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Free standing nanocellulose films – fabrication methods, surface engineering and recyclability

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Abstract

Free-standing nanocellulose films are among the predominant products derived from nanocellulose-based nanomaterials. These films have the potential to serve as alternatives to synthetic plastics in various applications. This review highlights the capacity of nanocellulose to develop films primarily used as barrier materials. Several methods are available for fabricating free-standing nanocellulose films and their composites. However, traditional techniques such as solvent casting and vacuum filtration are often time-consuming in the formation of wet films. Therefore, there is a need for faster fabrication methods. Spray coating emerges as a rapid and flexible process that accelerates the formation of nanocellulose films by spraying nanocellulose suspension onto polished stainless-steel surfaces. This method allows for surface engineering of the films, enabling the development of functional materials such as barriers and substrates for flexible electronics. The review summarizes various fabrication approaches suitable for large-scale production, emphasizing their efficiency and scalability. Additionally, considerations regarding the recyclability and surface engineering of nanocellulose films are discussed, highlighting their potential as functional materials within a circular economy framework. Nanocellulose films offer a sustainable alternative to conventional plastics, contributing to environmental conservation. Moreover, nanocellulose is an eco-friendly material with the capacity to combat microplastics and nanoplastics originating from synthetic plastics, thus supporting efforts toward reducing plastic pollution and promoting sustainability.

Keywords: Casting, Coating, Film's roughness and sustainability, Nanocellulose, Spraying, Vacuum filtration.

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Contents

Contribution of this paper to the literature

This review presents a comprehensive overview of spray-coated free-standing nanocellulose films, emphasizing substrate-induced surface engineering and single-step film formation. It highlights the need to explore previously unexamined relationships between processing methods and resulting structures. The review positions spray coating as a transformative technique capable of producing smooth, functional, and recyclable nanocellulose films. It offers a critical comparison of spray coating with traditional methods such as vacuum filtration and solvent casting, identifying optimal processing windows for the rapid fabrication of uniform, peelable nanocellulose films. This article serves as an instructional resource for undergraduate and graduate courses in nanotechnology.

1. Introduction

Nanocellulose is a biodegradable and renewable sustainable nanomaterial derived from cellulose-based natural materials such as wood pulp or greener biomass. It has a greater strength-to-weight ratio compared to conventional materials such as steel, making it highly suitable for developing composite material reinforcement and enhancing product performance. The production of nanocellulose requires less energy input and generates no toxic by-products, positioning it as a potential and environmentally friendly alternative to synthetic plastics. Free-standing nanocellulose films are thin or thick sheets made of nanocellulose fibers that can stand unsupported. These films can be transparent or opaque, depending on processing conditions and the source of the nanocellulose fibers from the feedstock. Due to their strength, lightness, and renewability, these films show promising applications in flexible electronic gadgets, packaging, filters, and medical devices. Various methods are employed to fabricate self-standing nanocellulose films, including solution or solvent casting, spin coating, layer-by-layer assembly, electrospinning, and physical vapor deposition. These techniques allow for the production of films with specific properties tailored to their intended applications, emphasizing nanocellulose's versatility as a sustainable material in advanced manufacturing and product development. These methods enable the fabrication of nanocellulose films with customized properties, highlighting their potential for use as functional products and their recyclability. Surface engineering of nanocellulose films for developing functional materials, such as solar cells and printed electronics, as well as recyclability, are also discussed in this review [1].

2. Fabrication Methods

There is a high demand for the use of freestanding nanocellulose (NC) films and their composites. Their applications are numerous, including barrier materials, tissue engineering scaffolds, and drug delivery devices. The market for NC is expected to grow to USD 700 million by 2023, with an annual growth rate of more than 33%, primarily driven by the pulp and paper sector. However, this growth is limited by the challenges associated with preparing NC films and composites using conventional methods [2]. The primary challenge lies in the processing time, which necessitates a rapid and versatile method to handle high-solid/fibre nanocellulose (NC) suspensions. This process aims to produce self-standing NC films that possess specific features such as mechanical strength, barrier properties, and surface roughness suitable for targeted applications. Various fabrication techniques are employed, including solvent casting, spin coating, Roll-to-Roll (R2R) coating, layer-by-layer assembly, vacuum filtration, and spraying. Among these, vacuum filtration remains a conventional method commonly used in laboratory settings for producing free-standing nanocellulose films and composites.

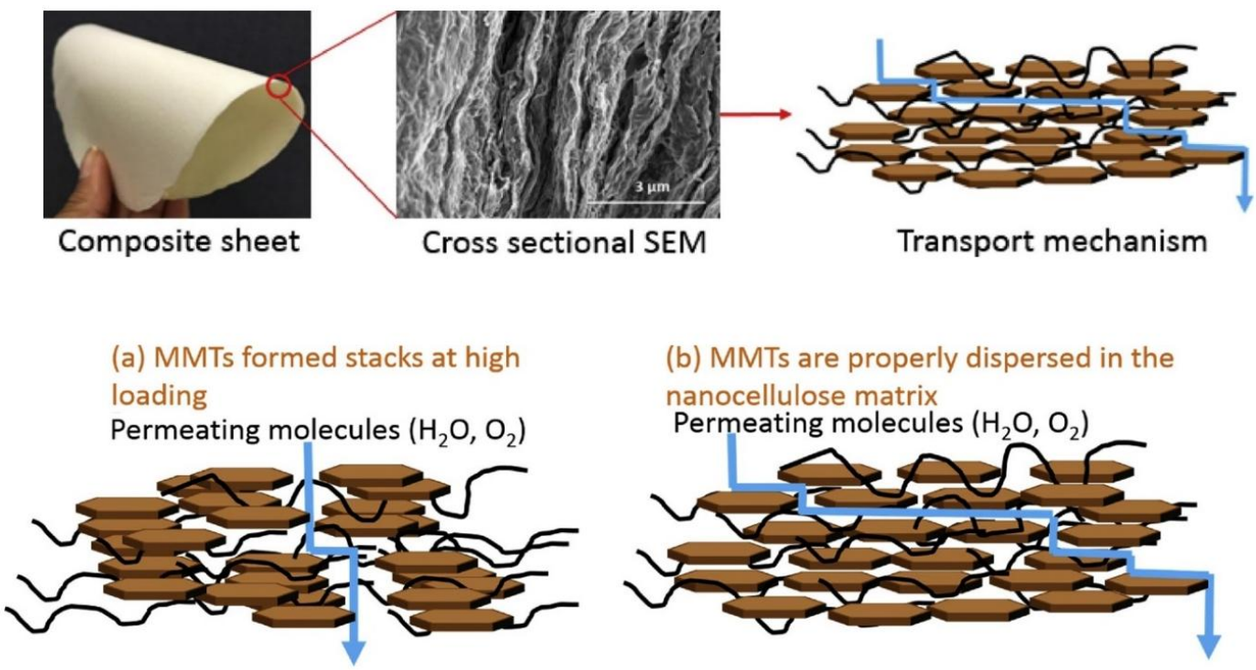

Figure 1. Mechanism of barrier performance in Nanocomposites.

