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Flexible Cellulose Nanofiber (CNF)-Nano-Montmorillonite (MMT) Composite Sheet Structure and Water Vapor Barrier Performance

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Abstract: One of the newly developed nanomaterials for functioning as high-performance packaging materials to replace synthetic plastics such as low-density and high-density polyethylene (LDPE, HDPE) is cellulose nanofiber (CNF). These substances are biodegradable, recyclable, and renewable. While cellulose nanofiber-based films have substantially better water vapor permeability than traditional packaging polymers, they have extremely low oxygen permeability. Water vapor permeability (WVP) of the spray-coated composites was decreased via spraying nano-montmorillonite (MMT) content into CNF suspension and also high-pressure homogenization of CNF-MMT suspension. The process for spraying cellulose nanofiber (CNF)-nano-montmorillonite (MMT) suspension on the stainless-steel surface was developed to produce a high-barrier performance composite. The two types of composites were prepared via spraying of raw CNF with MMT and fibrillated CNF with MMT via high-pressure homogenization. The structure and barrier performance of these composites were investigated with SAXS and ASTM E96/E96M-05. Before homogenization, the MMT is agglomerated, while after homogenization it is more exfoliated, which is split up into individual sheets. The water vapor permeability could be reduced by adding up to 20 wt. % montmorillonite and dispersing montmorillonite with two passes in a high-pressure homogenizer. With montmorillonite addition above 20 wt. %, the water vapor permeability started to increase due to aggregation of the montmorillonite in the homogenized composite. At the optimal addition level, the best performance achieved with spraying was a water vapor permeability of 8.3 x 10^{-12} g/m.s.pa. The air permeability of the composite was evaluated to be less than 0.003 µm/Pa.s. This value confirms an impermeable composite for packaging applications. Considering the orientation of MMT in the composite, the composite's structure can decide the barrier performance and can be altered by further fibrillation process of cellulose nanofibers via high-pressure homogenization.

Keywords: Cellulose nanofiber (CNF); Montmorillonite (MMT); XRD; Water vapor permeability; Structure of nanocomposite

1. Introduction

Synthetic plastics predominantly occupy a significant role in conventional packaging because of their comfort in processing methods and possess excellent barrier performance against air, water vapor, oxygen, carbon dioxide, and liquid water. However, it was mainly expensive in fabrication cost as the material was derived from fossil fuels. When compared with iron, glass, and ceramics, synthetic plastics are more flexible and potential for recycling and reprocessing. However, the waste from synthetic packaging has a negative impact on the environment. Plastic debris from this waste causes a contamination of the ecosystem, forming micro/nanoplastics contamination in the oceans and poisoning the wildlife as well as the ecosystem [1]. Petroleum-based packaging materials are not biodegradable and also cause severe environmental issues such as landfilling, harmful recycling processes with the emission of toxic gases, and leaching of toxic monomers in the watershed. These limitations have been driving researchers to find a sustainable approach to discovering new materials from natural sources and are becoming a top priority in the business of packaging materials nowadays.

Natural biopolymers are not exactly suitable for packaging applications due to their poor barrier performance against gases and vapors. Therefore, there is a requirement for sustainable composite developed from natural polymers that meet the requirements of high-performance barrier property. The new material for the design of the packaging should be novel and recyclable into a potential barrier material even after reuse/reprocessing or completely biodegradable when disposed into the environment. The barrier property of the material should be tailorable when combined with another material and flexible for forming into sheets/films or any other forms.

Cellulose is the predominant fibrous biopolymer applied in the development of green sustainable packaging material. It is renewable, eco-friendly, has good strength, and is capable of various chemical functionalization. Cellulose substrates such as paper, paper boards, container boards, and shipping sacks have been used as cellulose substrate packaging materials. It is low cost, widely available, less in weight, and tailoring its properties via adjusting the composition of the pulp, the manufacturing process and conditions, and its surface treatments. However, these materials are highly moisture-sensitive [2]. Yet they have poor barrier performance due to the presence of wide pores allowing a significant amount of gas and vapors to pass through. The cellulose substrates coating with wax or lamination of these substrates with synthetic plastics and substrates extrusion with aluminum were various approaches for increasing the barrier performance of the substrates. These coatings do have not any potential for reusability after recycling.

Utilizing cellulose nanofiber to make nanocomposite allows to enhance the mechanical strength and biocompatibility, and tune barrier potential against water vapor and other gaseous substances. Cellulose nanofiber (CNF) was produced from wood pulp and other cellulosic material via various methods of high-pressure homogenization, high-intensity ultrasonication, micro-grinding, micro-fluidization, electrospinning, steam explosion and chemical processes such as acid hydrolysis, enzymatic hydrolysis, 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO) oxidation and so on. CNF has good biocompatibility, biodegradability, and chemical stability. Recently, the research on the use of CNF in developing barrier materials for packaging applications has increased exponentially. Due to the high availability of CNF, it could minimize the cost of the starting material for packaging products from CNF and also offers a platform for recyclability and reusability leading to a sustainable pathway.

