Adeyeye, S. A. O.; Babu, A. S.; Parthasarathy, V. Review on Emerging Applications of Nano-biosensor in Food Safety. *J. Food Sci.* **2024**, *89* (7), 3950−3972.

(84) Aghaei, Z.; Emadzadeh, B.; Ghorani, B.; Kadkhodaee, R. Cellulose Acetate Nanofibres Containing Alizarin as a Halochromic Sensor for the Qualitative Assessment of Rainbow Trout Fish Spoilage. *Food Bioprocess Technol.* **2018**, *11* (5), 1087−1095.

(85) Lu, P.; Liu, R.; Liu, X.; Wu, M. Preparation of Self-Supporting Bagasse Cellulose Nanofibrils Hydrogels Induced by Zinc Ions. *Nanomaterials* **2018**, *8* (10), 800.

(86) Barandun, G.; Soprani, M.; Naficy, S.; Grell, M.; Kasimatis, M.; Chiu, K. L.; Ponzoni, A.; Güder, F. Cellulose Fibers Enable Near-Zero-Cost Electrical Sensing of Water-Soluble Gases. *ACS Sensors* **2019**, *4* (6), 1662−1669.

(87) Dodero, A.; Escher, A.; Bertucci, S.; Castellano, M.; Lova, P. Intelligent Packaging for Real-Time Monitoring of Food-Quality: Current and Future Developments. *Appl. Sci.* **2021**, *11* (8), 3532.

(88) Zhou, W.; Wu, Z.; Xie, F.; Tang, S.; Fang, J.; Wang, X. 3D Printed Nanocellulose-Based Label for Fruit Freshness Keeping and Visual Monitoring. *Carbohydr. Polym.* **2021**, *273*, No. 118545.

(89) Karzarjeddi, M.; Ismail, M. Y.; Antti Sirviö, J.; Wang, S.; Mankinen, O.; Telkki, V. V.; Patanen, M.; Laitinen, O.; Liimatainen, H. Adjustable Hydro-Thermochromic Green Nanofoams and Films Obtained from Shapable Hybrids of Cellulose Nanofibrils and Ionic Liquids for Smart Packaging. *Chem. Eng. J.* **2022**, *443* (April), 136369.

(90) Lu, P.; Yang, Y.; Liu, R.; Liu, X.; Ma, J.; Wu, M.; Wang, S. Preparation of Sugarcane Bagasse Nanocellulose Hydrogel as a Colourimetric Freshness Indicator for Intelligent Food Packaging. *Carbohydr. Polym.* **2020**, *249* (May), No. 116831.

(91) Sobhan, A.; Muthukumarappan, K.; Wei, L.; Zhou, R.; Tummala, H. Development of a Polylactic Acid-Coated Nano-cellulose/Chitosan-Based Film Indicator for Real-Time Monitoring of Beef Spoilage. *Anal. Methods* **2021**, *13* (23), 2612−2623.

(92) Li, L.; Wang, W.; Zheng, M.; Sun, J.; Chen, Z.; Wang, J.; Ma, Q. Nanocellulose-Enhanced Smart Film for the Accurate Monitoring of Shrimp Freshness via Anthocyanin-Induced Color Changes. *Carbohydr. Polym.* **2023**, *301* (PB), No. 120352.

(93) Yu, K.; Yang, L.; Zhang, S.; Zhang, N.; Xie, M.; Yu, M. Stretchable, Antifatigue, and Intelligent Nanocellulose Hydrogel Colorimetric Film for Real-Time Visual Detection of Beef Freshness. *Int. J. Biol. Macromol.* **2024**, *268* (P1), No. 131602.

(94) Ma, I. A. W.; Shafaamri, A.; Kasi, R.; Zaini, F. N.; Balakrishnan, V.; Subramaniam, R.; Arof, A. K. Anticorrosion Properties of Epoxy/

Nanocellulose Nanocomposite Coating. *BioResources* **2017**, *12* (2), 2912−2929.

(95) Ferreira, F. V.; Lona, L. M. F.; Pinheiro, I. F.; de Souza, S. F.; Mei, L. H. I. Polymer Composites Reinforced with Natural Fibers and Nanocellulose in the Automotive Industry: A Short Review. *J. Compos. Sci.* **2019**, *3* (2), 51.

(96) Natrayan, L.; Merneedi, A.; Bharathiraja, G.; Kaliappan, S.; Veeman, D.; Murugan, P. Processing and Characterization of Carbon Nanofibre Composites for Automotive Applications. *J. Nanomater.* **2021**, *2021*, 1.

(97) Tu, W.; Wang, S.; Deng, Q.; Li, D.; Zhang, Y.; Wang, Q.; Jiang, H. Review on Nanocellulose Composites and CNFs Assembled Microfiber Toward Automotive Applications. *Nanotechnol. Rev.* **2024**, *13* (1). DOI: 10.1515/ntrev-2024-0006.

(98) Yusuf, J.; Sapuan, S. M.; Ansari, M. A.; Siddiqui, V. U.; Jamal, T.; Ilyas, R. A.; Hassan, M. R. Exploring Nanocellulose Frontiers: A Comprehensive Review of Its Extraction, Properties, and Pioneering Applications in the Automotive and Biomedical Industries. *Int. J. Biol. Macromol.* **2024**, *255*, No. 128121.