Source: This image obtained from Garusinghe, et al. [3] and Honorato, et al. [4].

There are conventional and laboratory methods for fabrication of free-standing nanocellulose films. Some of the examples are 1. Vacuum Filtration: The wet film was formed through the filtration of the NC suspension using a membrane. 2. Spin coating: NC suspension was dispersed onto a substrate, and the film was formed, which is removable from the substrate. 3. Layer-by-layer assembly: Charged polymers and nanocellulose are alternately

deposited to produce a multilayer film that is removable. 4. Freeze-Drying: Nanocellulose suspension is frozen and lyophilized to produce a porous film. 5. Solvent Casting: Solvent-cast nanocellulose dissolved in solvent is cast on a substrate and the solvent is evaporated to produce a film. 6. Electrospinning involves the process of creating nanocellulose fibers by electrospinning them onto a collector, resulting in a nanofibrous film. These nanocellulose films are highly customizable in terms of porosity, thickness, and strength. Consequently, they are widely used in various applications such as biomaterials, packaging, and sensors.

2.1. Solvent Casting

Solvent casting is a common laboratory-scale technique used to produce nanocellulose films. It involves dispersing nanocellulose in a solvent to create a solution or suspension, which is then cast onto a substrate or into a Petri dish and subsequently dried to form a solid film. The key steps include selecting an appropriate solvent, uniformly dispersing the nanocellulose, casting the solution onto a surface, and allowing for stepwise evaporation. After drying, the final film's properties are characterized. This method is widely used in fields such as biomedicine, packaging, and electronics. The process duration ranges from three days to a week, depending on the nanocellulose concentration and the suspension's thickness. Evaporation time varies based on the water content in the suspension, which typically ranges from 1.13 wt.% to 2 wt.% of the nanocellulose content. Solvent casting is valued for its simplicity and scalability, enabling the production of nanocellulose films with tunable properties, making it a versatile technique for various applications [5, 6].

This technique offers the advantage of directly controlling the uniformity of NC films by adjusting thickness and basis weight through the pouring of a known quantity of the CNF suspension. However, after drying, the films often experience shrinkage and wrinkling, which can reduce uniformity and negatively impact the strength and other properties of the NC film. To produce high-quality films and sheets, it is essential to ensure a good distribution of NC within the suspension, thereby enhancing the film's overall consistency and performance [7].

Casting is a common laboratory-scale method for manufacturing clay-nanocellulose composites. A critical aspect of this process is the proper dispersion of clay in the suspension to prevent stacking and aggregation within the composites. Improving the dispersibility of MMT clay in the suspension is essential to prevent aggregation, which can compromise the barrier performance of the composite [8, 9]. Therefore, an additional step is necessary to enhance the dispersibility of clay platelets in the NC suspension before composite formation. Techniques such as intensive agitation through stirring and shear mixing are commonly employed to promote clay dispersibility. Ultrasonication has also been utilized to achieve a uniform dispersion of nano clay in suspension and to disrupt nano clay clusters or aggregates, although its feasibility for large-scale composite production may be limited [3].

Numerous instances of cast films demonstrate notable properties. For instance, a cast composite comprising vermiculite nanoplatelets in homogenized NC exhibited favorable oxygen and water vapor barrier characteristics, along with commendable tensile strength and stiffness. Another example involves a cast composite of cellulose foam with homogenized NC and Tween 80-2.5 wt.% MMT, which achieved a Water Vapor Permeability (WVP) of 216,000 $g \cdot \mu m \cdot m^{-2} \cdot day^{-1} \cdot KPa^{-1}$, a strength of 13.1±1.7 MPa, and a Young's modulus of 0.455 GPa. The reduced WVP and enhanced strength were attributed to the composite's lower MMT loading [10, 11].

Furthermore, a composite resulting from the casting of poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), NFC, and 50 wt.% sodium Na-MMT attained a WVP of 105 $g \cdot \mu m \cdot m^{-2} \cdot day^{-1} \cdot KPa^{-1}$, a tensile strength of 190±11 MPa, and a modulus of 15.9±0.3 GPa [12]. This cast composite exhibited improved WVP and strength due to the presence of biodegradable polymers and a high MMT content. The biodegradable polymer (PAA) facilitated clay particle dispersion and crosslinking between PVA and PAA [12]. Additionally, the NFC–vermiculite composite produced through two pressure homogenization stages followed by solution casting displayed a WVP of 60 $g \cdot \mu m \cdot m^{-2} \cdot day^{-1} \cdot KPa^{-1}$, a tensile strength of 244±24 MPa, and a modulus of 17.3±0.4 GPa. However, the extended processing time required for casting composite films poses a significant challenge for commercialization [10].

In solvent casting, the mixing of suspensions containing nanocellulose and clay platelets enhances dispersion, allowing for clay layer swelling. Consequently, the interaction between clay platelets and the fibrous film network results in a high-quality barrier composite film. However, the drying time for cast wet films exceeds three days, leading to clay platelet aggregation in composites with other polymers. To address this issue, additional steps are necessary to enhance clay dispersibility and improve interaction with nanocellulose suspension to form a composite. Techniques such as intensive stirring, shear mixing, and ultrasonication have been employed to promote clay dispersibility, although challenges remain for large-scale composite production. Typically, solvent casting is a time-consuming process involving blending the CNF suspension with MMT, followed by casting via pouring into a Petri dish. In this context, the main challenge is clay platelet aggregation in the CNF suspension, necessitating resolving steps to disperse and exfoliate clay for effective composite fabrication [13-15]. Figure 1 demonstrates a nanocellulose–MMT composite sheet, illustrating its layered cross-sectional morphology and the associated gas/water transport mechanism. Proper dispersion of MMT platelets creates a more tortuous diffusion pathway, which reduces water vapor permeation. Conversely, stacking of MMT at high loadings increases water vapor permeation channels, thereby enhancing permeability.

