



Research Article

Characterizations Of Free- Standing Nanocellulose Films

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ABSTRACT:

The distinct morphologies and functional properties of nanocellulose, which includes cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC), and amorphous nanocellulose, are determined by the sources and methods of extraction. NC exhibits enormous potential as a sustainable and renewable material in a variety of industrial sectors that are in line with environmental goals because of its high surface area, optical transparency, thermal stability, and capacity to form stable suspensions. The review describes the superior gas barrier qualities of dense, crystalline NC films under low to moderate relative humidity (RH) conditions by comparing the oxygen permeability (OP) and water vapor permeability (WVP) of NC films to those of conventional polymers. The limitations of NC films are examined in relation to porosity, crystallinity, processing techniques, and additives that affect barrier performance, especially the rise in permeability at higher RH brought on by plasticization and swelling effects. The sustainable nature of NC production is further highlighted by a review of environmental factors, such as energy consumption in mechanical fibrillation and chemical treatments to lower energy use. Overall, the study positions NC as a promising biomaterial with multipurpose capabilities in advanced material science by offering crucial insights into streamlining the production of nanocellulose films and customizing their properties for uses like electronics, biomedical devices, and sustainable packaging.

Keywords: Nanocellulose; Nanocomposites; Applications; Oxygen permeability and Water Permeability.

INTRODUCTION

Cellulose, the most prevalent natural polymer in plant cell walls, is the primary source of nanocellulose, a novel bio-based nanomaterial. It is made up of cellulose fibrils that are nanoscale and have at least one dimension in the nanometer range. These fibrils are usually 5–20 nanometers wide and up to several microns long. The distinct physicochemical characteristics of nanocellulose set it apart from regular cellulose due to its nanoscale structuring. Notably, nanocellulose has remarkable mechanical strength; its stiffness is on par with Kevlar, and its tensile strength exceeds that of steel. It is also non-toxic, biocompatible, lightweight, and biodegradable, which makes it appropriate for a variety of uses in electronics, composites, biomedicine, and packaging.

Each type of nanocellulose, including cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC), and amorphous nanocellulose, has unique morphologies and characteristics that are influenced

by the extraction process and source. Its versatility is further enhanced by its high surface area, optical transparency, thermal stability, and capacity to form stable suspensions with distinct rheological characteristics. Nanocellulose is a promising material for cutting-edge applications in a variety of industries because of its renewable nature and environmentally friendly qualities, which complement sustainable development goals. To fully utilize its potential, ongoing research focuses on functionalization techniques and scalable production methods.

Ultrathin, self-supporting membranes made entirely of nanocellulose fibrils that form a dense, highly entangled network structure are known as free-standing nanocellulose films. These films stand out from traditional cellulose materials due to their remarkable mechanical strength, optical transparency, and superior barrier qualities. These films, which are usually made by membrane filtration of nanocellulose hydrogels or suspensions or blade coating, can reach thicknesses as low as

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several hundred nanometers while still being flexible and long-lasting. Free-standing nanocellulose films are exciting prospects for use in flexible electronics, biodegradable packaging, energy storage membranes, and bio-inspired devices due to their high tensile strength and stiffness, which are attributed to the nanoscale dimensions and strong hydrogen bonding between cellulose fibrils. Their biodegradable and renewable qualities also fit in nicely with the objectives of sustainable material development. Nanocellulose's high purity and regulated fibrillation allow for multifunctional applications in cutting-edge technologies by allowing for the tuning of film characteristics like porosity, transparency, and gas barrier performance. All things considered, free-standing nanocellulose films are an environmentally friendly and adaptable platform material with enormous potential in a variety of scientific and industrial domains.

Because of their distinct structural features, free-standing nanocellulose films have remarkable mechanical and barrier qualities. Strong hydrogen bonds and aligned nanocellulose fibers give these films their high mechanical strength, even at extremely thin thicknesses (as low as 800 nm). The films' robust fibrillar network keeps them lightweight while preventing fracture and deformation. Nanocellulose films' dense, layered structure and crystallinity effectively block the transmission of gases and moisture, giving them exceptional resistance to oxygen and water vapor permeability. They are therefore ideal for uses that call for packaging materials or protective coatings. Their high transparency and optical clarity are also a result of their porous yet densely packed morphology, which is beneficial for advanced applications like cosmetics. Superior mechanical durability and efficient barrier performance are the overall results of the interaction of fiber orientation, high crystallinity, and purity in free-standing nanocellulose films. The biofabrication techniques for free-standing nanocellulose films and their characteristics are illustrated in this paper.

1.1. PROPERTIES OF NANOCELLULOSE FILMS

Nanocellulose films possess unique properties due to their nanoscale dimensions and renewable origin. These properties include high strength-to-weight

ratio, transparency, biodegradability, and flexibility. Nanocellulose films are also known for their excellent barrier properties against gases such as oxygen and water vapor, making them suitable for packaging applications. They exhibit high mechanical strength, stiffness, and thermal stability, which allows for various engineering applications. Additionally, nanocellulose films have a large surface area and can be easily functionalized to exhibit specific properties such as antimicrobial or superhydrophobic characteristics. Their renewable nature and sustainable production process make nanocellulose films an environmentally friendly alternative to conventional petroleum-based materials. Overall, the unique combination of properties of nanocellulose films makes them a promising material for a wide range of applications including flexible electronics, sensors, coatings, and biomedical devices. The characteristics of NC film are influenced by factors including thickness, basis weight, density, and porosity, which are closely tied to the properties of cellulose nano-fibrils, such as their diameter, aspect ratio, and the fabrication process utilized [1].