Cellulose nanofiber (CNF) consists of cellulose fibrils at the nanoscale embedded in the fibrous matrix producing a compact network structure with narrow pores. This CNF film has a notable mechanical property such as rigidity, tensile, flexural, and barrier properties such as good oxygen permeability and water vapor permeability. The cellulose nanofibrils have a high aspect ratio with a fibril diameter varying from 5 to 100 nm and a length of a few microns. As a result, the formed CNF film has a highly compact network by entanglement via hydrogen bonding. CNF was fabricated into films, membranes, aerogels, and nanocomposites with either organics polymers or inorganics fillers. Vacuum filtration, solvent casting, hot pressing, and spray coating are the methods for the fabrication of CNF film [3–6]. Spraying CNF on the polished stainless-steel surface to produce a smooth film is a rapid method and the basis weight and thickness of the film could be tailorable by adjusting CNF suspension consistency and process parameters in spray coating. The compact structure of sprayed CNF film has performed as a potential barrier against air and water vapor and an alternative to synthetic packaging material. The cellulose fibrils in the fibrous network produce an outstanding compactness through the interaction between the fibrils via hydrogen bonding and contribute to good barrier performance against gaseous substances [7].

Recently, spraying processes were used to fabricate nanocomposites such as graphite carbon black-micro fibrillated cellulose as an electrode and SiO2-microfibrillated cellulose nanopaper [8]. The operation time for the spraying process has an operation time of less than 30 minutes to form the MFC-SiO2 composite. The percentage of SiO2 in MFC suspension can be varied from 0 to 33 wt.% and does not affect the spraying time. As a result, the properties of the composite can be tailored depending on the SiO2 % in MFC suspension [9].

The oxygen permeability of CNF increased with the relative humidity of the surroundings. This is because nanocellulose fibers plasticize and are swelled by the adsorption of water molecules under a high moisture environment [10]. However, these films have a high water vapor permeability due to their high polar nature. In brief, the water vapor is absorbed by the cellulose fiber-fiber bond in the fibrous network. There is an increased diffusion pathway for enhancing barrier performance [10]. Because of the highly polar nature of CNF, the fiber-fiber bond was weakened through water sorption. As a consequence, the WVP of the film was increased, increasing the swelling of CNF film [11].

The incorporation of clay platelets into the cellulose nanofibril matrices shows improved properties such as stiff and strong composites with good elastic modulus and low gas permeability [12]. The cellulose nanofiber forms a fiber matrix network of dispersed clay platelets aggregates in the nanocomposite [13]. The oxygen permeability of nanocomposites with inorganics was quite appreciable and comparable with synthetic packaging materials and even better than that of commercial packaging materials [10]. In the design of barrier materials, water vapor permeability is a critical parameter to be controlled effectively for engineering packing materials and this property should be as low as much as possible for the extension of the shelf life of water-sensitive products such as foods and pharmaceuticals [11].

To improve the water vapor permeability of CNF, inorganics fillers have been incorporated into the fibrous matrix producing high-performance nanocomposites. Nanoinorganics provide a relatively larger surface area and favor the nanoclay–matrix interactions elevating the barrier performance and mechanical properties. The layered nanoclay into the polymer suspension enhances the tortuosity of the composite for water vapor/gas molecule diffusion, resulting in high barrier performance [12]. “Bentonite” montmorillonite (MMT) is a hydrated, alumina-silicate-layered clay that serves as reinforcement in nanocomposite materials and has a high surface area with a wide aspect ratio of 50 to 1000 [13]. MMT is composed of hard, impermeable filler and dioctahedral nanoclay with 2:1 layer coupling. It creates a maze-like structure that compels the transfer of air, oxygen, and water vapors to take a circuitous route, improving the composite’s barrier performance.

CNF-MMT Nanocomposites via vacuum filtration have low oxygen and water vapor permeability and high-performance composites [11, 14]. However, the time consumption for the production of nanocomposite via vacuum filtration is quite long, and sheet formation requires 30 mins to 4 days. Sometimes some of the nanoparticles will be drained out during the dewatering stage of vacuum filtration, affecting the sheet composition and porosity, resulting in poor properties of nanocomposites. The peeling of the composite from the filter surface is a quite challenge in vacuum filtration. In this method, the filtration time to form the sheet increased with basis weight and thickness [5]. Thus, this is a slow process and very limited in upscaling the process. Spray coating has been used to prepare the composites with cellulose nanofiber with varying content of fillers from 0 to 33% and consumed less than 30 mins for sheet formation. The filler concentration in CNF suspension does not affect the operation time for the spraying process. However, they replaced vacuum filtration with a spray coating but followed the conventional process such as transfer of sheet with blotter and vacuum dewatering, and then the film peeled off after drying [9].