2.2. Spin Coating

Spin coating is a technique used for the deposition of thin films by rapidly spinning a solution onto a substrate. This method involves preparing a well-dispersed nanocellulose solution in an appropriate solvent, often through techniques such as sonication. During the process, the solution is applied to the substrate, which is then spun at high speeds to facilitate the evaporation of the solvent, resulting in the formation of a uniform thin film. For applications requiring free-standing films, a sacrificial layer is typically employed to support the film during processing. Adjusting spin coating parameters, such as rotational speed, solution viscosity, and duration, is essential for achieving precise control over film thickness and quality. Although spin coating is highly effective for laboratory-scale experiments, it

is not suitable for large-scale commercial production due to scalability limitations. Nonetheless, it is valuable for testing biomolecule-cellulose interactions and other research applications. This technique has been utilized to enhance the gas barrier properties of cellulose nanocrystal films on various substrates, including polypropylene. Such films are promising for use in gas separation processes and as barrier materials in multilayer structures. Post-treatment processes, such as annealing, can further improve the mechanical and barrier properties of the films. In summary, spin coating is an effective method for producing ultra-thin nanocellulose films with nanometer-scale thicknesses. It involves high-speed spinning to remove excess suspension, resulting in uniform, thin layers. While not suitable for bulk manufacturing, it remains a valuable tool for laboratory investigations into biomolecule-biomaterial interactions and the development of advanced nanomaterials for specific applications [16-18].

2.3. Roll To Roll Coating

Roll-to-roll coating is a large-scale and continuous process used for applying nanocellulose onto substrates. This method involves passing the substrate through rollers, where nanocellulose is coated onto its surface. The thickness of the coating can be precisely controlled by adjusting the roller speed and the viscosity of the nanocellulose. This technique offers several advantages, including high yield, uniform coating thickness, and low-cost mass production, making it applicable across various industries. It has been employed to produce nanocellulose films with enhanced mechanical strength and barrier properties. These films exhibit regulated surface roughness and do not shrink over time. The low Oxygen Transmission Rate (OTR) of the films indicates excellent barrier properties, which are crucial for packaging applications. Additionally, the films demonstrate high tensile strength, and their application weight depends on the nanocellulose concentration and the wettability of the substrate. Overall, roll-to-roll coating provides a scalable and efficient method for manufacturing smooth, densely packed nanocellulose films at high speeds, suitable for use in packaging, electronics, and biomedical engineering [7, 19].

2.4. Layer-by-Layer Assembly

Layer-by-layer assembly involves the sequential layering of discrete nanocellulose sheets with positive and negative charges to create free-standing films with customizable properties. By controlling the number of layers and their composition, researchers can tailor the mechanical strength, flexibility, and transparency of the resulting films. The process allows for the incorporation of additives and functional groups, which can further enhance the properties of the films. This method is versatile and cost-effective, making it suitable for scaling up nanocellulose material production in various industries such as packaging, electronics, and biomedicine. In research applications, the technique typically involves depositing charged macromolecules and nanoparticles to form thin, functional films with precise control over thickness. For example, a study reported a film thickness of 5 micrometers and a surface roughness of 9 nanometers. However, it is important to note that this method is not ideal for large-scale commercial production of nanocellulose films due to limitations in scalability and throughput [20]. Over the past thirty years, layer-by-layer assembly under mild reaction conditions has been employed as a method for modifying the surface of cellulose fiber sheets. Notably, the dimensions and morphology of the substrate do not hinder this process. The drying of the coating on substrates is a time-intensive step, although specific details are lacking in existing literature. Films produced through this technique can exhibit flexibility in composition, customizable thickness, and consistent performance. By applying multiple coatings on the base substrates, the thickness of the composite can be tailored. The multilayer coating of montmorillonite (MMT) on base substrates influences the strength of the composites and may lead to MMT aggregation. For example, layer-by-layer coating of MMT on biodegradable polymer films has been shown to improve barrier properties, such as decreasing oxygen permeability. MMT surface coating on sisal fiber cellulose microcrystals by this method has also been used to create flame-retardant materials [21, 22].

2.5. Vacuum Filtration

Vacuum filtration is a commonly used method for creating nanocellulose films. In this process, a nanocellulose suspension is poured onto a filter membrane supported by a vacuum setup. The vacuum pressure pulls the liquid through the filter, leaving a nanocellulose layer on the membrane. As water is removed, nanocellulose fibers form a dense network, resulting in a compact film. This method offers several advantages, including efficient water removal through vacuum application, precise control over the NC film thickness, and scalability for laboratory and pilot-scale production. It is considered a conventional technique for fabricating nanocellulose films for various applications, such as barrier sheets and nanocomposites with inorganic materials. Figure 2 illustrates the sequential steps involved in the vacuum filtration process for producing freestanding nanocellulose films.

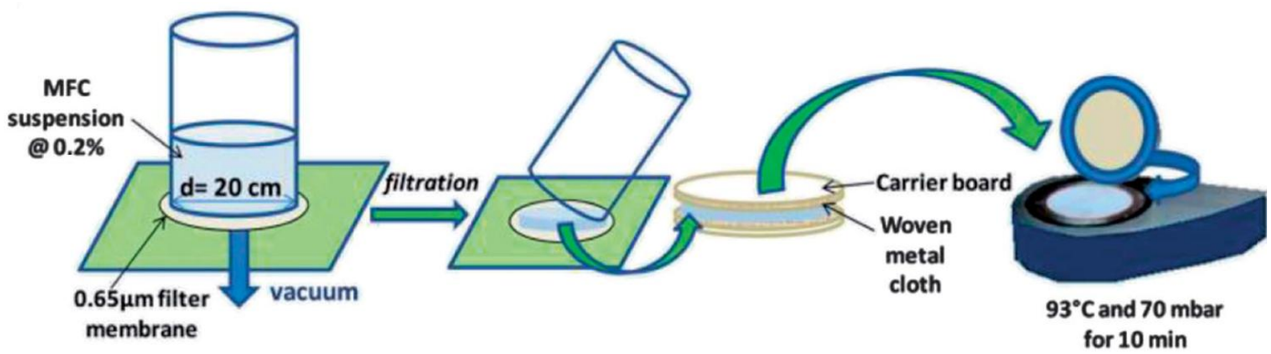

Figure 2. Vacuum filtration for NC film fabrication.
Source: Reprinted, adapted with permission from Sehaqui, et al. [23] and Czerwonatis [24].