1.1.1. THICKNESS AND BASIS WEIGHT

Nanocellulose films are known for their high strength and excellent barrier properties, making them attractive for various applications. The thickness of nanocellulose films can vary depending on the production method and intended use. Typically, nanocellulose films have thicknesses ranging from a few nanometers to a few micrometers. Basis weight, on the other hand, refers to the weight of the nanocellulose film per unit area. It is often expressed in grams per square meter (g/m²) or other similar units. The basis weight of nanocellulose films can also vary based on factors such as the type of nanocellulose used, the processing conditions, and the desired properties of the final product. Both thickness and basis weight play crucial roles in determining the mechanical strength, optical properties, barrier performance, and overall functionality of nanocellulose films. Researchers and manufacturers often optimize these parameters to meet specific requirements for diverse applications, including packaging, coatings, biomedical devices, and electronics. By controlling the thickness and basis weight of nanocellulose films, tailored properties can be achieved for

different industrial and commercial needs. The characteristics and properties of NC film, such as strength, density, and barrier performance, are significantly influenced by the thickness and basis weight of the film. Additionally, the fabrication method employed plays a crucial role in determining the specific characteristics of the NC film. For instance, in vacuum filtration, NC films typically range in thickness from 50 to 100 μm and have a basis weight varying between 60 to 80 g/m^2 . It is

1.1.1. APPARENT DENSITY

The apparent density of nanocellulose films refers to the mass per unit volume of the film, including both the cellulose material and any void spaces within the film. It is an important parameter that can influence the properties and performance of the films. The apparent density of nanocellulose films can be influenced by various factors such as the type of nanocellulose used, the preparation method, and any additives or processing conditions employed. Lower apparent densities typically indicate a more porous structure, while higher densities suggest a more compact and dense material. Measuring the apparent density of nanocellulose films is typically done by weighing a known volume of the film and calculating the mass per unit volume. This information can be valuable for understanding the structural characteristics of the films and optimizing their properties for specific applications. Overall, the apparent density of nanocellulose films is a critical parameter to consider when designing and engineering these materials for various applications in areas such as packaging, biomedical devices, and electronics. The fibrous network density in NC film plays a crucial role in determining its barrier and mechanical properties [75]. This density is influenced by interactions among fibrils and the processing of the film. The method used to prepare NC film impacts its density through factors such as agglomeration and surface uniformity. The presence of clumps of cellulose nanofibers during film processing can also affect its density. In cases where NC film is partially homogenized or non-homogenized, a decrease in film density may be observed during vacuum filtration. Conversely, when fibers are homogenized, the resulting NC film demonstrates densification with reduced thickness due to the compact packing of nanofibrils. For

noted that an increase in the concentration of NC suspension leads to longer dewatering times during the forming process, particularly for higher basis weight NC films. On the other hand, casting, which is a straightforward method, results in non-uniform NC films due to the formation of shrinkage and wrinkles. Cast NC films typically exhibit thickness variations ranging from 5 to 30 μm [2].

instance, the average density of microfibrillated cellulose (MFC) film produced via vacuum filtration was reported to be 820 kg/m^3 [3].

1.2. FILM UNIFORMITY

Uniformity of nanocellulose films is crucial for their performance in various applications. Achieving uniformity in nanocellulose films involves controlling factors such as the dispersion of nanocellulose particles, the deposition process, and the drying conditions. 1. Dispersion: Proper dispersion of nanocellulose particles in the suspension is essential to ensure uniformity. Techniques such as high-shear mixing, sonication, or homogenization can be used to achieve a well-dispersed nanocellulose suspension. 2. Deposition process: The method used to deposit the nanocellulose suspension onto a substrate plays a significant role in achieving uniformity. Techniques like spin coating, dip coating, or spray coating can be employed to control the thickness and uniformity of the film. 3. Drying conditions: Proper drying conditions are essential to prevent the formation of cracks, defects, or uneven areas in the nanocellulose film. Controlling factors such as temperature, humidity, and drying rate can help ensure a uniform and smooth film surface. Overall, maintaining uniformity in nanocellulose films is essential to enhance their mechanical, optical, and barrier properties for applications in areas such as flexible electronics, packaging, and biomedical devices. In the production of cellulose fiber-based products like paper and paperboard, the quality of the film or sheet is assessed based on its uniformity. This characteristic serves as a key indicator for evaluating the consistency of NC film, directly impacting its surface quality, strength, and printability [76]. To determine the relative formation value (RFV) of the

sheet or film, a paper perfect formation tester is utilized. The RFV serves as a metric for assessing the uniformity of the NC film, with a RFV value of ≥ 1 indicating good uniformity and a value of < 1 suggesting poorer formation quality [4].

1.3. MECHANICAL PROPERTIES

Nanocellulose films exhibit remarkable mechanical properties due to their unique structure and composition. These free-standing films are lightweight, strong, and have high tensile strength, making them suitable for various applications. The mechanical properties of nanocellulose films are influenced by factors such as the type of nanocellulose used (e.g., cellulose nanocrystals or cellulose nanofibrils), the manufacturing process, and the presence of additives or reinforcements. Nanocellulose films typically have high modulus of elasticity, high tensile strength, and good flexibility. The films can exhibit both high strength and toughness, making them ideal for use in applications where a balance between stiffness and ductility is required. Additionally, nanocellulose films have low thermal expansion coefficients and high thermal stability, further enhancing their mechanical properties. Overall, the mechanical properties of free-standing nanocellulose films make them attractive materials for a wide range of applications, including packaging, electronics, biomedical devices, and structural composites. Researchers continue to explore ways to further enhance the mechanical properties of nanocellulose films through innovative processing techniques and the incorporation of additional reinforcements or functionalization strategies.

The robustness of nanocellulose (NC) films plays a crucial role in upholding their functionality in barrier materials, membranes, and composites. It is imperative for NC films to possess adequate reinforcement for the matrix. Within NC films, fibers interconnect to create a dense network held together by hydrogen bonds between adjacent fibers, thereby enhancing the film's strength, modulus, and density. The strength of NC films is influenced by various factors including the diameter and length of fibrils, the biomass source, and the quality of fiber interactions within the network. Additionally, the

fabrication techniques employed and the characteristics of cellulose nanofibrils significantly impact the strength of NC films. A comparative analysis of the mechanical properties of nanocellulose films produced through different methods is presented in Table 1. The data in Table 1 indicates that spraying is the most expedient method for NC film formation, yielding properties akin to those obtained through conventional methods like vacuum filtration.