(99) Buckner, C. A.; Lafrenie, R. M.; Dénommée, J. A.; Caswell, J. M.; Want, D. A.; Gan, G. G.; Leong, Y. C.; Bee, P. C.; Chin, E.; Teh, A. K. H.; Picco, S.; Villegas, L.; Tonelli, F.; Merlo, M.; Rigau, J.; Diaz, D.; Masuelli, M.; Korrapati, S.; Kurra, P.; Puttugunta, S.; Picco, S.; Villegas, L.; Tonelli, F.; Merlo, M.; Rigau, J.; Diaz, D.; Masuelli, M.; Tascilar, M.; de Jong, F. A.; Verweij, J.; Mathijssen, R. H. J. Nature-Inspired Nano Cellulose Materials, Advancements in Nano Cellulose Preparation and Versatile Applications. In *Nanocellulose-Sources, Preparations, and Applications*; IntechOpen, 2024; Vol. *11*. DOI: 10.5772/intechopen.114222.

(100) Shanmugam, K. Nanocellulose as Sustainable Eco-Friendly Nanomaterials: Production, Characterization, and Applications. *Dermatological Health* **2024**, *2* (3), 8−33, DOI: 10.26689/dh.v2i3.7611.

(101) Yousefi, H.; Su, H. M.; Imani, S. M.; Alkhaldi, K.; Filipe, C. D.; Didar, T. F. Intelligent Food Packaging: A Review of Smart Sensing Technologies for Monitoring Food Quality. *ACS Sensors* **2019**, *4* (4), 808−821.

(102) Dias, O. A. T.; Konar, S.; Leão, A. L.; Yang, W.; Tjong, J.; Sain, M. Current State of Applications of Nanocellulose in Flexible Energy and Electronic Devices. *Front. Chem.* **2020**, *8* (May). DOI: 10.3389/fchem.2020.00420.

(103) Perdani, C. G.; Gunawan, S. A Short Review: Nanocellulose for Smart Biodegradable Packaging in the Food Industry. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *924* (1), 012032.

(104) Li, S.; Chen, H.; Liu, X.; Li, P.; Wu, W. Nanocellulose as a Promising Substrate for Advanced Sensors and Their Applications. *Int. J. Biol. Macromol.* **2022**, *218* (July), 473−487.

(105) Niu, Z.; Yuan, W. Highly Efficient Thermo- And Sunlight-Driven Energy Storage for Thermo-Electric Energy Harvesting Using Sustainable Nanocellulose-Derived Carbon Aerogels Embedded Phase Change Materials. *ACS Sustain. Chem. Eng.* **2019**, *7* (20), 17523−17534.

(106) Norrrahim, M. N. F.; Mohd Kasim, N. A.; Knight, V. F.; Ujang, F. A.; Janudin, N.; Abdul Razak, M. A. I.; Shah, N. A. A.; Noor, S. A. M.; Jamal, S. H.; Ong, K. K.; Wan Yunus, W. M. Z. Nanocellulose: The next Super Versatile Material for the Military. *Mater. Adv.* **2021**, *2* (5), 1485−1506.

(107) Smalyukh, I. I. Thermal Management by Engineering the Alignment of Nanocellulose. *Adv. Mater.* **2021**, *33* (28), 1−11.

(108) Apostolopoulou-Kalkavoura, V.; Munier, P.; Bergström, L. Thermally Insulating Nanocellulose-Based Materials. *Adv. Mater.* **2021**, *33* (28). DOI: 10.1002/adma.202001839.

(109) Dallaev, R. Advances in Materials with Self-Healing Properties: A Brief Review. *Materials (Basel).* **2024**, *17* (10), 2464.

(110) Khalid, M. Y.; Arif, Z. U.; Al Rashid, A.; Bukhari, S. M. Z. S.; Hossain, M.; Koç, M. Shape-Memory and Self-Healing Properties of Sustainable Cellulosic Nanofibers-Based Hybrid Materials for Novel Applications. *Giant* **2024**, *19* (May), No. 100299.

(111) Chi, K.; Catchmark, J. M. Improved Eco-Friendly Barrier Materials Based on Crystalline Nanocellulose/Chitosan/Carboxymethyl Cellulose Polyelectrolyte Complexes. *Food Hydrocoll.* **2018**, *80*, 195−205.

(112) Asha, V.; Sivaranjana, P. Development of Biodegradable Films Using Nanocellulose for Food Packaging Application − Review. *Azerbaijan Chem. J.* **2023**, *2023* (1), 30−54.

(113) Patil, T. V.; Patel, D. K.; Dutta, S. D.; Ganguly, K.; Santra, T. S.; Lim, K. T. Nanocellulose, a Versatile Platform: From the Delivery of Active Molecules to Tissue Engineering Applications. *Bioact. Mater.* **2022**, *9* (April 2021), 566−589.

(114) Carvalho, A. P. A.; de Értola, R.; Conte-Junior, C. A. Nanocellulose-Based Platforms as a Multipurpose Carrier for Drug and Bioactive Compounds: From Active Packaging to Transdermal and Anticancer Applications. *Int. J. Pharm.* **2024**, *652* (January). DOI: 10.1016/j.ijpharm.2024.123851.

(115) La Fuente Arias, C. I.; Kubo, M. T. K.; Tadini, C. C.; Augusto, P. E. D. Bio-Based Multilayer Films: A Review of the Principal Methods of Production and Challenges. *Critical Reviews in Food Science and Nutrition* **2023**, *63*, 2260.

(116) Grzebieniarz, W.; Biswas, D.; Roy, S.; Jamróz, E. Advances in Biopolymer-Based Multi-Layer Film Preparations and Food Packaging Applications. *Food Packag. Shelf Life* **2023**, *35* (June 2022). DOI: 10.1016/j.fpsl.2023.101033.

(117) Alias, A. R.; Wan, M. K.; Sarbon, N. M. Emerging Materials and Technologies of Multi-Layer Film for Food Packaging Application: A Review. *Food Control* **2022**, *136* (August 2021), No. 108875.