A rapid method for fabricating CNF film is to spray it onto a stainless-steel plate. This technique can create films with a diameter of 15.9 cm in less than a minute [5]. The spraying procedure is remarkable for contour coating and contactless coating with the base surface. The topography of the base surface often has little impact on the coating procedure. By changing the spray coating technique's process parameters and CNF suspension concentration, it is possible to produce films with higher basis weights and more consistent thicknesses [5–6]. A novel process that is independent of process variables like suspension concentration and nanoclay loading in the suspension is the preparation of CNF-MMT nanocomposite via spraying and functionalization by the addition of particular nanoparticles/nanofillers in the cellulose nanofiber suspension.

During this process, the composite was fabricated and the barrier performance of the composite relies on the MMT location in the composite. However, the effect of composite structure on the barrier performance of the CNF-MMT composite remains obscure. This work investigates the effect of the CNF-MMT composite structure on the water vapor permeability as one of the important barrier properties of the CNF-MMT composite and the structure of the composite evaluated via SAXS.

2. Materials and methods

2.1. Cellulose nanofiber

In the documented scientific literature, the terminology for cellulose nanofiber (CNF) was repeatedly modified. Nanocellulose (NC), micro-fibrillated cellulose (MFC), cellulose nano-fibrils, and nano-fibrillated cellulose (NFC) are further names for CNF. In the experiment at hand, cellulose nanomaterial was referred to as CNF/NC. The present CNF experiment employed DAICEL Chemical Industries Limited's (Celish KY-100S) feedstock, which ranged in fiber percentage from 23% to 25%. According to Raj, the cellulose nanofibrils of DAICEL NC (Celish KY-100S) have an average diameter of around 70 nm and a mean fiber length of about 8 m [15]. A 142 x 28 aspect ratio for the KY 100S was determined using KY-100S by DAICEL. To create KY 100S, cellulose pulp was micro-fibrillated under intense water pressure. According to Raj et al., KY100S has a crystallinity index of 78. 2.0% wt. CNF suspensions were made by dissolving 25-weight percent of KY 100S's fiber in deionized water as described in the scientific literature and then disintegrating the mixture for 15,000 revolutions at 3000 rpm [15].

2.2. Nanoclay

A montmorillonite (MMT) nanoparticle called Closite Na++ was given by IMCD Australia Limited in Mulgrave, VIC 3170, Australia by BYK Additives and Instruments, Germany. Closite Na++ has an average dry particle size of 25 m (d50), a packed bulk density of 568 g/l, a density of 2.86 g/cm^3, and X-ray data that support a d001 of 1.17 nm.

2.3. Preparation of nanoclay-cellulose nanofiber suspension

The 2 wt. % of CNF suspension was prepared and disintegrated as per the reported procedure in scientific literature. The nanoclay addition is based on fiber (solid content) in the nanocellulose and varies by 5 wt %, 10 wt%, 20 wt.%, 30 wt.%, 50 wt.%, and 75 wt.% into 960 g of water and vigorously mixed and disintegrated with nanocellulose to make suspension for spraying. The MMT-nanocellulose suspension is used to prepare the composite with 5 wt. %, 10 wt.%, 20 wt.%, 30 wt.%, 50 wt.%, and 75 wt.% of Closite Na++.

2.4. Homogenization

Homogenization of CNF-MMT suspension is implemented to process the nanocomposite with a good tortuous path. The 2 wt.% CNF-MMT suspension was homogenized at 1000 bar and subjected to 2 passes in GEA High-Pressure Homogenizer. The high-pressure homogenized suspension was used for the fabrication of composite via spraying. The method for homogenization of CNF suspension with MMT is here. The further reduction of DIACEL nanocellulose into a nanoscale diameter of fibrils, the nanocellulose suspension with MMT concentration of interest was homogenized in GEA Niro Soavi (laboratory scale) high-pressure homogenizer. The 2 wt. % suspension with MMT underwent 2 passes at 1000 bar pressure. The homogenized suspension was then used for spraying on the polished metal surface to make a nanocomposite.