1.4. BARRIER PROPERTIES

Free-standing nanocellulose films exhibit excellent barrier properties due to their unique structure and composition. The nanocellulose material is derived from renewable sources such as wood pulp or agricultural residues, making it an environmentally friendly option for barrier applications. The high aspect ratio and nanoscale dimensions of cellulose nanofibers contribute to the barrier properties by creating a dense network that restricts the passage of gases and liquids. The hydrogen bonding between cellulose molecules further enhances the barrier performance by creating a tight intermolecular network. Nanocellulose films also have low porosity, which minimizes the diffusion of molecules through the film. This, combined with the high surface area of nanocellulose, provides an effective barrier against oxygen, water vapor, and other molecules. The mechanical properties of nanocellulose films, such as high tensile strength and flexibility, contribute to their barrier performance by maintaining structural integrity under different environmental conditions. Overall, free-standing nanocellulose films offer an attractive solution for various barrier applications in packaging, biomedical devices, and electronics due to their sustainable nature and excellent barrier performance. Cellulose nanofibers possess the ability to create a dense fibrous structure that contributes to their barrier performance. In comparison to both synthetic plastics and other natural polymers, nanocellulose exhibits lower oxygen permeability and reasonable water vapor permeability. A study depicted in Figure 1 illustrates the oxygen permeability (OP) and water vapor permeability (WVP) of traditional synthetic films and biopolymer films, highlighting the superior barrier performance of nanocellulose in contrast to other biopolymers [40]. Oxygen and water vapor permeability represent the primary barrier properties of nanocellulose film, with Figure 1 demonstrating that the barrier properties of nanocellulose film surpass those of other biopolymers. Additionally,

Figure 2 illustrates the diffusion pathway of nanocellulose concerning oxygen and water vapor. However, Figure 2 did not explore the three-dimensional movements of water vapor and gas around the cellulose nanofibers. The primary mechanism involves diffusion around the cellulose nanofibers, with gases typically circulating around the fiber's circumference rather than along its length. Permeating gases tend to follow the shortest path rather than the longest path available.

The barrier properties of free-standing nanocellulose films play a crucial role in various applications, particularly in packaging, where they need to protect contents from external factors such as moisture, oxygen, and light. Here are some key aspects of the barrier properties of nanocellulose films: **Water Vapor Transmission Rate (WVTR):** Nanocellulose films typically exhibit low WVTR due to the dense network structure formed by nanocellulose fibrils. This property makes them effective barriers against moisture, preventing the ingress of water vapor into packaged goods. **Oxygen Transmission Rate (OTR):** Oxygen barrier properties are essential for preserving the freshness and shelf life of perishable products. Nanocellulose films can be engineered to have low OTR by optimizing factors such as film thickness, nanocellulose concentration, and degree of crystallinity. **Gas Permeability:** Apart from oxygen, nanocellulose films may also exhibit barrier properties against other gases such as carbon dioxide and nitrogen. This property is crucial in applications where the preservation of product quality relies on controlling gas exchange with the surrounding

environment. **UV Barrier:** Nanocellulose films can provide UV barrier properties, protecting light-sensitive products from degradation caused by exposure to UV radiation. This is particularly important in packaging applications for products such as pharmaceuticals, cosmetics, and food items. **Tunable Barrier Performance:** The barrier properties of nanocellulose films can be tailored by adjusting parameters such as film composition, processing conditions, and post-treatment methods. Incorporating additives or nanofillers into the nanocellulose matrix can further enhance barrier performance. **Flexibility and Conformability:** Nanocellulose films can conform to the shape of the packaged product, providing effective barrier protection even in complex packaging geometries. Their flexibility allows for the creation of packaging solutions that minimize material usage while maximizing barrier performance. **Environmental Sustainability:** One of the key advantages of nanocellulose films is their renewable and biodegradable nature, making them environmentally friendly alternatives to conventional barrier materials such as plastics. This sustainability aspect is increasingly important in the development of eco-friendly packaging solutions. Overall, nanocellulose films offer promising barrier properties that make them attractive for various packaging applications, where effective protection against external factors is essential for maintaining product quality and extending shelf life. Ongoing research and development efforts continue to advance the understanding and optimization of nanocellulose-based barrier materials for a wide range of industrial applications.

Table 1-Properties of NC films [5]

Fabrication Method	Time Consumption Film formation	Elastic modulus GPa	Tensile strength MPa	Tensile Index Nm/g	Basis Weight g/m ²
Spraying of NC On nylon fabric	10–27 min	17.5–21	50–150	45–104	13.7–124
Membrane filtration	NA	10.7–13.7	129–214	NA	NA
Vacuum Filtration	10 mins	NA	NA	94	56.4
Filtration (Fabric Filter)		15.7–17.5	104–154	129–146	17–35
Membrane filtration	55 min	13.4±0.2	232	-	56
Paper Filtration	2880 mins	10–10.6	127–135	-	-
Membrane Filtration	-	11.9±0.8	135±18		62.4
Filtration on Fabric	60 – 180 mins	8.1–11	121–230	-	55

1.1.2. OXYGEN PERMEABILITY (OP)

Oxygen permeability of free-standing nanocellulose films is a critical property that determines their potential applications in various industries such as food packaging, biomedical devices, and gas separation membranes. Nanocellulose films offer an interesting combination of properties, including high strength, flexibility, and renewable nature, making them attractive for oxygen barrier applications. The oxygen permeability of nanocellulose films is influenced by several factors such as film thickness, porosity, crystallinity, and chemical modifications. Thinner films and higher crystallinity tend to result in lower oxygen permeability due to reduced pathways for gas diffusion. Furthermore, the presence of defects, such as cracks or voids, can also affect oxygen permeability by providing pathways for gas molecules to pass through. Researchers are actively exploring different strategies to enhance the oxygen barrier properties of nanocellulose films, including the incorporation of nanofillers, surface modifications, and blending with other polymers. By optimizing the structure and composition of nanocellulose films, it is possible to tailor their oxygen permeability to meet specific application requirements.

The oxygen permeability of free-standing nanocellulose films can vary depending on several factors, including the type of nanocellulose used, film thickness, density, and processing methods. Generally, nanocellulose films exhibit excellent barrier properties against oxygen due to their dense network structure and high crystallinity. However,

the exact oxygen permeability of nanocellulose films can be influenced by the following factors:

Nanocellulose Type: Different types of nanocellulose, such as cellulose nanocrystals (CNCs) or cellulose nanofibrils (CNFs), may exhibit variations in oxygen permeability due to differences in their structure, morphology, and surface properties.

Film Thickness: Thinner films typically offer better barrier properties against oxygen compared to thicker films. This is because thinner films have shorter diffusion paths for oxygen molecules to penetrate, resulting in lower permeability.

Film Density: The density of the nanocellulose film can affect its oxygen permeability. Higher film density, achieved through compression or densification processes, can reduce the amount of free volume within the film matrix, thereby decreasing oxygen permeability.

Crystallinity: Nanocellulose films with higher crystallinity tend to have lower oxygen permeability due to the tighter packing of cellulose chains and reduced free volume available for gas diffusion.

Processing Methods: The fabrication method used to prepare nanocellulose films can influence their oxygen permeability. Techniques such as casting, compression molding, or layer-by-layer assembly may result in variations in film structure and properties, affecting oxygen barrier performance.