(118) Pankaj, S. K.; Thomas, S. *Cold Plasma Applications in Food Packaging*; Elsevier Inc., 2016. DOI: 10.1016/B978-0-12-801365-6.00012-3.

(119) Bukhari, M. D.; Gohar, G. A.; Akhtar, A.; Ullah, S.; Akram, M.; Abid, J.; Raza, H. Adhesion Theories and Effect of Surface Roughness on Energy Estimation and Wettability of Polymeric Composites Bonded Joints: A-Review. *VW Appl. Sci.* **2019**, *2* (1), 74−86.

(120) Nabels-Sneiders, M.; Barkane, A.; Platnieks, O.; Orlova, L.; Gaidukovs, S. Biodegradable Poly(Butylene Succinate) Laminate with Nanocellulose Interphase Layer for High-Barrier Packaging Film Application. *Foods* **2023**, *12* (22), 4136.

(121) Wang, L.; Chen, C.; Wang, J.; Gardner, D. J.; Tajvidi, M. Cellulose Nanofibrils Versus Cellulose Nanocrystals: Comparison of Performance in Flexible Multilayer Films for Packaging Applications. *Food Packag. Shelf Life* **2020**, *23* (September 2019). DOI: 10.1016/j.fpsl.2020.100464.

(122) Lee, K.; Kwon, G.; Jeon, Y.; Jeon, S.; Hong, C.; Choung, J. W.; You, J. Toward Millimeter Thick Cellulose Nanofiber/Epoxy Laminates with Good Transparency and High Flexural Strength. *Carbohydr. Polym.* **2022**, *291* (April), No. 119514.

(123) Pankaj, S. K.; Bueno-Ferrer, C.; Misra, N. N.; Milosavljević, V.; O'Donnell, C. P.; Bourke, P.; Keener, K. M.; Cullen, P. J. Applications of Cold Plasma Technology in Food Packaging. *Trends Food Sci. Technol.* **2014**, *35* (1), 5−17.

(124) Perera, K. Y.; Prendeville, J.; Jaiswal, A. K.; Jaiswal, S. Cold Plasma Technology in Food Packaging. *Coatings* **2022**, *12* (12), 1−19.

(125) Hoque, M.; McDonagh, C.; Tiwari, B. K.; Kerry, J. P.; Pathania, S. Effect of Cold Plasma Treatment on the Packaging Properties of Biopolymer-Based Films: A Review. *Appl. Sci.* **2022**, *12* (3), 1346.

(126) Dimic-Misic, K.; Kostić, M.; Obradović, B.; Kramar, A.; Jovanović, S.; Stepanenko, D.; Mitrović-Dankulov, M.; Lazović, S.; Johansson, L. S.; Maloney, T.; Gane, P. Nitrogen Plasma Surface Treatment for Improving Polar Ink Adhesion on Micro/Nanofibrillated Cellulose Films. *Cellulose* **2019**, *26* (6), 3845−3857.

(127) Rashvand, M.; Matera, A.; Altieri, G.; Genovese, F.; Nikzadfar, M.; Feyissa, A. H.; Di Renzo, G. C. Effect of Dielectric Barrier Discharge Cold Plasma on the Bio-Nanocomposite Film and Its

Potential to Preserve the Quality of Strawberry under Modified Atmosphere Packaging. *Food Bioprocess Technol.* **2023**, 2022.

(128) Pasquier, E.; Mattos, B. D.; Koivula, H.; Khakalo, A.; Belgacem, M. N.; Rojas, O. J.; Bras, J. Multilayers of Renewable Nanostructured Materials with High Oxygen and Water Vapor Barriers for Food Packaging. *ACS Applied Materials Interfaces* **2022**, *14*, 30236 DOI: 10.1021/acsami.2c07579.

(129) Satam, C. C.; Irvin, C. W.; Lang, A. W.; Jallorina, J. C. R.; Shofner, M. L.; Reynolds, J. R.; Meredith, J. C. Spray-Coated Multilayer Cellulose Nanocrystal - Chitin Nanofiber Films for Barrier Applications. *ACS Sustain. Chem. Eng.* **2018**, *6* (8), 10637−10644.

(130) Tyagi, P.; Lucia, L. A.; Hubbe, M. A.; Pal, L. Nanocellulose-Based Multilayer Barrier Coatings for Gas, Oil, and Grease Resistance. *Carbohydr. Polym.* **2019**, *206* (October 2018), 281−288.

(131) Huang, X.; Ji, Y.; Guo, L.; Xu, Q.; Jin, L.; Fu, Y.; Wang, Y. Incorporating Tannin Onto Regenerated Cellulose Film Towards Sustainable Active Packaging. *Ind. Crops Prod.* **2022**, *180* (October 2021), No. 114710.

(132) Lavrič, G.; Oberlintner, A.; Filipova, I.; Novak, U.; Likozar, B.; Vrabič-Brodnjak, U. Functional Nanocellulose, Alginate and Chitosan Nanocomposites Designed as Active Film Packaging Materials. *Polymers (Basel).* **2021**, *13* (15), 2523.

(133) Vaezi, K.; Asadpour, G.; Sharifi, S. H. Effect of Coating with Novel Bio Nanocomposites of Cationic Starch/Cellulose Nanocrystals on the Fundamental Properties of the Packaging Paper. *Polym. Test.* **2019**, *80* (August). DOI: 10.1016/j.polymertest-ing.2019.106080.