As discussed earlier, vacuum filtration is a laboratory-scale technique used to fabricate freestanding nanocellulose (NC) films. This method is a conceptual design similar to a paper-making machine. Vacuum filtration involves pouring NC suspension into a metal mesh-filtered column to produce a wet NC fiber film. The mesh size determines

NC retention and drainage time. Various filter media used in vacuum filtration for NC film production include hydrophilic polytetrafluoroethylene (PTFE) membranes with a pore size of 0.1 μm, Millipore filter membranes with a pore size of 0.65 μm, polyamide filter cloth, cellulose filter membranes, woven filter fabrics, and copper wire with an opening of 125 μm. When employing woven filter fabrics, it is essential to ensure a sufficiently high solids content to facilitate the formation of an interconnected fiber network. The wet NC film formed on the mesh is subsequently subjected to air or drum drying [23, 25-28].

The duration required for laboratory sheet production through filtration has exhibited considerable variation, influenced by the fiber type and filter medium. Filtration times have ranged from 45 minutes to 3-4 hours when utilizing fine filter media. This filtration duration can be reduced to 8 minutes by employing a filter medium with larger pores, such as woven fabric, in conjunction with increased vacuum pressure. Notably, the use of coarser NC necessitated longer filtration times, with homogenization to reduce fiber diameter resulting in a 10-minute filtration time to produce a film with a basis weight of 60 g/m^2 [23, 26, 28].

While vacuum filtration is a conventional approach for NC film fabrication, it is constrained by an increase in drainage time corresponding to the film's basis weight. The escalation of film thickness and basis weight in tandem with drainage time exhibits an exponential relationship. The thickness of NC films produced via filtration typically ranges from 50 to 100 μm. A significant challenge in this method is the detachment of the film from the filter after couching, occasionally leaving a filter mark on the NC film that compromises its uniformity. Despite the method's capacity to yield NC films with commendable barrier and mechanical properties, the prolonged preparation time poses a hindrance to scaling up the process for commercial NC film production [7, 28].

2.6. Nanocomposite Via Filtration

The process of vacuum filtration involves creating composite sheets using cellulose fibers or cellulose-based materials, where a suspension of cellulose nanofibrils combined with nano-inorganics is collected on a filter to produce the composites [3, 12, 29]. The wet composites collected on the filter are then subjected to couching, pressing, and drying procedures. During the mixing phase, the inorganic components are evenly dispersed within the three-dimensional fibrous network.

MMT–NC composites have been successfully fabricated through vacuum filtration, demonstrating reduced permeability to oxygen and water vapor. Studies have shown that the water vapor permeability (WVP) of MMT–NC composites produced via filtration is approximately 13.3 ± 2.0 g·μm/m^2·day·kPa when the composites contain 16.7 wt.% of MMT. However, an increase in MMT content by 0.2 wt.% in the NC suspension has been found to prolong drainage time during the filtration process, posing challenges for commercial viability. For instance, composite films containing 25 wt.% clay loaded in Eucalyptus NC and P. radiata NC, prepared through vacuum filtration, exhibited varying water vapor transmission rates (WVTR) ranging from 183 to 197 g/m·day. The incorporation of clay from 0 wt.% to 25 wt.% resulted in a decrease in WVTR from 299 to 197 in P. radiata NC composites and from 285 to 183 in Eucalyptus NC composites. However, the specific processing time required for these composites was not detailed in the literature [4, 30].

2.7. Impregnation Processes

This approach has been employed for the fabrication of composites on a small scale within a laboratory setting. Initially, a thin cellulose film was created through membrane filtration. Subsequently, nanoparticles were introduced into the film using a solvent carrier. The impregnated composite exhibits superior dimensional stability, flame retardancy, and mechanical strength [31]. However, their barrier performance was not specifically reported in their findings.

2.8. Hot Pressing

Hot pressing is a widely used method for fabricating free-standing nanocellulose films. Nanocellulose fibers are initially dispersed in a solvent to create a suspension. This suspension is then poured into a mold, where it is compressed and heated. During this process, the solvent evaporates, and the fibers bond together, forming a strong and flexible film. Precise control of temperature, pressure, and processing time is essential to produce high-quality films. The mechanical strength and transparency of the films can be tailored by adjusting these processing parameters. Hot pressing is effective in producing nanocellulose films with potential applications in packaging, electronics, and biomedical engineering. Additionally, hot pressing is employed to produce nanocellulose-inorganic composite materials used as barriers, typically as the final step after filtration. This process is conducted at approximately 105°C and 150 bar, with a heating and cooling duration of three to four hours, ensuring optimal bonding and material properties. The Water Vapor Permeability (WVP) of TMA-NFC/Mica R120 is 2200 g·μm·m^{-2}·day^{-1}·kPa^{-1} at 23°C and 50% relative humidity, with a strength of 104±5 MPa and a Young's modulus of 10.3±1.1 GPa. The WVP of TMA-NFC/Vermiculite is 1400 g·μm·m^{-2}·day^{-1}·kPa^{-1}, with a strength of 135±5 MPa and the same Young's modulus [4, 32].

2.9. Spray Coating

Spray coating is a broad technique involving the deposition of a thin material layer onto surfaces, applicable to nanocellulose films. Achieving a good coating depends on proper mixing and atomization of the spray solution. Critical parameters such as spray pressure, nozzle diameter, and the distance from the surface influence the quality of the coating. Advantages of this method include precise control over thickness, excellent coverage of intricate shapes, and scalability for large-scale applications. However, there are potential drawbacks, including nozzle clogging and the possibility of non-uniform coatings. With proper tuning and optimization, spray coating can be a valuable technique for producing nanocellulose films across various applications [33-35]. The spraying process enables contour coating without direct contact with the surface, remaining unaffected by the surface's topography. Research indicates that the strength of films produced through spray coating is comparable to those made through casting. The spraying process involves the formation of a spray jet of liquid, followed by atomization of the jet into a mist. Atomization occurs through two mechanisms: liquid lamella disintegration and disintegration of the liquid

jet. The resulting fine droplets coalesce on the contact surface, forming a film due to the film-forming properties of the polymers through hydrogen bonding. Once dried, the film can be peeled from the substrate. Figure 3 illustrates the steps involved in the spraying process [24, 35-37].