Additives: Incorporating additives or nanofillers into nanocellulose films can modify their barrier properties. For example, the addition of hydrophobic materials or nanoparticles can further reduce oxygen permeability by creating barriers or enhancing film density.

Post-Treatment: Post-treatment processes, such as chemical crosslinking

or surface modification, can improve the barrier properties of nanocellulose films by enhancing their structural integrity and reducing molecular mobility. Overall, nanocellulose films have the potential to offer excellent oxygen barrier properties, making them attractive candidates for applications where oxygen sensitivity is a concern, such as food packaging, barrier coatings, and oxygen-sensitive electronic devices. However, it's essential to consider the specific requirements of each application and optimize the film properties accordingly to achieve the desired level of oxygen barrier performance.

The infiltration of oxygen and various gases, including volatile organic compounds, can lead to the deterioration of food quality. Oxygen in the atmosphere can interact with the carbon-carbon double bond found in unsaturated fatty acids present

in oils and fats, causing rancidity. Nanocellulose (NC) films, due to their low oxygen permeability (OP), serve as effective barriers to safeguard food products. By preventing undesired chemical reactions like oxidation, these films can prolong the shelf life of food items and help maintain their flavor and aroma. The oxygen permeability of nanocellulose films is assessed and compared with that of synthetic plastics in Table 6. The data on the oxygen permeability of synthetic plastics and nanocellulose films are presented in Table 6 [40]. This table also illustrates the impact of relative humidity on NC films and carboxymethylated NC films in comparison to synthetic plastics. At lower relative humidity levels, NC films exhibit minimal oxygen permeability, which increases as the relative humidity percentage rises. This increase is relatively similar to that observed in traditional synthetic plastics. Table 7 provides information on the water vapor permeability of biopolymer films and conventional synthetic plastic films.

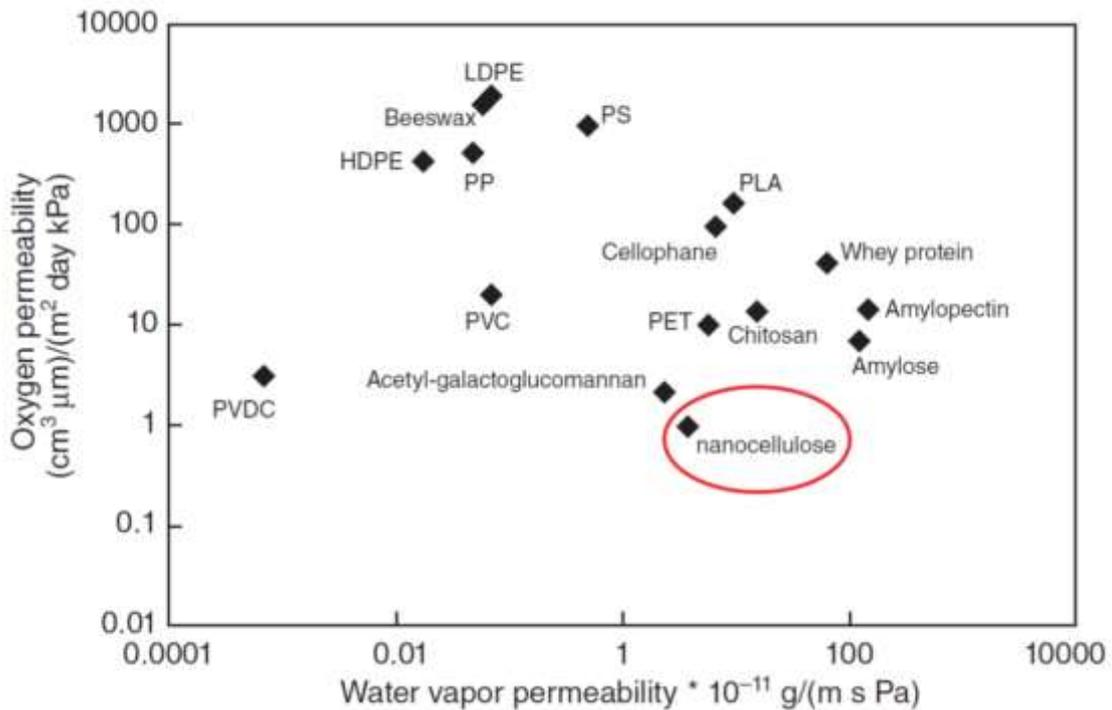


Figure 1-Overview of Barrier Materials, obtained from Aulin et al 2011 [6]. The Oxygen permeability was measured at 23°C and 50% RH.

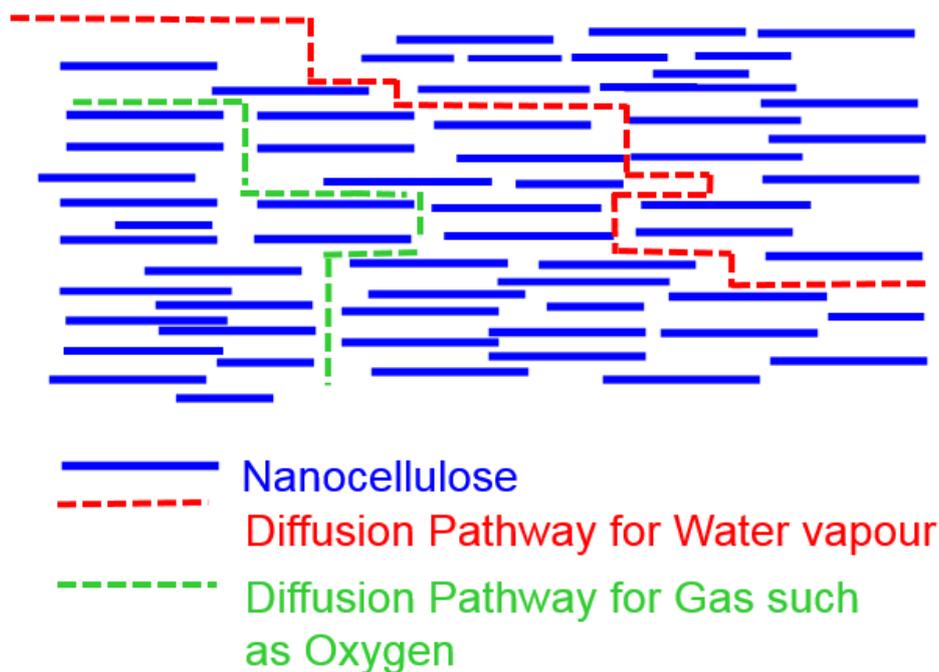


Figure 2-Simple diagram of the structure of NC film giving it good barrier performance against oxygen and water vapour ((Nair, 2014) [7]