(134) Chen, C.; Zong, L.; Wang, J.; Xie, J. Microfibrillated Cellulose Reinforced Starch/Polyvinyl Alcohol Antimicrobial Active Films with Controlled Release Behavior of Cinnamaldehyde. *Carbohydr. Polym.* **2021**, *272* (April), No. 118448.

(135) Mujtaba, M.; Morsi, R. E.; Kerch, G.; Elsabee, M. Z.; Kaya, M.; Labidi, J.; Khawar, K. M. Current Advancements in Chitosan-Based Film Production for Food Technology; A Review. *Int. J. Biol. Macromol.* **2019**, *121*, 889−904.

(136) Kumar, S.; Mukherjee, A.; Dutta, J. Chitosan Based Nanocomposite Films and Coatings: Emerging Antimicrobial Food Packaging Alternatives. *Trends Food Sci. Technol.* **2020**, *97*, 196−209.

(137) Akter, T.; Nayeem, J.; Quadery, A. H.; Abdur Razzaq, M.; Tushar Uddin, M.; Shahriar Bashar, M.; Sarwar Jahan, M. Micro-crystalline Cellulose Reinforced Chitosan Coating on Kraft Paper. *Cellul. Chem. Technol.* **2020**, *54* (1−2), 95−102.

(138) Gao, Q.; Lei, M.; Zhou, K.; Liu, X.; Wang, S.; Li, H. Preparation of a Microfibrillated Cellulose/Chitosan/Polypyrrole Film for Active Food Packaging. *Prog. Org. Coatings* **2020**, *149* (August), No. 105907.

(139) Duarte, M. M.; Tomasi, J. C.; Helm, C. V.; Amano, E.; Lazzarotto, M.; Godoy, R. C. B.; Nogueira, A. C.; Wendling, I. Caffeinated and Decaffeinated Mate Tea: Effect of Toasting on Bioactive Compounds and Consumer Acceptance. *Rev. Bras. Ciências Agrárias - Brazilian J. Agric. Sci.* **2020**, *15* (3), 1−10.

(140) Missio, A. L.; Mattos, B. D.; Otoni, C. G.; Gentil, M.; Coldebella, R.; Khakalo, A.; Gatto, D. A.; Rojas, O. J. Cogrinding Wood Fibers and Tannins: Surfactant Effects on the Interactions and Properties of Functional Films for Sustainable Packaging Materials. *Biomacromolecules* **2020**, *21* (5), 1865−1874.

(141) Graham, N.; Gang, F.; Fowler, G.; Watts, M. Characterisation and Coagulation Performance of a Tannin-Based Cationic Polymer: A Preliminary Assessment. *Colloids Surfaces A Physicochem. Eng. Asp.* **2008**, *327* (1−3), 9−16.

(142) Pei, Y.; Tang, K; Zheng, X.; Liu, J.; Zhao, J.; Liu, S.; Yang, W. A Cellulose/Tannin Hydrogel and Its Preparation Method. CN104262650A, 2016.

(143) Pei, Yi.; Chen, Y.; Xu, G.; Tang, K.; Zheng, X.; Liu, J. Cellulose/Tannin Micro and Nanofibers and Their Preparation Method. CN105536727B, 2018.

(144) Xu, Q.; Jin, L.; Wang, Y.; Sun, Q.; Chen, H. Method for Preparing a Recyclable Cellulose/Tannin Nanofiber Microgel Adsorbent. CN109279903A, 2019.

(145) Gao, Li; Sun, Y.; Wang, J.; Zhang, W.; Chen, J.. Preparation Method of a High-Performance Biodegradable Film. CN106189270, 2016.

(146) Xu, Q.; Wang, Y.; Jin, L.; Wang, Y.; Qin, M. Adsorption of Cu (II), Pb (II) and Cr (VI) from Aqueous Solutions Using Black Wattle Tannin-Immobilized Nanocellulose. *J. Hazard. Mater.* **2017**, *339*, 91−99.

(147) Limaye, M. V.; Schütz, C.; Kriechbaum, K.; Wohlert, J.; Bacsik, Z.; Wohlert, M.; Xia, W.; Pléa, M.; Dembele, C.; Salazar-Alvarez, G.; Bergström, L. Functionalization and Patterning of Nanocellulose Films by Surface-Bound Nanoparticles of Hydrolyzable Tannins and Multivalent Metal Ions. *Nanoscale* **2019**, *11* (41), 19278−19284.

(148) Asante, B.; Sirviö, J. A.; Li, P.; Lavola, A.; Julkunen-Tiitto, R.; Haapala, A.; Liimatainen, H. Adsorption of Bark Derived Polyphenols onto Functionalized Nanocellulose: Equilibrium Modeling and Kinetics. *AIChE J.* **2020**, *66* (2). DOI: 10.1002/aic.16823.

(149) Kriechbaum, K.; Bergström, L. Antioxidant and UV-Blocking Leather-Inspired Nanocellulose-Based Films with High Wet Strength. *Biomacromolecules* **2020**, *21* (5), 1720−1728.

(150) Kim, T. J.; Silva, J. L.; Kim, M. K.; Jung, Y. S. Enhanced Antioxidant Capacity and Antimicrobial Activity of Tannic Acid by Thermal Processing. *Food Chem.* **2010**, *118* (3), 740−746.

(151) Pulido, R.; Bravo, L.; Saura-Calixto, F. Antioxidant Activity of Dietary Polyphenols As Determined by a Modified Ferric Reducing/Antioxidant Power Assay. *J. Agric. Food Chem.* **2000**, *48* (8), 3396−3402.

(152) Antonia, de S. L.; Laynne, H. de C. L.; Davi, da S.; Livio, C. C. N.; Jose, A. D. L. Incorporation of Tannic Acid in Formulations for Topical Use in Wound Healing: A Technological Prospecting. *African J. Pharm. Pharmacol.* **2015**, *9* (26), 662−674.