2.5. Spraying of nanoclay montmorillonite (MMT)-cellulose nanofiber suspension

The CNF-MMT composite was prepared through spray coating as reported for the preparation of pure nanocellulose film. In this method, cellulose nanofiber (CNF)-Montmorillonite (MMT) suspension was sprayed on the stainless-steel plate on a moving conveyor. The velocity of the conveyor was maintained to be 1.25 ± 0.25 cm/sec. The professional spray system Wagner Pro 117 was used for spraying suspension at a spray pressure of 200 bar. In the spray system, an elliptical spray jet with an angle of 50° from the spray nozzle 517 was able to develop coverage of 22.5 cm suspension on the base surface. The distance from the spray nozzle to the square stainless-steel plate was 50 ± 1.0 cm. The steady state in the spray coating experimental setup was allowed to run the system for 30 seconds to avoid any discontinuity in the spray jet. The sprayed composite film was very wet and dried in a laminar flow chamber under standard laboratory conditions for 24 hours. The well-dried composite film was easily peeled from the stainless-steel plate. The developed composite film was used for evaluating barrier potential and other characterization. **Figure 1** shows the spray coating experimental setup for the fabrication of CNF-MMT composites.

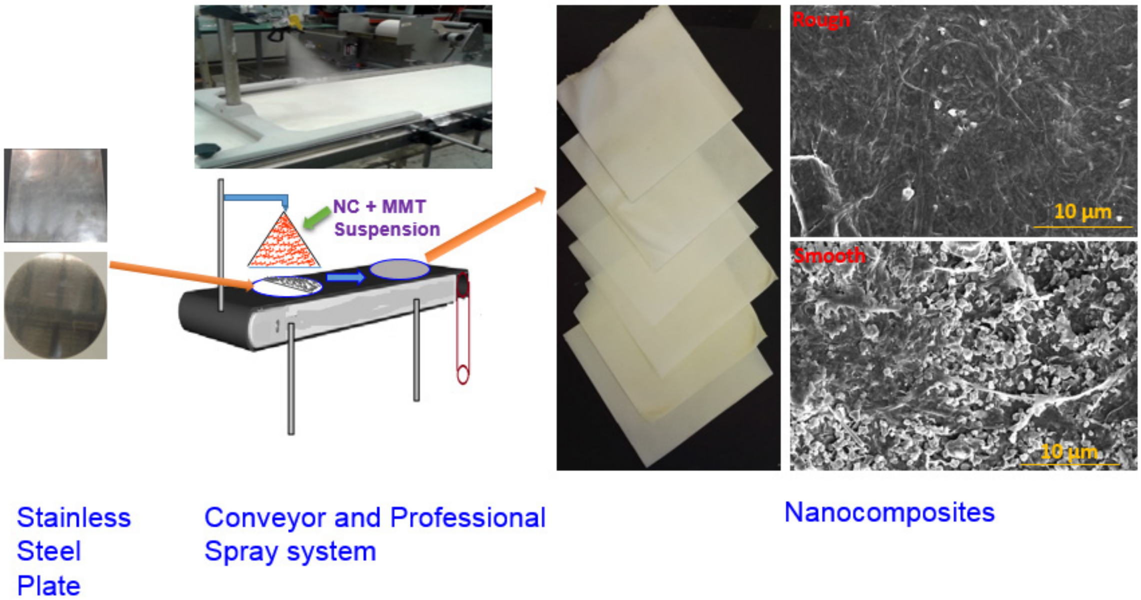


Figure 1. An experimental setup for spraying of nanocellulose suspension with MMT

2.6. Air permeance

The L&W air permeance tester which has a measuring range from 0.003 to 100 µm/Pa.S was used to investigate the air permanence of the spray-coated nanocomposite. The mean value of air permeance from 3 different areas of each composite sheet was reported. The Technical Association of the Pulp and Paper Industry (TAPPI) standard T 460-om-2 has been used to measure the air permeance of the composite.

2.7. Water vapor permeability

ASTM standard (E96/E96M-05) method was used to evaluate the water vapor permeability (WVP) of the composites. This test was normally carried out at 23°C and 50% relative humidity. Before the testing, the composites were dried for at least 24 hours at a temperature of 105 °C in an air oven. The cup was filled with 40 g of dried anhydrous $CaCl_2$. The composites were used to cover the cups. The weight of the cup, $CaCl_{2,}$ and test specimen was evaluated every 4 hours. The water vapor transmission rate (WVTR) is defined as the slope of the line between the weight of moisture absorbed in $CaCl_2$ in the cup and time. The WVTR of composites was normalized with the thickness of the composites and converted into water vapor permeability (WVP). The mean value of three parallel tests of each NC-MMT composite was reported. Simultaneously, the test without $CaCl_2$ in the cups as blank was carried out.

2.8. Cross-sectional investigation of nanocomposite

The SEM FEI Magellan 400 was utilized to investigate the cross-section of the nanocomposite and surface of the composite. The specimen was soaked in liquid nitrogen and fractured with a tweezer and then the specimen was fixed onto a metal sample holder and the coating with a thin layer of conductive metal such as iridium. After that, the coated specimen was subjected to SEM imaging.