Table 1-Oxygen Permeability of NC and Synthetic Plastics [7]

Materials	OP (cc μm^2 day KPa)	Conditions
NC	0.6	65% RH
NC carboxymethylated	0.0006	0% RH
NC Carboxy methylated	0.85	50% RH
Cellophane	0.41	0% RH
Polyethene (PE)	50–200	50% RH
Polyvinylidene chloride (PVdC)	0.1–3	-
Polyvinyl alcohol (PVOH)	0.20	0% RH
Ethylene vinyl alcohol (EVOH)	0.01–0.1	0% RH

Table 7. Water vapour permeability of biopolymer films and conventional synthetic plastics films:

Type of Film material	Water vapour permeability (WVP) 10^{-11} g/m.s.Pa	Test conditions	Reference
Polyvinylidene Chloride (PVDC)	0.0007 – 0.0024	38°C, 0-90% RH	[8]
LDPE	0.07 -0.1	38°C, 0-90% RH	[8]
PP	0.05	38°C, 0-90% RH	[8]
PS	0.5	38°C, 0-90% RH	[8]
Bee wax	0.06	25°C,0-100%	[8]
Cellophane	6.9	25°C,0-90%	[8]
Chitosan	13	25°C,76.2%	[9]

Nanocellulose (NC) film exhibits effective oxygen barrier properties of up to 65% relative humidity (RH) according to a study [10]. Within this RH range, the barrier performance of nanocellulose film is comparable to that of synthetic polymers [11], making it a viable option for packaging dry foods. Dense NC films, achieved through structural modifications to enhance nanofibril entanglements, result in a more compact surface and intricate internal diffusion pathway, leading to reduced permeability to gases and water vapor [12]. The presence of crystalline regions, in particular, contributes to heightened impermeability [13].

1.1.2.1. LIMITATIONS OF NC WITH RESPECT TO OP

The oxygen permeability (OP) of nanocellulose (NC) film exhibits low values similar to those of synthetic plastics at 0% relative humidity (RH), but

rises with increasing RH levels, with a notable decrease in performance observed above 65% RH. In contrast to synthetic plastics, NC demonstrates superior oxygen barrier properties at 0% RH and satisfactory barrier characteristics at higher humidities of 50% or 65% RH. This performance advantage over polyethylene is significant, with NC film displaying rigidity and resistance at low humidity levels, transitioning to a rubbery and viscous state at higher RH due to elevated moisture content softening the cellulose nanofibrils and weakening the cellulose chains. Consequently, the increased interfibrillar space and local deformation facilitate enhanced permeation of oxygen molecules through the film [10]. The OP values for NC film are measured at 0.6 cc μm^2 day kPa at 65% RH, 0.85 cc μm^2 day kPa at 50% RH, and 0.011 (cm³ μm)/(m² day kPa) at 0% RH. A comparison of the OP of microfibrillated cellulose (MFC) at different humidity levels and against synthetic

plastics is detailed in Table 8. Additionally, Table 9 illustrates that the OP of cellulose nanofiber (CNF) film decreases with increasing film thickness and rises with RH levels [14].

Nanocellulose films have shown promising potential as barriers to oxygen permeability due to their dense structure and high aspect ratio of nanocellulose particles. However, there are some limitations to consider: 1. Moisture Sensitivity: Nanocellulose films can be sensitive to moisture, which may affect their barrier properties. High humidity levels can lead to swelling and reduced barrier performance against oxygen permeability. 2. Thickness Variability: Achieving consistent and uniform thickness in nanocellulose films can be

challenging, which may result in variations in oxygen permeability across the film. 3. Structural Integrity: Nanocellulose films may lack the mechanical strength required to maintain barrier properties under certain conditions, leading to potential defects or cracks that can compromise oxygen barrier performance. 4. Surface Roughness: The surface roughness of nanocellulose films may impact their ability to create a uniform barrier against oxygen permeability, especially at the nanoscale level where defects can occur. Overall, while nanocellulose films offer promising oxygen barrier properties, these limitations need to be addressed to optimize their performance in various applications requiring effective oxygen barrier materials.

Table 8-OP of MFC [15]

Material	OP (cm ³ µm)/(m ² day kPa)	Relative humidity (%)
MFC	0.011	0
MFC	3.52 - 5.03	50
PET	10 - 50	50
PLA	184	0
LDPE	1900	50

Table 9-Reported oxygen permeability of selected carboxymethylated nanofibril (CNF) films

Material	OP (cm ³ .µm)/ (m ² .day.kPa)	Film thickness µm	Conditions
CNF (carboxymethylated)	0.009	2.54	0% RH
CNF (carboxymethylated)	0.0006	3.19	0% RH
CNF (carboxymethylated)	0.85	3.19	50% RH



1.1.2.2. WATER VAPOUR BARRIER PROPERTIES:

Paper and paper board, which are composed of cellulose fibres, provide structural support for protecting contents. However, their susceptibility to water vapor and oxygen is attributed to the presence of large pores and the hydrophilic properties of cellulose fibers. Nanocellulose, on the other hand, features a fibrous network with smaller pores and exhibits improved resistance to water vapor. By integrating cellulose reinforcing materials into the fibrous network, the barrier performance has been significantly enhanced, leading to a reduction in water vapor permeability [10].

Nanocellulose films exhibit excellent water vapor barrier properties due to their densely packed structure and high aspect ratio. The nanocellulose network creates tortuous pathways that impede the diffusion of water molecules, making it an effective barrier against water vapor transmission. Additionally, the hydrogen bonding between cellulose nanofibrils enhances the mechanical strength of the film, further improving its barrier properties. The nanoscale dimensions of cellulose fibrils also contribute to the exceptional barrier performance by reducing the chances of water molecule permeation. The high surface area-to-volume ratio of nanocellulose films allows for efficient coverage of surfaces, creating a uniform barrier against water vapor. Moreover, the renewable and biodegradable nature of nanocellulose makes it an attractive alternative to synthetic water vapor barrier materials. Nanocellulose films can be easily produced from sustainable sources such as wood pulp or agricultural residues, offering an environmentally friendly solution for packaging and barrier applications. Overall, the water vapor barrier properties of free-standing nanocellulose films make them a promising material for various industrial applications, including food packaging, electronics, and pharmaceuticals.