(153) Liu, H.-F.; Zhang, F.; Lineaweaver, W. C. History and Advancement of Burn Treatments. *Ann. Plast. Surg.* **2017**, *78*, S2−S8.

(154) Rivero, S.; García, M. A.; Pinotti, A. Crosslinking Capacity of Tannic Acid in Plasticized Chitosan Films. *Carbohydr. Polym.* **2010**, *82* (2), 270−276.

(155) Rubentheren, V.; Ward, T. A.; Chee, C. Y.; Nair, P. Physical and Chemical Reinforcement of Chitosan Film Using Nanocrystalline Cellulose and Tannic Acid. *Cellulose* **2015**, *22* (4), 2529−2541.

(156) Lamarra, J.; Rivero, S.; Pinotti, A. Nanocomposite Bilayers Based on Poly(Vinyl Alcohol) and Chitosan Functionalized with Gallic Acid. *Int. J. Biol. Macromol.* **2020**, *146*, 811−820.

(157) Hu, Z.; Cranston, E. Surface Modification of Cellulose Nanocrystals, US9815910B2, December 2015.

(158) Zhang, Z.-Y.; Sun, Y.; Zheng, Y.-D.; He, W.; Yang, Y.-Y.; Xie, Y.-J.; Feng, Z.-X.; Qiao, K. A Biocompatible Bacterial Cellulose/Tannic Acid Composite with Antibacterial and Anti-Biofilm Activities for Biomedical Applications. *Mater. Sci. Eng., C* **2020**, *106*, No. 110249.

(159) Brett, C. J.; Mittal, N.; Ohm, W.; Gensch, M.; Kreuzer, L. P.; Körstgens, V.; Månsson, M.; Frielinghaus, H.; Müller-Buschbaum, P.; Söderberg, L. D.; Roth, S. V. Water-Induced Structural Rearrangements on the Nanoscale in Ultrathin Nanocellulose Films. *Macromolecules* **2019**, *52* (12), 4721−4728.

(160) Shanmugam, K. Scanning Electron Microscopic Evaluation of Spray Coated Micro-Fibrillated Cellulose on the Packaging Paper. *J. Mater. Sci. Surf. Eng.* **2021**, *8* (1), 966−970.

(161) Nadeem, H.; Athar, M.; Dehghani, M.; Garnier, G.; Batchelor, W. Recent Advancements, Trends, Fundamental Challenges and Opportunities in Spray Deposited Cellulose Nanofibril Films for Packaging Applications. *Sci. Total Environ.* **2022**, *836* (May), No. 155654.

(162) Sadeghifar, H.; Venditti, R.; Jur, J.; Gorga, R. E.; Pawlak, J. J. Cellulose-Lignin Biodegradable and Flexible UV Protection Film. *ACS Sustain. Chem. Eng.* **2017**, *5* (1), 625−631.

(163) Calvo, M. E.; Castro Smirnov, J. R.; Míguez, H. Novel Approaches to Flexible Visible Transparent Hybrid Films for Ultraviolet Protection. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50* (14), 945−956.

(164) Butt, S. T.; Christensen, T. Toxicity and Phototoxicity of Chemical Sun Filters. *Radiat. Prot. Dosimetry* **2000**, *91* (1), 283−286.

(165) Tu, Y.; Zhou, L.; Jin, Y. Z.; Gao, C.; Ye, Z. Z.; Yang, Y. F.; Wang, Q. L. Transparent and Flexible Thin Films of ZnO-Polystyrene Nanocomposite for UV-Shielding Applications. *J. Mater. Chem.* **2010**, *20* (8), 1594.

(166) Picard, G.; Simon, D.; Kadiri, Y.; LeBreux, J. D.; Ghozayel, F. Cellulose Nanocrystal Iridescence: A New Model. *Langmuir* **2012**, *28* (41), 14799−14807.

(167) Meng, Y.; Lu, J.; Cheng, Y.; Li, Q.; Wang, H. Lignin-Based Hydrogels: A Review of Preparation, Properties, and Application. *Int. J. Biol. Macromol.* **2019**, *135*, 1006−1019.

(168) Szalaty, T. J.; Klapiszewski, Ł.; Jesionowski, T. Recent Developments in Modification of Lignin Using Ionic Liquids for the Fabrication of Advanced Materials—A Review. *J. Mol. Liq.* **2020**, *301*, No. 112417.

(169) Hambardzumyan, A.; Foulon, L.; Chabbert, B.; Aguié-Béghin, V. Natural Organic UV-Absorbent Coatings Based on Cellulose and Lignin: Designed Effects on Spectroscopic Properties. *Biomacromolecules* **2012**, *13* (12), 4081−4088.

(170) Collins, M. N.; Nechifor, M.; Tanasă, F.; Zănoagă, M.; McLoughlin, A.; Stróżyk, M. A.; Culebras, M.; Teacă, C.-A. Valorization of Lignin in Polymer and Composite Systems for Advanced Engineering Applications − A Review. *Int. J. Biol. Macromol.* **2019**, *131*, 828−849.

(171) Farooq, M.; Zou, T.; Riviere, G.; Sipponen, M. H.; Österberg, M. Strong, Ductile, and Waterproof Cellulose Nanofibril Composite Films with Colloidal Lignin Particles. *Biomacromolecules* **2019**, *20* (2), 693−704.

(172) Herrera, M.; Thitiwutthisakul, K.; Yang, X.; Rujitanaroj, P. on; Rojas, R.; Berglund, L. Preparation and Evaluation of High-Lignin Content Cellulose Nanofibrils from Eucalyptus Pulp. *Cellulose* **2018**, *25* (5), 3121−3133.