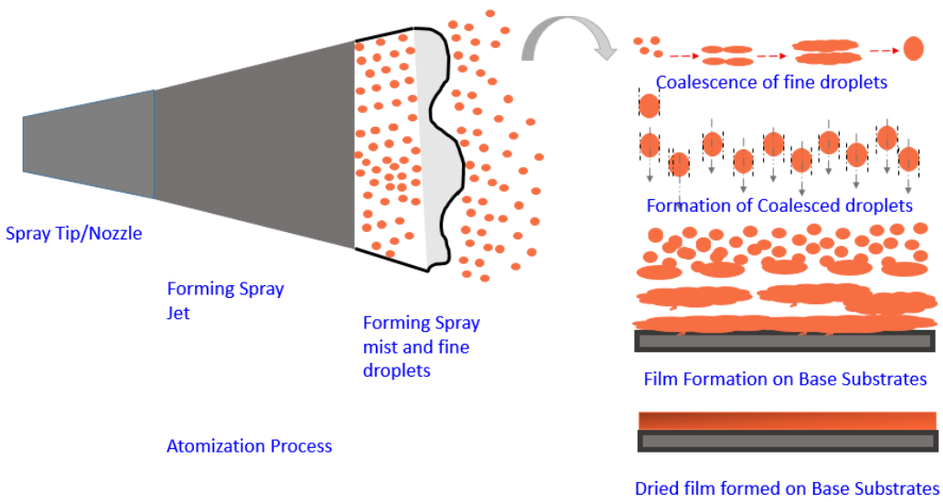

Figure 3. Mechanism of Spraying.

Compared to traditional laboratory methods for producing nanocellulose (NC) films, spraying has been identified as an initial technique for creating a coating layer on cellulosic substrates or solid surfaces. This process has been utilized in various applications, such as enhancing the barrier and mechanical properties of paper substrates by spraying nanocellulose onto them. Additionally, efforts have been made to create free-standing nanocellulose paper as barrier materials by spraying NC onto nylon fabric. To improve mechanical qualities and barrier performance, chitin and cellulose nanofiber spray coatings onto polylactic acid films have also been investigated. The creation of free-standing NC films using the spraying method, which can be divided into two approaches: spraying on an impermeable substrate or spraying on a permeable substrate is the main focus of this work [33, 38, 39].

2.9.1. Spraying of NC on Permeable Substrates

Spray coating offers a wider range of coating basis weights compared to filtration methods, and the spraying process remains unaffected by nanocellulose suspension concentration as long as it maintains suitable viscosity. Researchers have used nanocellulose (NC) spraying to create barrier layers on cellulosic fibrous substrates, with up to 2 wt.% NC reducing water removal during drying [40].

2.9.2. Spraying of NC on Impermeable Substrates

The application of nanocellulose (NC) through spraying onto smooth and polished solid surfaces has been studied for the production of free-standing NC films. A recent approach involved spraying microfibrillated cellulose (MFC) onto a preheated metal surface to create MFC films with three-dimensional structures. The resulting films exhibited varying basis weights and thicknesses, ranging from 59 to 118 g/m² and 46 to 68 µm, respectively. However, challenges such as the formation of cracks and wrinkles on the NC film surface were observed. Attempts to mitigate these issues by reducing water content were made, but spraying with both 4.5 wt.% and 9 wt.% NC led to the generation of disrupted spray jets due to the gel-like properties of MFC, resulting in the production of cracked films. Notably, the study did not report the replication and assessment of the surface roughness of the spray-coated NC films from the substrate. In a separate investigation, ethyl cellulose was effectively dispersed in water with the addition of a plasticizer, and the resulting liquid was sprayed onto Teflon plates. This method yielded a uniform and consistent cellulose film with superior tensile strength compared to cast films. Furthermore, the application of cationic chitin fibers and anionic cellulose nanofibers through spray coating on poly(lactic acid) (PLA) films was explored to enhance barrier performance. The multilayer spray coating of these fibrous materials on PLA resulted in reduced oxygen permeability, although it exhibited lower haze compared to films spray-coated solely with chitin nanofibers or cellulose nanofibers [35, 36, 39].

2.9.3. Limitations In Spraying of NC on Permeable Surface

The application of spray coating was utilized to deposit a nanocellulose (NC) suspension onto a permeable nylon fabric substrate with specific characteristics. Following the spraying process, excess water was removed from the NC-coated fabric using vacuum filtration. This spraying technique was found to be time-consuming, requiring approximately 10 to 20 minutes for completion. The study indicated that NC films were produced using a homogenized NC suspension with a consistent concentration of 2 wt. %. However, details regarding the surface roughness of the NC film and the impact of suspension consistency on film properties were not provided. The thickness and basis weight of the resulting NC film were adjusted within the range of 10 µm to 72 µm and 13.7 g/m² to 124 g/m², respectively, by varying the conveyor speed in the experimental setup from 0.5 to 3 m/min. The flow rate of the microfibrillated cellulose (MFC) slurry from the spray system nozzle remained constant at 0.75 kg/min. Subsequent to spraying, the filtration time ranged from 15 seconds to 90 seconds. The wet MFC film underwent a dewatering process by being sandwiched between new nylon fabrics and blotting papers, followed by compression with a 3 kg roll and vacuum drying at 90°C. The drying times for films with different basis weights were reported as 10 minutes for a 55 g/m² film and 25 minutes for a thicker film. Although the presence of nylon fabric imprints on the spray-coated nanomaterial was noted, a detailed evaluation of these imprints was not conducted [35]. Furthermore, the influence of the substrate surface on the properties of the NC film was not explored in the study. Figure 4 illustrates a typical operation of the spray coating process.

The spraying method resulted in the production of nanocellulose (NC) films or barrier layers with increased thickness and basis weight on cellulosic substrates when compared to vacuum filtration. By homogenizing microfibrillated cellulose onto a moving nylon fabric on a conveyor belt set at a speed of 0.5 m/min, a yield of 124 g/m² of the NC film was achieved. The sprayed films exhibit favorable Young's modulus properties, with a value of 18 GPa, and an air permeability of less than 0.7 nm·Pa^{-1}·s^{-1} [35]. Although spraying has not been utilized for discrete NC film production, the impact of suspension consistency on sheet quality generated through spraying remains unexplored in relation to hand sheets produced via vacuum filtration. Further research is needed to investigate the influence of suspension consistency and spray process parameters on key characteristics of NC films, including uniformity, surface roughness, smoothness, thickness, and coat weight.