The water vapor permeability of free-standing nanocellulose films can vary depending on several factors, including the type of nanocellulose used, film thickness, porosity, and processing methods. Generally, nanocellulose films exhibit good barrier properties against water vapor due to their dense network structure and hydrophilic nature. However, the exact water vapor permeability of nanocellulose films can be influenced by the following factors:

Nanocellulose Type: Different types of nanocellulose, such as cellulose nanocrystals (CNCs) or cellulose nanofibrils (CNFs), may exhibit variations in water vapor permeability due to differences in their structure, morphology, and surface properties.

Film Thickness: Thinner films typically offer better barrier properties against water vapor compared to thicker films. This is because thinner films have shorter diffusion paths for water vapor molecules to penetrate, resulting in lower permeability.

Porosity: The porosity of the nanocellulose film can affect its water vapor permeability. Higher porosity, which may be influenced by factors such as film density and processing conditions, can increase water vapor permeability by providing pathways for water vapor diffusion.

Crystallinity: Nanocellulose films with higher crystallinity tend to have lower water vapor permeability due to the tighter packing of cellulose chains and reduced free volume available for water vapor diffusion.

Processing Methods: The fabrication method used to prepare nanocellulose films can influence their water vapor permeability. Techniques such as casting, compression molding, or layer-by-layer assembly may result in variations in film structure and properties, affecting water vapor barrier performance.

Additives: Incorporating additives or nanofillers into nanocellulose films can modify their barrier properties. For example, the addition of hydrophobic materials or nanoparticles can further reduce water vapor permeability by creating barriers or enhancing film density.

Post-Treatment: Post-treatment processes, such as chemical crosslinking

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or surface modification, can improve the barrier properties of nanocellulose films by enhancing their structural integrity and reducing molecular mobility. Overall, nanocellulose films have the potential to offer good water vapor barrier properties, making them suitable for applications where moisture protection is essential, such as food packaging, barrier coatings, and moisture-sensitive electronic devices. However, it's essential to consider the specific requirements of each application and optimize the film properties accordingly to achieve the desired level of water vapor barrier performance.

1.1.2.3. MECHANISM OF BARRIER PERFORMANCE

In order to comprehend the barrier mechanism of NC film, the process of oxygen and water vapor diffusion from regions of high concentration to low concentration across an NC film involves three distinct steps.

1. Penetrating molecules that have been absorbed onto the surface of the nanocrystalline film.
2. Movement of these molecules as they diffuse within the structure of the film.
3. The molecule is released from the opposite side of the nanocrystalline film

The permeability through a NC film mostly depends on diffusion rate internal to the film.

Equation 1- Permeability of gas or water vapour through films

$$P = D * S$$

Where P is the permeability, D is the diffusion coefficient and S is the solubility coefficient.

The permeability coefficient P is evaluated from the application of Henry's Law of Solubility to Fick Laws of diffusion and is given by

Equation 2-Permeability coefficient

$$P = \frac{D * S * q * l}{A * t * \Delta P}$$

Where q is the amount of gas or water vapour passing through the film, l is the flow path or thickness, A is the cross-sectional area, t is time, and p is the pressure difference across the film [7].

The relative permeability of the composite film is given by

$$\frac{P}{P_o} = \frac{1 - \phi}{\tau}$$

Where P = Permeability of the composite film

P_o = Permeability of pure film (no filler in the film)

ϕ = Volume fraction of the filler

τ = Tortuosity of the composite

The permeability of the composite material is influenced by tortuosity, which can be adjusted by various factors such as the type of nanoclay filler used, its aspect ratio, aggregation within the composite (intercalation and exfoliation), and the orientation of the clay within the composite sheet or film. Barrier performance against gases is also elucidated by the properties of the materials [16]. Films made from hydrophilic polymers are effective barriers against oxygen and grease under dry conditions. Nano cellulose films, characterized by a high number of hydrogen bonds, have the ability to form robust films that reduce the permeation of oxygen and volatile compounds [17] This gas barrier feature can be utilized to prolong the shelf life of food products and prevent contamination. The dense arrangement of cellulose nanofibrils in nanocellulose films hinders the passage of oxygen and other gaseous molecules through the film [18].

At higher relative humidity levels, the oxygen permeability of carboxymethylated nanocellulose films produced through solvent casting significantly increases due to the plasticizing and swelling of cellulose nanofibrils with water [7]. The porosity of nanocellulose films is a crucial factor affecting oxygen permeation and barrier performance. The oxygen transmission rate of the film decreases with increasing film thickness, as the tortuous pathway lengthens, enhancing the film's barrier properties. The surface pores of the film are poorly connected, acting as an impermeable barrier to oxygen penetration. The internal structure of nanocellulose films, including crystalline and amorphous regions in cellulose nanofibrils, contributes to their barrier

performance. The crystalline regions are impermeable to gases, while the dense amorphous regions resist gas permeation. Additionally, the size of the fibrils influences barrier performance by promoting the formation of a compact film [19] [14].

The solubility of gases is another critical factor determining the barrier performance of nanocellulose films. Non-polar gases like oxygen and nitrogen exhibit low solubility in the hydrophilic nanocellulose polymer, resulting in effective barriers against these gases.

$$P = \frac{j(\Delta x)}{A(\Delta p)}$$

The oxygen permeability of biopolymer films can be calculated using the provided equation, where P represents the oxygen permeability coefficient of the biopolymer film in amol/m s Pa , J is the oxygen transmission rate through the film in amol/s , t is the film thickness in meters, ΔP is the differential partial pressure across the film in Pa, and A is the surface area of the film in square meters [20] [18].

1.2. METHODS FOR IMPROVING THE BARRIER PERFORMANCE

There are several methods for enhancing the barrier performance of free-standing nanocellulose films:

1. **Surface Modification:** Modifying the surface of the nanocellulose film by coating it with materials such as polymers or nanoparticles can create a more effective barrier against gases and liquids.
2. **Crosslinking:** Introducing crosslinks between cellulose chains can improve the mechanical strength and barrier properties of the film.
3. **Layer-by-Layer Assembly:** Alternating layers of nanocellulose with other materials through layer-by-layer assembly can create a barrier with enhanced properties.
4. **Nanocomposite Formation:** Incorporating nanoparticles or other nanomaterials into the nanocellulose film can improve barrier performance.
5. **Chemical Modification:** Chemical treatments such as acetylation or esterification can alter the properties of nanocellulose films, improving their barrier performance.
6. **Nanostructuring:** Creating nanostructured surfaces

on the nanocellulose film can enhance barrier properties by reducing diffusion pathways for gases and liquids. By employing these methods, researchers can tailor the properties of nanocellulose films to achieve the desired barrier performance for various applications.