(173) Zhang, T.; Zhang, W.; Zhang, Y.; Shen, M.; Zhang, J. Gas Phase Synthesis of Aminated Nanocellulose Aerogel for Carbon Dioxide Adsorption. *Cellulose* **2020**, *27* (6), 2953−2958.

(174) Feldman, D. Lignin Nanocomposites. *J. Macromol. Sci. Part A* **2016**, *53* (6), 382−387.

(175) Michelin, M.; Marques, A. M.; Pastrana, L. M.; Teixeira, J. A.; Cerqueira, M. A. Carboxymethyl Cellulose-Based Films: Effect of Organosolv Lignin Incorporation on Physicochemical and Antioxidant Properties. *J. Food Eng.* **2020**, *285*, No. 110107.

(176) Xiong, F.; Wu, Y.; Li, G.; Han, Y.; Chu, F. Transparent Nanocomposite Films of Lignin Nanospheres and Poly(Vinyl Alcohol) for UV-Absorbing. *Ind. Eng. Chem. Res.* **2018**, *57* (4), 1207−1212.

(177) Yetiş, F.; Liu, X.; Sampson, W. W.; Gong, R. H. Acetylation of Lignin Containing Microfibrillated Cellulose and Its Reinforcing Effect for Polylactic Acid. *Eur. Polym. J.* **2020**, *134* (May), 109803.

(178) Chihaoui, B.; Tarrés, Q.; Delgado-Aguilar, M.; Mutjé, P.; Boufi, S. Lignin-Containing Cellulose Fibrils as Reinforcement of Plasticized PLA Biocomposites Produced by Melt Processing Using PEG as a Carrier. *Ind. Crops Prod.* **2022**, *175*, No. 114287.

(179) Parit, M.; Saha, P.; Davis, V. A.; Jiang, Z. Transparent and Homogenous Cellulose Nanocrystal/Lignin UV-Protection Films. *ACS Omega* **2018**, *3* (9), 10679−10691.

(180) Luo, J.; Su, Y.; Chen, J.; Wang, X.; Liu, J. Pretreatment of Lignin-Containing Cellulose Micro/Nano-Fibrils (LCMNF) from Corncob Residues. *Cellulose* **2021**, *28* (8), 4671−4684.

(181) Xu, Y.; Kuang, Y.; Salminen, P. J.; Chen, G. The Influence of Nano-Fibrillated Cellulose as a Coating Component in Paper Coating. *BioResources* **2016**, *11* (2). DOI: 10.15376/biores.11.2.4342-4352.

(182) Aulin, C.; Salazar-Alvarez, G.; Lindström, T. High Strength, Flexible and Transparent Nanofibrillated Cellulose−Nanoclay Biohybrid Films with Tunable Oxygen and Water Vapor Permeability. *Nanoscale* **2012**, *4* (20), 6622.

(183) Nair, S. S.; Zhu, J.; Deng, Y.; Ragauskas, A. J. High Performance Green Barriers Based on Nanocellulose. *Sustain. Chem. Process.* **2014**, *2* (1), 1−7.

(184) de Almeida, J. C.; de Barros, A.; Odone Mazali, I.; Ferreira, M. Influence of Gold Nanostructures Incorporated into Sodium Montmorillonite Clay Based on LbL Films for Detection of Metal Traces Ions. *Appl. Surf. Sci.* **2020**, *507* (July 2019), No. 144972.

(185) Giannakas, A. E.; Salmas, C. E.; Leontiou, A.; Moschovas, D.; Baikousi, M.; Kollia, E.; Tsigkou, V.; Karakassides, A.; Avgeropoulos, A.; Proestos, C. Performance of Thyme Oil@Na-Montmorillonite and Thyme Oil@Organo-Modified Montmorillonite Nanostructures on the Development of Melt-Extruded Poly-L-Lactic Acid Antioxidant Active Packaging Films. *Molecules* **2022**, *27* (4), 1231.

(186) Choudalakis, G.; Gotsis, A. D. Permeability of Polymer/Clay Nanocomposites: A Review. *Eur. Polym. J.* **2009**, *45* (4), 967−984.

(187) Rhim, J.-W.; Park, H.-M.; Ha, C.-S. Bio-Nanocomposites for Food Packaging Applications. *Prog. Polym. Sci.* **2013**, *38* (10−11), 1629−1652.

(188) McAdam, C. P.; Hudson, N. E.; Liggat, J. J.; Pethrick, R. A. Synthesis and Characterization of Nylon 6/Clay Nanocomposites Prepared by Ultrasonication and in Situ Polymerization. *J. Appl. Polym. Sci.* **2008**, *108* (4), 2242−2251.

(189) Gleason, M. H.; Daniel, D. E.; Eykholt, G. R. Calcium and Sodium Bentonite for Hydraulic Containment Applications. *J. Geotech. Geoenvironmental Eng.* **1997**, *123* (5), 438−445.

(190) Hubbe, M. A.; Ferrer, A.; Tyagi, P.; Yin, Y.; Salas, C.; Pal, L.; Rojas, O. J. Nanocellulose in Packaging. *BioResources* **2017**, *12* (1), 2143−2233.

(191) Huang, C.; Fang, G.; Tao, Y.; Meng, X.; Lin, Y.; Bhagia, S.; Wu, X.; Yong, Q.; Ragauskas, A. J. Nacre-Inspired Hemicelluloses Paper with Fire Retardant and Gas Barrier Properties by Self-Assembly with Bentonite Nanosheets. *Carbohydr. Polym.* **2019**, *225*, No. 115219.