2.9.4. Spray Coating for Composites Layer Development

In recent developments, the application of nanocellulose combined with inorganic materials onto porous surfaces such as paper and cardboard has emerged as an effective method for creating composite barrier layers. This technique offers the coating a maximum surface area with minimal operational time [35, 41].

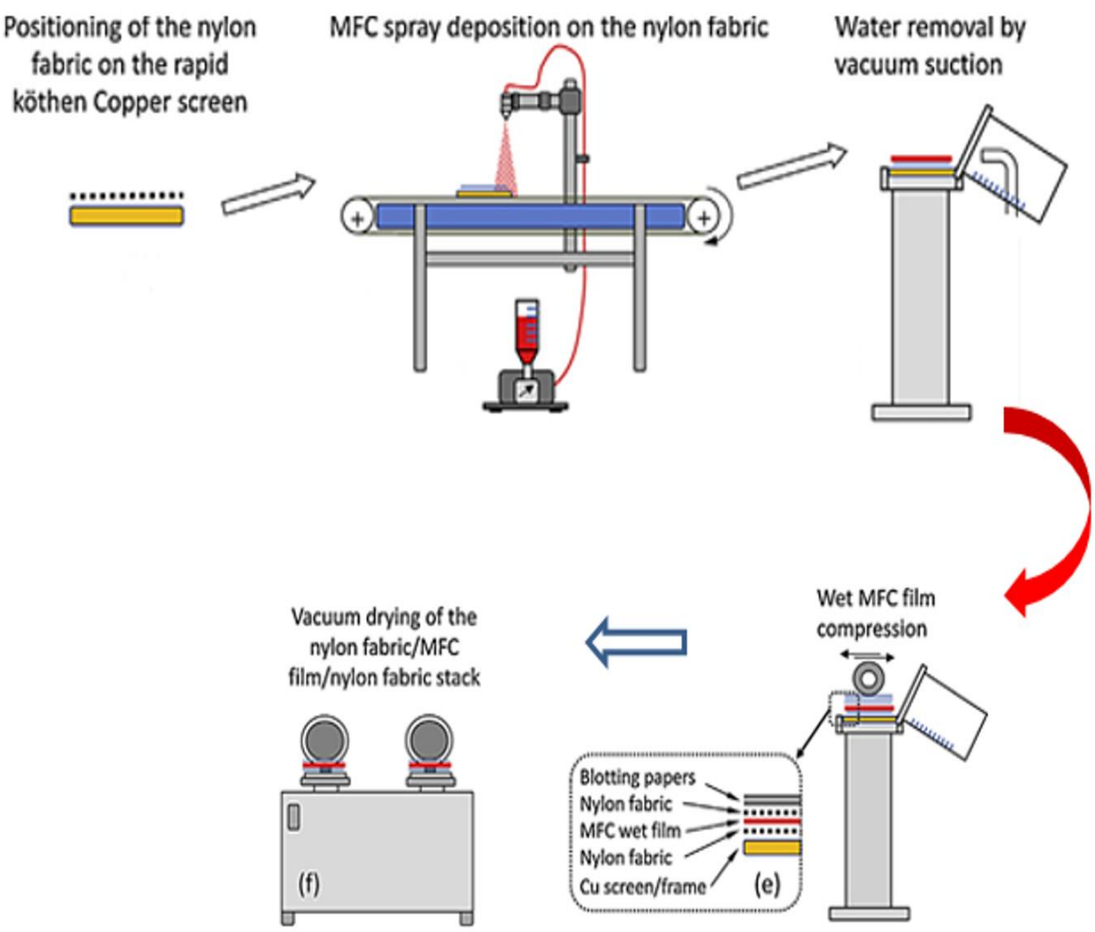

Figure 4. Spray coating to prepare NC film.
Source: The image obtained from Beneventi, et al. [33] and Herrera [6].

The spray coating was used to fabricate microfibrillated cellulose (MFC)-SiO_2 composites with a minimal operation time of less than 30 minutes on a base sheet of approximately 310 cm², independent of the SiO_2 concentration. The addition of SiO_2 in the spraying suspension, ranging from 0 to 33 wt. %, allowed for customization of the composite properties. Control over the coating layer weight on cellulosic substrates was achieved by adjusting the conveyor velocity in the experimental setup and the inorganic content in the nanocellulose (NC) suspension. These composites exhibited effective air impermeability, indicating favorable barrier performance. Additionally, a composite comprising graphite and MFC was produced through the spraying method [34, 41].

The application of cellulose nanofibrils combined with nano clay (MMT) on Kraft paper and printing paper substrates significantly improved their barrier properties against oxygen and water vapor, as well as their tensile strength. Producing composite barrier layers on paper substrates required operation times of 30 seconds and 50 seconds for clay suspensions ranging from 0 wt.% to 5 wt.%. Notably, at clay composite layer concentrations of 3 wt.% and 5 wt.% with basis weights of 22 g/m² and 29 g/m², the oxygen barrier permeance was measured at 88,600 ± 2,000 cm³/m²/day and 36,400 ± 1,100 cm³/m²/day, respectively. The water vapor barrier performance of these composites was recorded at 14 g/m²/day and 8 g/m²/day. The process of creating barrier layers on paper substrates with thicknesses of 19 µm and 29 µm took less than 30 seconds through a spraying process, which involved removing water from the sprayed suspensions via vacuum filtration. Enhancing the wettability between substrates and cellulose nanofibrils required surface treatments such as wetting and corona discharge treatment. Although the concentration of nanocellulose (NC) varied between 1 wt.% and 2 wt.%, the impact of NC suspension concentration on the properties of the composite layers was not thoroughly explored. Some instances of surface non-uniformity, including agglomeration, were observed [42].

Furthermore, the layered spray coating of cationic chitin fibers and anionic cellulose fibers on PLA films was investigated to modify the barrier and mechanical properties of the films. This method facilitated the creation of

multi-layer coatings on PLA films, resulting in an oxygen permeability (OP) of 22 cm^3 μm/m^2/day/kPa at 50% RH for the composite layer with PLA film, compared to the plain PLA film's OP of 70 cm^3 μm/m^2/day/kPa at 50% RH. The water vapor transmission rate (WVTR) of the composite layer with PLA film was reported at 60 g water/m^2/day at 50% RH, slightly lower than that of the pure PLA film [39].