Various methods can be used to improve the barrier performance of nanocellulose (NC) films, such as modifying cellulose fibrils chemically, incorporating additives, applying coatings, implementing cross-linking treatments, and retaining residual lignin in the NC. Additionally, the inclusion of montmorillonite (MMT) or similar nanoparticles can impact the water vapor resistance of NC films. The introduction of vermiculite into NC films has been shown to enhance their oxygen resistance, even under high humidity conditions. Incorporating MMT into biopolymers to create nanocomposites can enhance their strength and thermal stability. Clays like MMT, which have a high aspect ratio, can effectively reinforce biopolymeric matrices [18-23]. Bentonite, also known as MMT, is a common clay used in composite development and is characterized by its alumina-silicate layered structure. MMT serves as a nanoscale filler that provides reinforcement in nanocomposites due to its high surface area and aspect ratio. MMT is considered safe for use as a food additive at a concentration of 5 wt.% in Australia. Nanocomposites made from nanocellulose and MMT exhibit low oxygen and water vapor permeability. Incorporating clay into biopolymer networks can enhance mechanical properties, increase glass transition temperature, and improve thermal resistance. However, adding clay to nanocellulose can reduce the transparency of NC films. Sodium Montmorillonite, derived from bentonite, contains impurities like feldspar, calcite, silica, and gypsum. Bentonite's main component, Montmorillonite, tends to agglomerate into lamellar packages, resulting in an irregular shape. Natural bentonite is non-swellable due to the presence of calcium and magnesium ions, but alkaline activation can convert these ions into sodium ions in MMT. This cation exchange process involves treating MMT with soda ash to replace calcium and magnesium ions with sodium ions, allowing the activated [18-27].

The types of clay used in making nanocomposites play a crucial role in determining their barrier effectiveness. Clays are generally categorized as either swellable or non-swellable. Non-swellable clays like kaolinite and illite do not expand, while swellable clays like montmorillonites such as bentonite and vermiculite can swell and shrink based on the interlayer cations present, such as Na^+ , Ca^{++} , and Mg^{++} . Montmorillonite (MMT) is a type of bentonite with exchangeable interlayer cations like Na^{++} or Ca^{++} along with Mg^{++} . Calcium bentonite, a natural form of Ca^{++} MMT, has low swelling properties, but when converted to the sodium form, the Na^{++} ion significantly boosts water absorption and promotes exfoliation due to weaker linkages. The impact of these interlayer cations on barrier performance, particularly water vapor permeability, has not been extensively studied, but it is anticipated that their distinct swelling characteristics could have a significant influence on the barrier properties of the composite [28] [29].

1.2.1. ROLE OF CLAYS INTO THE NANOCELLULOSE NETWORK

Nanoclays play a significant role in enhancing the properties of nanocellulose films by improving their mechanical strength, barrier properties, and thermal stability. When incorporated into the nanocellulose network, nanoclays act as reinforcing agents by forming a strong interfacial interaction with the cellulose chains. This leads to

improved mechanical properties such as increased tensile strength, modulus, and toughness of the resulting nanocomposite films. Additionally, nanoclays help in reducing water vapor permeability and gas barrier properties of the nanocellulose films, making them suitable for packaging applications where moisture and gas resistance are crucial. The presence of nanoclays also enhances the thermal stability of nanocellulose films, making them more resistant to high temperatures. Moreover, the combination of nanocellulose and nanoclays can lead to the development of sustainable and environmentally friendly materials with improved properties, which can find applications in various fields such as food packaging, biomedical devices, and electronics. Overall, the incorporation of nanoclays into the nanocellulose network offers a promising approach to create advanced materials with enhanced performance characteristics.

The packaging sector favors inexpensive additives and environmentally friendly materials that are widely accepted for easy processing by the industry. Inorganic layers, typically around 1 nm thick and varying in length up to several microns depending on the type of silicates or clays, are commonly used as additives. As previously mentioned, the addition of clay particles in the diffusion path of the film enhances the tortuosity of the NC film, leading to improved barrier performance and potential of the nanocomposite.

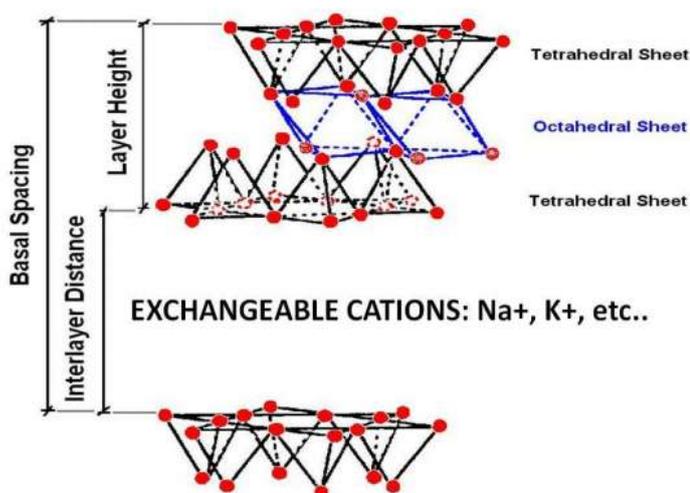


Figure 31-Structure of MMT. The image obtained from [30]

1.2.2. STRUCTURE OF NANOCELLULOSE COMPOSITE

Nanostructured cellulose composites show promise for barrier applications due to their unique properties. These composites typically consist of nano-sized cellulose particles dispersed in a polymer matrix. The structure of nano-cellulose composites for barrier applications is crucial for their performance. The arrangement of cellulose nanoparticles within the polymer matrix plays a key role in determining the barrier properties of the composite. A well-dispersed and oriented structure of nano-cellulose particles can create tortuous pathways that impede the movement of gas molecules and liquids, enhancing the barrier properties of the material. The incorporation of surface modifications or coatings on the cellulose nanoparticles can further improve the barrier performance by reducing the permeability of the composite to different molecules. In addition, the interfacial interactions between the cellulose nanoparticles and the polymer matrix are essential for the overall performance of the composite. Strong adhesion between the cellulose particles and the polymer can prevent the formation of gaps or defects that could compromise the barrier properties. Overall, the optimal structure of nano-cellulose composites for barrier applications involves a well-dispersed, oriented arrangement of nanoparticles within the polymer matrix, combined with appropriate surface modifications and strong interfacial interactions to enhance barrier performance.