(192) Zheng, M.; Tajvidi, M.; Tayeb, A. H.; Stark, N. M. Effects of Bentonite on Physical, Mechanical and Barrier Properties of Cellulose Nanofibril Hybrid Films for Packaging Applications. *Cellulose* **2019**, *26* (9), 5363−5379.

(193) Punia Bangar, S.; Ilyas, R. A.; Chowdhury, A.; Navaf, M.; Sunooj, K. V.; Siroha, A. K. Bentonite Clay as a Nanofiller for Food Packaging Applications. *Trends Food Sci. Technol.* **2023**, *142*, No. 104242.

(194) Yong, C.; Mei, C.; Guan, M.; Wu, Q.; Han, J.; Sun, X. A Comparative Study of Different Nanoclay-Reinforced Cellulose Nanofibril Biocomposites with Enhanced Thermal and Mechanical Properties. *Compos. Interfaces* **2018**, *25* (4), 301−315.

(195) Williams, R.; English, R.; Graveson, I.; Monin, S. Method for Producing a Nanocrystalline Cellulose (CNC) - Reinforced Cellulosic Fiber or Filament. EP2889399A1, December 2015.

(196) Panga, M. K. R.; Lafitte, V. G. H.; Hutchins, R. D.; Enkababian, P. Water Control Agent for Oilfield Application. US10815414, October 2020.

(197) Hu, D.; Zhang, Z.; Liu, M.; Lin, J.; Chen, X.; Ma, W. Multifunctional UV-Shielding Nanocellulose Films Modified with Halloysite Nanotubes-Zinc Oxide Nanohybrid. *Cellulose* **2020**, *27* (1), 401−413.

(198) Berglund, L.; Liu, A. Strong Nanopaper, US8658287B2, December 2014.

(199) Hitzky, E. R.; Aranda Gallego, M. P.; Darder Colom, M. M.; Barbero, M. M. G. C. R. Composite material of nanocellulose and fibrous clays, method of production and use thereof. WO2016001466A1, June 2015.

(200) Martin, C.; Barker, R.; Watkins, E. B.; Dubreuil, F.; Cranston, E. D.; Heux, L.; Jean, B. Structural Variations in Hybrid All-Nanoparticle Gibbsite Nanoplatelet/Cellulose Nanocrystal Multi-layered Films. *Langmuir* **2017**, *33* (32), 7896−7907.

(201) Chemin, M.; Heux, L.; Guérin, D.; Crowther-Alwyn, L.; Jean, B. Hybrid Gibbsite Nanoplatelet/Cellulose Nanocrystal Multilayered Coatings for Oxygen Barrier Improvement. *Front. Chem.* **2019**, *7*. DOI: 10.3389/fchem.2019.00507.

(202) Kan, K. H. M.; Li, J.; Wijesekera, K.; Cranston, E. D. Polymer-Grafted Cellulose Nanocrystals as PH-Responsive Reversible Flocculants. *Biomacromolecules* **2013**, *14* (9), 3130−3139.

(203) Ávila Ramírez, J. A.; Fortunati, E.; Kenny, J. M.; Torre, L.; Foresti, M. L. Simple Citric Acid-Catalyzed Surface Esterification of Cellulose Nanocrystals. *Carbohydr. Polym.* **2017**, *157*, 1358−1364.

(204) Chen, Q.; Shi, Y.; Chen, G.; Cai, M. Enhanced Mechanical and Hydrophobic Properties of Composite Cassava Starch Films with Stearic Acid Modified MCC (Microcrystalline Cellulose)/NCC (Nanocellulose) as Strength Agent. *Int. J. Biol. Macromol.* **2020**, *142*, 846−854.

(205) Mashkour, M.; Afra, E.; Resalati, H.; Mashkour, M. Moderate Surface Acetylation of Nanofibrillated Cellulose for the Improvement of Paper Strength and Barrier Properties. *RSC Adv.* **2015**, *5* (74), 60179−60187.

(206) Fujisawa, S.; Okita, Y.; Saito, T.; Togawa, E.; Isogai, A. Formation of N-Acylureas on the Surface of TEMPO-Oxidized Cellulose Nanofibril with Carbodiimide in DMF. *Cellulose* **2011**, *18* (5), 1191−1199.

(207) Russell, J. L.; Muller, F.; Coutts, D.; Serobian, A. K.; Winter, P.; Pivonka, N. Treatment and Kits for Creating Transparent Renewable Surface Protective Coatings, NZ576658, December 2011.

(208) Etchells, M.; Versteylen, S. Food Preservation Systems, US7585530, December 2007.

(209) Wu, M.; Huang, Y.; Kuga, S.; Huang, P. Method for Preparing Cellulose Nanofiber Capable of Being Stably Dispersed, US20140299019A1, December 2017.

(210) Huang, F.-Y. Thermal Properties and Thermal Degradation of Cellulose Tri-Stearate (CTs). *Polymers (Basel).* **2012**, *4* (2), 1012−1024.

(211) Qiu, X.; Hu, S. Smart" Materials Based on Cellulose: A Review of the Preparations, Properties, and Applications. *Materials (Basel).* **2013**, *6* (3), 738−781.

(212) Amaliyah, S. Synthesis and Characterization of Cellulose Stearate Ester From Bacterial Cellulose and Stearic Acid Enzymatically Using Immobilized Lipase. *Molekul* **2016**, *11* (2), 256.

(213) Kulomaa, T.; Matikainen, J.; Karhunen, P.; Heikkilä, M.; Fiskari, J.; Kilpeläinen, I. Cellulose Fatty Acid Esters as Sustainable Film Materials − Effect of Side Chain Structure on Barrier and Mechanical Properties. *RSC Adv.* **2015**, *5* (98), 80702−80708.