2.9.5. Spray Coating for Developing Free-Standing Nanocomposite

Spraying is a rapid technique for producing nanocomposite (NC) films, with operational durations of less than 30 minutes. This method is efficient for manufacturing composites and is used in NC-MMT (montmorillonite) composite materials. Traditional methods such as vacuum filtration or casting are time-consuming and often face issues like drying and wrinkling [35]. Vacuum filtration, in particular, requires a minimum operational time of 24 hours to 4 days for nanocomposite production. Challenges include separating the film from the filter and handling the wet film after peeling before drying. These conventional methods also face limitations in customizing the basis weight and thickness of the composites.

2.9.6. Pros and Cons of the Different Methods

To summarize, casting techniques are slow and can lead to poor film quality due to wrinkling. Filtration methods are time-consuming and have limitations regarding suspension concentrations. Peeling and filter marking are common issues associated with filtration. Research on spraying methods for NC sheets has not yet explored the limits of sprayable NC suspension, the impact of the base surface on film properties, or the influence of suspension and spraying parameters on the uniformity of NC films.

2.9.7. Ideal Requirement of Preparation of NC Films

In order to successfully prepare free-standing nanocellulose films, several important requirements must be considered. These include the use of high-quality raw materials, such as cellulose derived from renewable sources like wood pulp, cotton, or agricultural residues. The raw materials should be processed to produce nanocellulose with desirable characteristics, including a high aspect ratio and uniformity. Dispersibility plays a crucial role in achieving uniformity and homogeneity in the final film, which can be accomplished through appropriate dispersion methods. The addition of a binder or matrix substance may be necessary to provide cohesion and mechanical strength; suitable options include biocompatible polymers or other biological substances. The film formation process must be carefully controlled to attain specific properties such as thickness, porosity, and mechanical performance. Various drying and crosslinking techniques such as air drying, freeze-drying, or chemical crosslinking should be employed to enhance the mechanical strength and stability of the films. Surface modification can also be applied to introduce additional functionalities or improve biocompatibility with other materials. Comprehensive characterization of nanocellulose films is essential to ensure they meet the desired specifications and performance standards. Addressing these requirements systematically enables researchers and engineers to produce high-quality, freestanding nanocellulose films tailored for specific applications, including packaging, biomedical devices, and environmentally friendly materials.

In comparison to synthetic plastic films, the production rate of nanocellulose (NC) films is notably sluggish [8]. Accelerating the manufacturing process of nanocellulose (NC) films is essential to expand their applications across various fields, including packaging, air and water filtration, membrane technology, and tissue engineering. To enable the commercial-scale production of NC films, it is crucial to develop methods that enhance film performance concerning water vapor and oxygen barrier properties. Additionally, customizing the thickness and basis weight of NC films without increasing operational time is vital. Adjusting the concentration of NC suspension allows for the manipulation of the film's strength and bulk characteristics, ensuring the production of uniform films. Incorporating nanoparticles to create composite materials should be achievable without affecting processing variables. Producing NC films in a single operation can eliminate the need for subsequent procedures such as dewatering, vacuum drying, or couching of the wet film. Furthermore, generating refined nanocellulose films with controllable surface roughness is important for developing advanced materials, and this can be achieved without requiring additional treatments.

3. Recyclability of Nanocellulose Films

Nanocellulose films are promising materials due to their renewability, biodegradability, and strength. They can be recycled through various processes, including dissolving them in specific solvents or mechanically breaking them down into finer fibers.

Multiple recycling cycles are feasible without significant loss of material properties, making them attractive as environmentally friendly packaging options. Additionally, they can be made compatible with existing recycling infrastructure, facilitating easier integration into current waste management systems. However, challenges remain in efficiently collecting, sorting, and processing nanocellulose-based materials on a commercial scale. Ongoing research and development efforts aim to address these issues and optimize recycling processes. While nanocellulose films hold potential as recyclable products, further technological and infrastructural advancements are necessary to maximize their recyclability. Safety and sustainability are critical considerations in the development of food packaging materials, as both cellulose macrofibers and nanocellulose are biodegradable and pose minimal risk of entering or disrupting the food chain [43, 44]. Nanocellulose is susceptible to microbial degradation in the environment, serving as a substrate for cellulose-degrading organisms such as fungi and bacteria due to the small size of cellulose nanofibrils.

Consequently, nanocellulose can function as a biodegradable and sustainable barrier material. Cellulose nanofibers can be sourced from renewable and widely available global resources. Nanocellulose aligns with the sustainable packaging principles outlined by the Sustainable Packaging Alliance (SPA). The sustainability potential of nanocellulose in packaging applications is illustrated in Table 1, with a key focus on the energy consumption associated with nanocellulose production and recycling for film manufacturing.

Table 1. Sustainability features of cellulosic nanofibers.

Principle	Strategies of sustainable packaging	Cellulosic nanofibers in packaging
Effective	Minimal waste production	1. Biodegradable 2. Recyclable 3. High abundance 4. Eco-friendly
	High functionality	1. Potential for recyclability and reusability; 2. Light in weight; 3. High mechanical strength and stiffness; 4. Excellent durability; 5. High barrier performance against water vapour and oxygen and air
	Cost effective	1. Abundant; 2. Recyclable; 3. Reusable into secondary barrier material
Efficient	Maximize product-to-packaging ratio	1. High potential 2. Durable; 3. Flexible nature
	Maximize materials efficiency	Potential for recycling with very minimal degradation
Cyclic	Recyclable; Reusable; Biodegradable	Natural biopolymers such as cellulose and nanocellulose
Clean / Safe	Minimal airborne and waterborne emissions to environment; Minimize greenhouse gas emissions; Reduce toxicity and litter impacts	Minimal ecological impact with cellulose nanofibers; Minimal greenhouse gas emissions; Biodegradable nature, effective disposal after use

Source: Honorato, et al. [4].