2.9. SAXS

SAXS measurements were performed on the original composite sheets [27]. The transmission mode was carried out at an energy of 8 keV at 2 samples to detector distances (7 m and 1 m). The measured q ranges were between q = 0.001 and 0.2 $Å^{-1}$. The PILATUS 1 M detector has been used to detect the X-rays scattered from the composite sample. The pixel size in the detector was maintained to be 172 um x 172 um. The curve from scattered data was processed after the data reduction and radial averaging by the in-house beamline software ScatterBrain. Silver behenate and glassy carbon were used to calibrate the q scale and normalize scattering curves to an absolute scattering cross-section.

3. Result and discussion

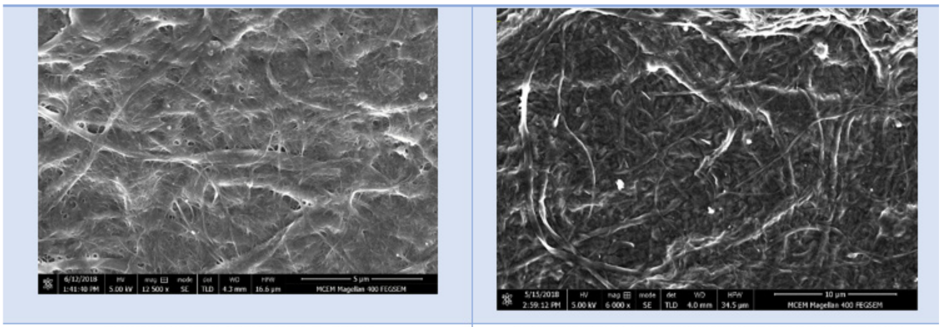
Spraying CNF-MMT suspension on polished stainless steel is a novel approach to the fabrication of the nanocomposite for barrier applications. Spraying provides least the operation time for forming the composite film. The operating time for forming the composite film was less than a minute, The CNF and MMT concentration in the suspension was independent of the operation time for the spraying processes. In vacuum filtration, Increasing CNF-MMT concentration in the suspension would increase dewatering time exponentially. As a consequence, the time consumed for forming the composite film on the filter mesh in vacuum filtration varies from 30 minutes to 24 hours. The spray-coated CNF-MMT composite has two unique surfaces namely a rough surface which is exposed to air (also called a free surface) and a smooth surface which is exposed to a polished metal side. The roughness of a smooth surface was lower than that of a rough surface. The smooth surface of the composite film is glossy and shiny which can be used for further development of various functional materials such as printed electronics and flexible electronics.

The MMT-nanocellulose composites were prepared via spray coating, engineering its barrier performance, and tailoring their bulk properties by adding the percentage of MMT from 0 % to 30 wt. %. The air and water vapor permeability (WVP) properties of nanocomposites via spraying were evaluated for each type of composite. Spray-coated nanocomposites were flexible and foldable, more uniform in thickness. The nanocomposites are yellowish due to the increased MMT content in the nanocomposites. The reason for the yellowing of the surface of nanocomposites is due to the absorption spectra of MMT in the nanocomposites and similar observations were reported in the previous literature [11, 16]. The colored nanocomposite as a finishing quality could be produced by spray coating and simply adjusting MMT loading in the nanocellulose suspension.

3.1. Surface appearance of nanocomposites

Figure 2 shows the rough surface of pure nanocellulose film and 30% MMT-nanocellulose composites prepared with and without homogenization. The distribution of MMT platelets on the surface of the spray-coated composite has been observed. MMT particles were embedded well and impregnated in a cellulose nanofibrils network. MMT nanoclay particle’s size varies from 20 nm to 50 nm and capacity is embedded into the pores of the CNF fibrous matrix. Sometimes MMT platelets were formed as stacks or aggregates in the fabrication of composite. It results that MMT aggregates/stacks cause exfoliation in the composite. As a consequence, it results in poor water vapor barrier performance. The 10 µm and 100 µm SEM micrographs of these spray-coated nanocomposites confirm the distribution of MMT in the nanocomposites at various magnifications. The EDX spectrum of nanocomposites confirms the presence of the nanoclay on the surface of the nanocomposite due to the presence of elements like Si and Na along with carbon and oxygen from cellulose molecules.