The structure of nanocellulose composites depends on several factors, including the type of nanocellulose used, the matrix material, processing methods, and any additives or reinforcements incorporated into the composite. Here's an overview of the typical structures found in nanocellulose composites:

Nanocellulose Network: The nanocellulose component forms a network structure within the composite. Depending on the form of nanocellulose used (e.g., cellulose nanocrystals, cellulose nanofibrils), this network can consist of individual nanocellulose particles dispersed

throughout the matrix or interconnected fibrillar structures.

Matrix Material: The matrix material surrounds and encapsulates the nanocellulose network. It can be a polymer, biopolymer, or other suitable material chosen based on the desired properties and applications of the composite. The matrix provides structural support, mechanical strength, and cohesion to the composite.

Interfacial Region: The interface between the nanocellulose and the matrix is critical for determining the properties of the composite. Proper adhesion and interactions between the nanocellulose and matrix materials are essential for achieving good mechanical properties and load transfer within the composite. Surface modifications or compatibilizers may be used to enhance interfacial interactions.

Filler-Matrix Interaction: Depending on the compatibility between the nanocellulose and matrix materials, filler-matrix interactions can vary. Strong interactions can lead to improved mechanical properties, while weak interactions may result in phase separation or reduced composite performance.

Orientation and Alignment: The orientation and alignment of nanocellulose within the composite can significantly influence its mechanical and barrier properties. Techniques such as shear flow during processing or alignment in external fields (e.g., magnetic or electric fields) can be used to control the orientation of nanocellulose particles or fibrils within the composite.

Porosity and Microstructure: The presence of nanocellulose within the composite can influence its microstructure and porosity. Nanocellulose networks may contribute to the formation of interconnected pores or channels within the composite, which can affect properties such as permeability, swelling behavior, and surface area.

Additives and Reinforcements: Additional additives or reinforcements, such as nanoparticles, fibers, or fillers, may be incorporated into the composite to further enhance its properties. These additives can provide additional functionality, improve mechanical strength, or modify other characteristics of the composite. Overall, the structure of nanocellulose composites is complex and can be tailored through material selection, processing techniques, and the addition of additives to achieve desired properties for specific

applications, such as packaging, automotive, aerospace, and biomedical materials.

There are three different types of structures found in composites: phase separated nanocomposites, intercalated nanocomposites, and exfoliated nanocomposites. These structures are determined by the method of fabrication, the arrangement of clay platelets, and the size of nanocellulose fibrils, all of which influence the barrier performance of the composite material. In phase separated nanocomposites, the clay platelets are not mixed with the polymer, leading to their aggregation within

the composite and resulting in poor barrier performance. In intercalated nanocomposites, the clay platelets are inserted between polymer fibers, creating an ordered structure with alternating layers of nanocellulose and clay at a nanometer scale. Exfoliated nanocomposites feature well-separated clay platelets dispersed within the nanocellulose region, with extensive penetration of nanocellulose into the clay layers. The orientation of clay platelets in nanocomposites, as depicted in Figure 4, plays a crucial role in determining the barrier mechanism of the composite material [31] [32].

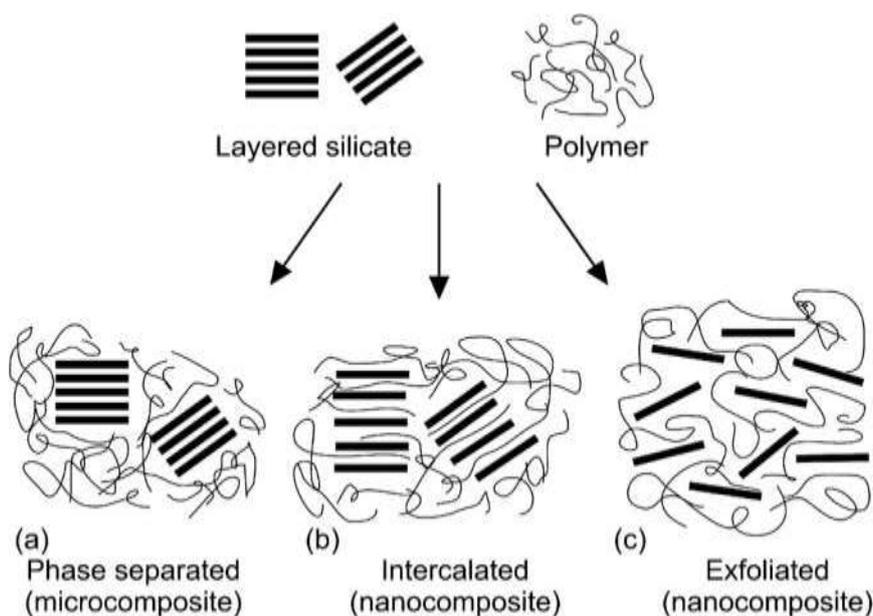


Figure 42-Structure of nanocomposite. The image obtained from Alexandre, M et al , 2000 [33]

operational durations typically under 30 minutes [34]. This method has proven to be efficient for manufacturing composites, leading to its utilization in the creation of NC–MMT Composite materials. Traditionally, the fabrication of free-standing NC films involved either vacuum filtration or casting techniques. However, these methods are known for their time-intensive nature, taking anywhere from 10 minutes to 3 days for film formation, with issues such as drying and wrinkling posing limitations. Vacuum filtration, in particular, necessitates a minimum operational time of 24 hours to 4 days for

nanocomposite production, with challenges in separating the film from the filter and handling the wet film post-peeling before drying. These conventional approaches also face constraints in customizing the basis weight and thickness of the composites.

1.3. CONCLUSION

In recent times, nanocellulose films and their composites have shown promise for a variety of applications across different industries. These films have been primarily utilized in functions such as barriers, air filtration, antimicrobial coatings,

substrates for electronic devices, and light-emitting diodes, among others, with the aim of replacing conventional synthetic plastics. Both free-standing nanocellulose films and their composite counterparts offer a wide range of properties and

applications, making them attractive materials for various industries seeking sustainable and functional packaging solutions, biomedical devices, and advanced materials.

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