Cellulose fibers possess a significant number of hydrogen bonds that serve to uphold the fibrous structure and various levels of organization within wood. The energy necessary to disrupt the inter-fibrillary hydrogen bonding in cellulose is notably high, typically falling within the range of 19 to 21 MJ/kg mol. In the context of mechanical homogenization for the large-scale manufacturing of nanocellulose, energy consumption can vary between 20,000 and 30,000 kWh per ton. Specifically, the energy demand for producing nanocellulose from bleached eucalyptus pulp via the grinding process typically falls within the range of 5 to 30 kWh per kilogram. To mitigate energy consumption in nanocellulose production, strategies such as chemical or biological treatments have been employed to reduce energy usage to approximately 1,000 kWh per ton [45].

The mechanical fibrillation process is a widely utilized technique for the fabrication of nanofibers, with an energy consumption rate of approximately 70000 kWh per ton [46]. To reduce the energy demands associated with nanocellulose production, various chemical treatments such as TEMPO-oxidation, carboxymethylation, and enzymatic treatment are employed. For instance, TEMPO treatment has been shown to significantly decrease energy consumption from 194,400 kWh per ton [47] (when utilizing repeated passes in a homogenizer) to 1,944 kWh per ton. However, it should be noted that extended chemical treatments are necessary, and certain chemical processes may pose risks. Furthermore, the energy consumption associated with enzymatic treatment of fibers followed by mechanical fibrillation exceeds that of chemical treatment of fibers combined with mechanical processes [48].

The energy required for the production of nanocellulose through different mechanical processes follows the order of high-pressure homogenization > microfluidization > grinder. Specifically, the energy consumption for processing nanocellulose with pre-treatment was approximately 9,180 kJ/kg for microfluidization, 9,090 kJ/kg for the grinder, and 31,520 kJ/kg for the homogenizer [49, 50]. Nanocellulose has the potential to serve as a raw material for the development of barrier films, offering an environmentally friendly alternative to synthetic plastic films. However, when comparing the energy consumption involved in manufacturing nanocellulose films to that of synthetic plastic films, it is found that nanocellulose film production consumes approximately ten times more energy. Consequently, ongoing research is focused on developing methods for nanocellulose production that reduce energy consumption [51, 52].

Cellulose fiber substrates, such as paper and paperboard, possess recyclable, renewable, and biodegradable properties. However, their barrier performance against oxygen and water vapor is limited due to the presence of large pores in the fibrous structure. Strategies such as lamination and extrusion with synthetic plastics have been employed to enhance the barrier properties of cellulose fiber substrates, but recycling these coated materials has proven to be challenging [53]. In the context of laminated and composite packaging materials, the strong bonding between layers complicates the recycling process [8].

Polyolefin film recycling, such as LDPE, requires more than half the energy of virgin polyolefin film; however, recycling nanocellulose films consumes significantly less energy [17]. Roll-to-roll coating was used to fabricate a secondary barrier material from LDPE with a nanocellulose (NC) coating. The oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) of the recycled film decreased after recycling, with NC agglomerates having an insignificant impact on barrier performance. The barrier properties of the recycled film declined after recycling, and NC agglomerates had no effect on this decline.

4. Surface Engineering of Nanocellulose Films

Surface modification of free-standing nanocellulose films involves tailoring the surface roughness of the films to improve their performance and functionality in applications such as printed and flexible electronics. This can be achieved through chemical treatments, coatings, and functionalization. Chemical treatments involve applying various reagents to alter the surface chemistry of nanocellulose, which can enhance its adhesion, wettability, and compatibility with other materials. The surface of nanocellulose can also be coated with polymers or nanoparticles to modify its properties for specific applications. Functionalization entails the adsorption of functional groups or molecules onto the nanocellulose surface to impart new functionalities or properties.

Modification of the surface of free-standing nanocellulose films enhances their mechanical strength, heat resistance, barrier functionality, and adhesion. These improvements enable their application in packaging, paper production, biomedical devices, and electronics. Surface modification and engineering are sustainable and flexible methods that allow the properties of nanocellulose films to be tailored according to specific application requirements. Surface patterning techniques can be employed to create patterned or structured surfaces on nanocellulose films, providing functionalities such as high wettability, anti-fouling properties, or optical features. Biomimetic surface modification techniques can also be utilized to engineer nanocellulose films with particular functionalities, including superhydrophobic surfaces or shark skin-like morphologies, which mimic natural structures for enhanced performance.

In addition, surface roughness is an important consideration in the synthesis of functional materials from nanocellulose. Minimizing surface roughness is crucial for the production of flexible electronics because a smooth surface is required to ensure even deposition of conductive ink on the substrate. The process used for preparing nanocellulose films is another approach. The mean roughness of nanocellulose films obtained through the roll-to-roll technique is approximately 450 nm on the base surface side and 800 nm on the free side of the film.

The distribution of fibril sizes within the nanocellulose network and the roughness of the base surface are key parameters that govern surface roughness, as previously discussed [7]. However, the primary objective of this study on spray coating is to customize the surface roughness of the film by spraying nanocellulose onto various substrates with differing degrees of roughness. This objective aims to elucidate the factors influencing smoothness and to explore how films with minimal roughness can be utilized in diverse applications such as flexible electronics and solar cells.

5. Perspective and Conclusion

Nanocellulose films and their composites have potential applications across various industries, including barriers, air filtration, antimicrobial coatings, substrates for electronic devices, and light-emitting diodes. Currently, the production processes are slow and limited, which impacts the properties of the films. This chapter proposes a more efficient and rapid manufacturing process for nanocellulose (NC) films and their composites, emphasizing flexibility in customizing properties to meet specific functional requirements. It analyzes the barrier and mechanical performance of NC films produced using rapid spraying techniques. Notably, spraying methods provide a faster way to form NC films on different surfaces, and incorporating nano-inorganic materials has been shown to improve barrier performance and strength, resulting in nanocomposites. Free-standing nanocellulose films can be fabricated through methods such as casting or evaporation, where a nanocellulose suspension is cast onto a substrate and the solvent is evaporated to produce a thin film; layer-by-layer assembly, which involves depositing alternating layers of nanocellulose and oppositely charged polyelectrolytes onto a substrate; and spin coating, where a nanocellulose solution is spin-coated onto a substrate followed by solvent evaporation. These techniques are typically time-consuming and labor-intensive, making them suitable primarily for laboratory-scale research. Both free-standing nanocellulose films and their composite variants offer a broad range of properties and applications, making them attractive materials for industries seeking sustainable and functional packaging solutions, biomedical devices, and advanced materials.

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