Pure MFC (Unhomogenized) | **30% Closite Na MMT Nanocellulose Unhomogenized**



Pure NC (Homogenized) | **30% Closite Na MMT Nanocellulose Unhomogenized**

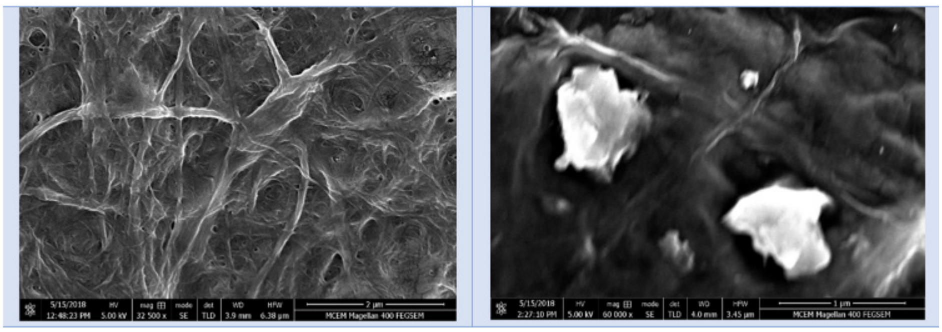
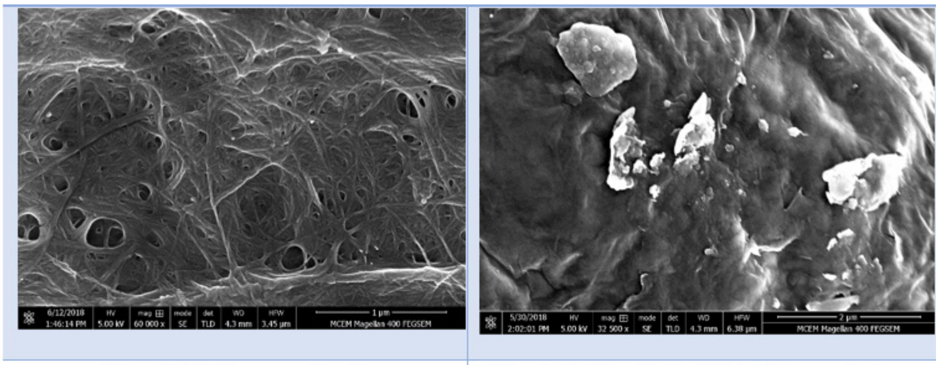


Figure 2. Surface appearance of spray-coated 30 wt.% nanocomposites

Figure 3 reveals the rough surface of the 10 wt. % spray-coated nanocomposite and the presence of the MMT platelets on the composite. When compared with high-pressure homogenized plain nanocellulose films and composite, the cellulose fibrils are closely packed via forming hydrogen bonding with neighbor fibers forming an outstanding network with less porous than that of original nanocellulose films and composite. After homogenization of nanocellulose suspension with clay, fibrillation among the cellulose nanofibrils is better due to more interaction between reduced cellulose nanofibrils via hydrogen bonding and results in the formation of a good compact fibrous network.

Pure MFC (Unhomogenized) **10 wt.% Closite Na MMT Nanocellulose Unhomogenized**



Pure NC (Homogenized) **10 wt. % Closite Na MMT Nanocellulose Unhomogenized**

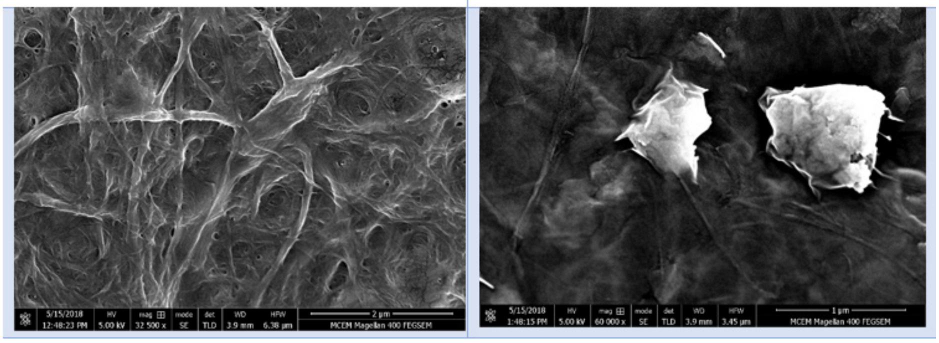
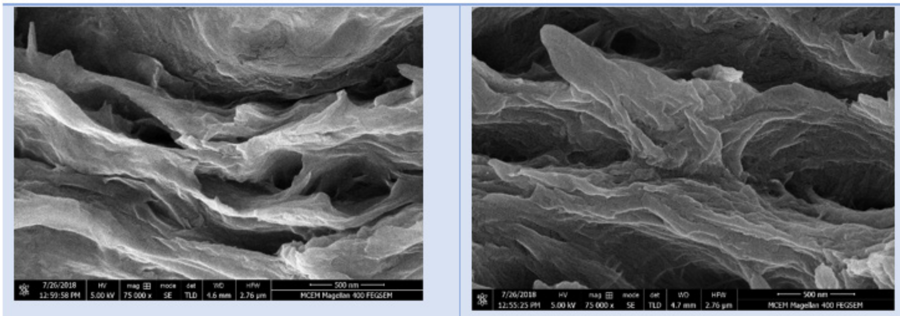