(214) Uschanov, P.; Johansson, L.-S.; Maunu, S. L.; Laine, J. Heterogeneous Modification of Various Celluloses with Fatty Acids. *Cellulose* **2011**, *18* (2), 393−404.

(215) Hosseinpourpia, R.; Adamopoulos, S.; Walther, T.; Naydenov, V. Hydrophobic Formulations Based on Tall Oil Distillation Products for High-Density Fiberboards. *Materials (Basel).* **2020**, *13* (18), 4025.

(216) Pacaphol, K.; Aht-Ong, D. The Influences of Silanes on Interfacial Adhesion and Surface Properties of Nanocellulose Film Coating on Glass and Aluminum Substrates. *Surf. Coat. Technol.* **2017**, *320*, 70−81.

(217) Surya, I.; Hazwan, C. M.; Abdul Khalil, H. P. S.; Yahya, E. B.; Suriani, A. B.; Danish, M.; Mohamed, A. Hydrophobicity and Biodegradability of Silane-Treated Nanocellulose in Biopolymer for High-Grade Packaging Applications. *Polymers (Basel).* **2022**, *14* (19), 4147.

(218) Anžlovar, A.; Krajnc, A.; Žagar, E. Silane Modified Cellulose Nanocrystals and Nanocomposites with LLDPE Prepared by Melt Processing. *Cellulose* **2020**, *27* (10), 5785−5800.

(219) Panaitescu, D. M.; Gabriela, M.; Nicolae, C.; Gabor, A. R.; Damian, C. M.; Ianchi, R. Effect of Medium-Chain-Length Alkyl Silane Modified Nanocellulose in Poly (3-Hydroxybutyrate) Nanocomposites. *Polymers* **2024**, *16* (21), 3069 DOI: 10.3390/polym16213069.

(220) Poothanari, M. A.; Leterrier, Y. Fluorine Free Surface Modification of Microfibrillated Cellulose-Clay Composite Films: Effect of Hydrophobicity on Gas Barrier Performance. *Surfaces* **2024**, *7* (2), 283−295.

(221) Liu, D.; Gao, Y.; Song, Y.; Zhu, H.; Zhang, L.; Xie, Y.; Shi, H.; Shi, Z.; Yang, Q.; Xiong, C. Highly Sensitive Multifunctional Electronic Skin Based on Nanocellulose/MXene Composite Films with Good Electromagnetic Shielding Biocompatible Antibacterial Properties. *Biomacromolecules* **2022**, *23* (1), 182−195.

(222) Tian, J.; Kong, Y.; Qian, S.; Zhang, Z.; Xia, Y.; Li, Z. Mechanically Robust Multifunctional Starch Films Reinforced by Surface-Tailored Nanofibrillated Cellulose. *Compos. Part B Eng.* **2024**, *275* (February), No. 111339.

(223) Yook, S.; Park, H. H.; Park, H. H.; Lee, S.-Y.; Kwon, J.; Youn, H. J. Barrier Coatings with Various Types of Cellulose Nanofibrils and Their Barrier Properties. *Cellulose* **2020**, *27* (8), 4509−4523.

(224) Zhang, Z.; Tingaut, P.; Rentsch, D.; Zimmermann, T.; Sèbe, G. Controlled Silylation of Nanofibrillated Cellulose in Water: Reinforcement of a Model Polydimethylsiloxane Network. *ChemSusChem* **2015**, *8* (16), 2681−2690.

(225) Peresin, M. S.; Kammiovirta, K.; Heikkinen, H.; Johansson, L.-S.; Vartiainen, J.; Setälä, H.; Österberg, M.; Tammelin, T. Understanding the Mechanisms of Oxygen Diffusion through Surface Functionalized Nanocellulose Films. *Carbohydr. Polym.* **2017**, *174*, 309−317.

(226) Li, Y.; Jia, P.; Xu, J.; Wu, Y.; Jiang, H.; Li, Z. The Aminosilane Functionalization of Cellulose Nanofibrils and the Mechanical and CO_2 Adsorption Characteristics of Their Aerogel. *Ind. Eng. Chem. Res.* **2020**, *59* (7), 2874−2882.

(227) Li, Y.; Li, L.; Sun, J. Bioinspired Self-Healing Superhydrophobic Coatings. *Angew. Chem.* **2010**, *122* (35), 6265−6269.

(228) Teisala, H.; Tuominen, M.; Kuusipalo, J. Superhydrophobic Coatings on Cellulose-Based Materials: Fabrication, Properties, and Applications. *Adv. Mater. Interfaces* **2014**, *1* (1), No. 1300026.

(229) Bajpai, S.; Nemade, P. R. Silane and Fluorine Free Facile Hydrophobicization of Water Hyacinth Biomass for Oil-Water Separations. *Chemosphere* **2024**, *358* (November 2023), No. 142164.

(230) Kan, L.; Zhang, X.; Huang, Q.; Wang, Y.; Tian, M.; Huang, Q.; Wei, W.; Zhang, F.; Wang, X. Fabrication of Cellulose-Based and Fluorine/Silane Free Superhydrophobic Paper by a Green and Sustainable Approach. *Ind. Crops Prod.* **2023**, *203* (August), No. 117226.

(231) Ye, M.; Wang, S.; Ji, X.; Tian, Z.; Dai, L.; Si, C. Nanofibrillated Cellulose-Based Superhydrophobic Coating with Antimicrobial Performance. *Adv. Compos. Hybrid Mater.* **2023**, *6* (1), 1−10.