Figure 3. Surface of the spray-coated 10 wt.% nanocomposite

Figure 4 reveals the SEM micrograph on the cross-sectional view of both composites prepared via spraying. The aggregation of MMT as clumps was observed in the interior of the original composites and MMT was aggregated and concentrated on the edges of one part of the original nanocomposites. It means that clay platelets were not penetrated into the interior of the fibrous network. The mean diameter of raw CNF is ~70nm with a mean length of fiber around 8μm and an average aspect ratio of 142 ± 28. The size of Bentonite MMT (nanoclay) particles varied from 20 to 50 nm in length. In original composites, MMT platelets were not intercalated between nanocellulose fibrils due to their large aspect ratio. As a consequence, the spray-coated original composites retain an exfoliated structure where MMT platelets are concentrated and aggregated on a portion of the composite and not uniformly separated within the cross-section of the composites. In the case of composites with a high-pressure homogenization step, MMT platelets are well distributed in the interior nanocomposites, and MMT platelets were intercalated uniformly in between the cellulose nanofibrils. The SEM micrographs reveal the MMT platelets equally entangled between cellulose nanofibrils. The average diameter of nanocellulose after high-pressure homogenization is 20 nm with 5 μm in length of cellulose fibers, the aspect ratio of homogenized nanocellulose is evaluated to be 286. Due to the reduction of nanocellulose fibers via high-pressure homogenization, cellulose nanofibrils are easily penetrated into MMT platelet layers resulting in nanocomposite with an intercalated structure.

Pure nanocellulose spray-coated (Unhomogenized)

Pure nanocellulose spray-coated Homogenized sheet



30 Wt. % MMT Original Composites

30 Wt% MMT Composites with high-pressure homogenization

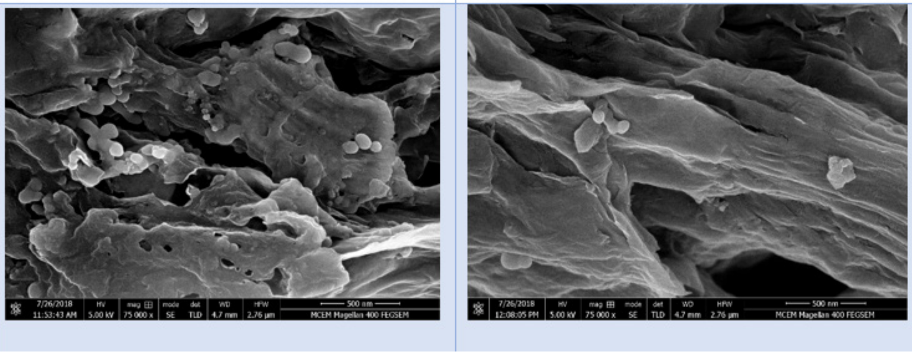


Figure 4. Cross-sectional view of the original composite and composite with high-pressure homogenization

3.3. Flexible spray coating process for preparation of nanocomposite

Figure 5 reveals the surface and topography of CNF-MMT composites. The MMT particles were scattered in the network of cellulose nanofibrils in the composite. In the raw or original composite, the MMT particles were aggregated and showed large clumps on the surface of the composite. This aggregation of MMT causes the exfoliation of MMT particles in cellulose nanofibrils. As a result, the WVP of the composite is not much decreased. In composite prepared via spraying of high-pressure homogenized CNF-MMT suspension, CNF are well fibrillated and reduced the fiber diameter from 70 nm to 20 nm and MMT platelets are sectioned into the individual particles and allowed for well mixing with fibrillated CNF. As a result, the MMT particles were intercalated in the cellulose nanofibrils matrix, allowing the reduction of the WVP of the composite.

Figure 6 reveals the original composite and composite prepared via spraying of high-pressure homogenization of 2 % wt. CNF+ 30 wt, % MMT. As the discussion was given in **Figure 5**, the same phenomena have been observed in 30 wt.% MMT composite. In addition to that, an increase in MMT concentration in the composite could elevate the WVP of the composite. Generally, Bentonite MMT was highly hygroscopic and increased the quantity of MMT in the composite leading to more water absorption. This phenomenon was observed in the plot of WVP versus MMT percentage.

Figure 7 and **Figure 8** reveal the cross-sectional images of the composite and pure CNF film. In the cross-section of the original composites, the MMT stacks were observed in the interior of the cellulose nanofibrils network and caused the exfoliation of the MMT in the composite. In homogenized composites, the MMT stacks are broken into MMT layer particles and mixed well with cellulose nanofibrils matrix resulting in intercalated composites. The WVP of the homogenized composite has a lower value than that of the original composites.

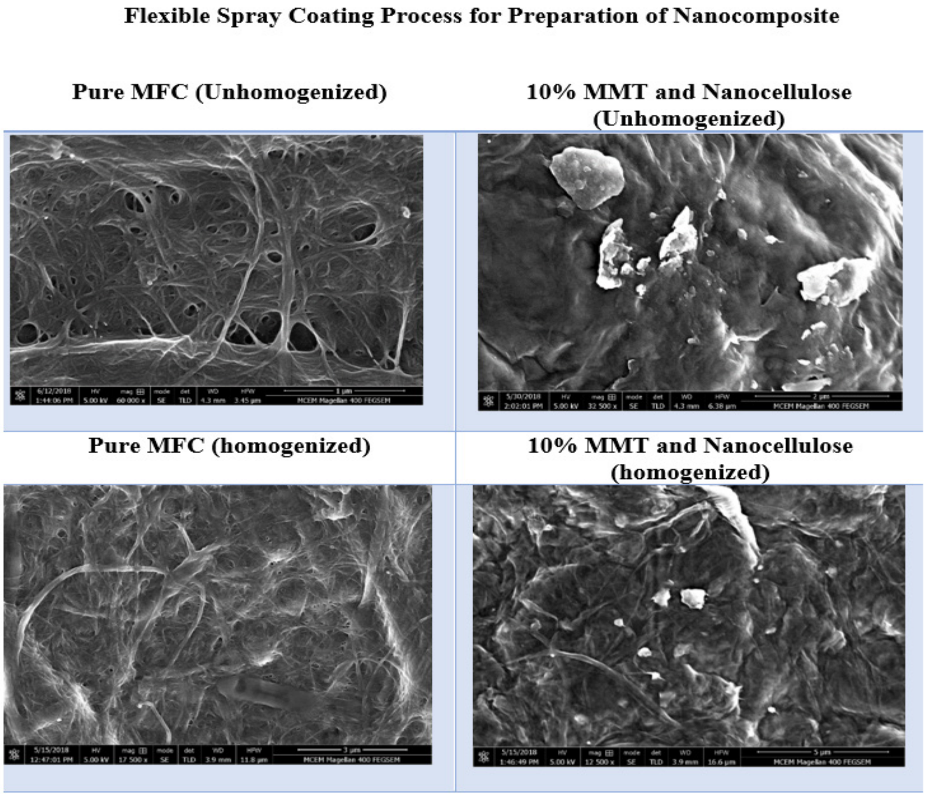


Figure 5. Surface morphology of 10 wt.% MMT original composites and composites with high-pressure homogenization step

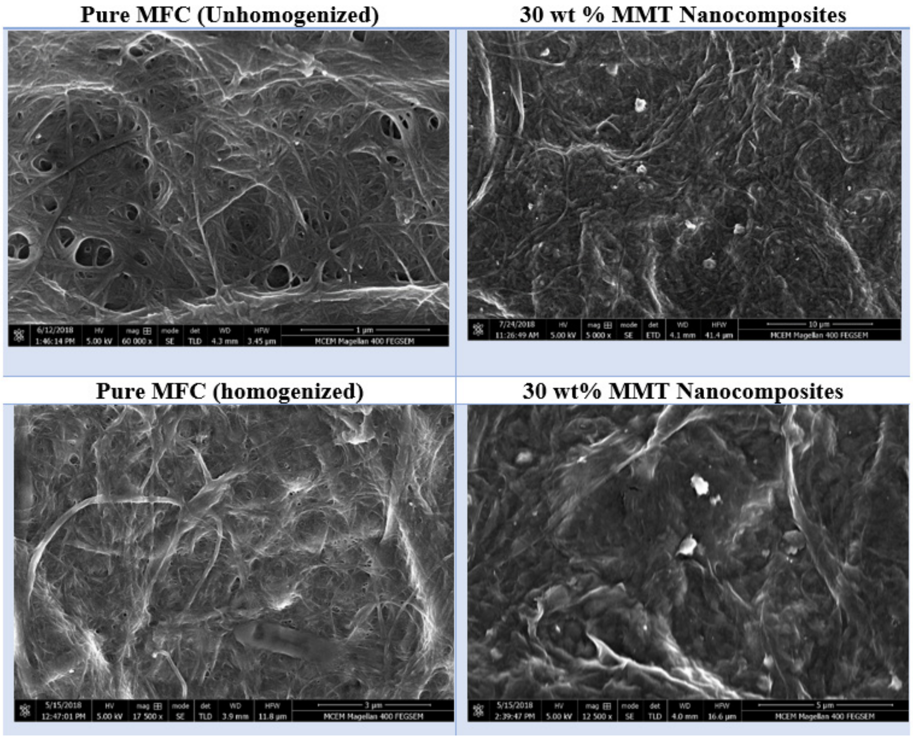
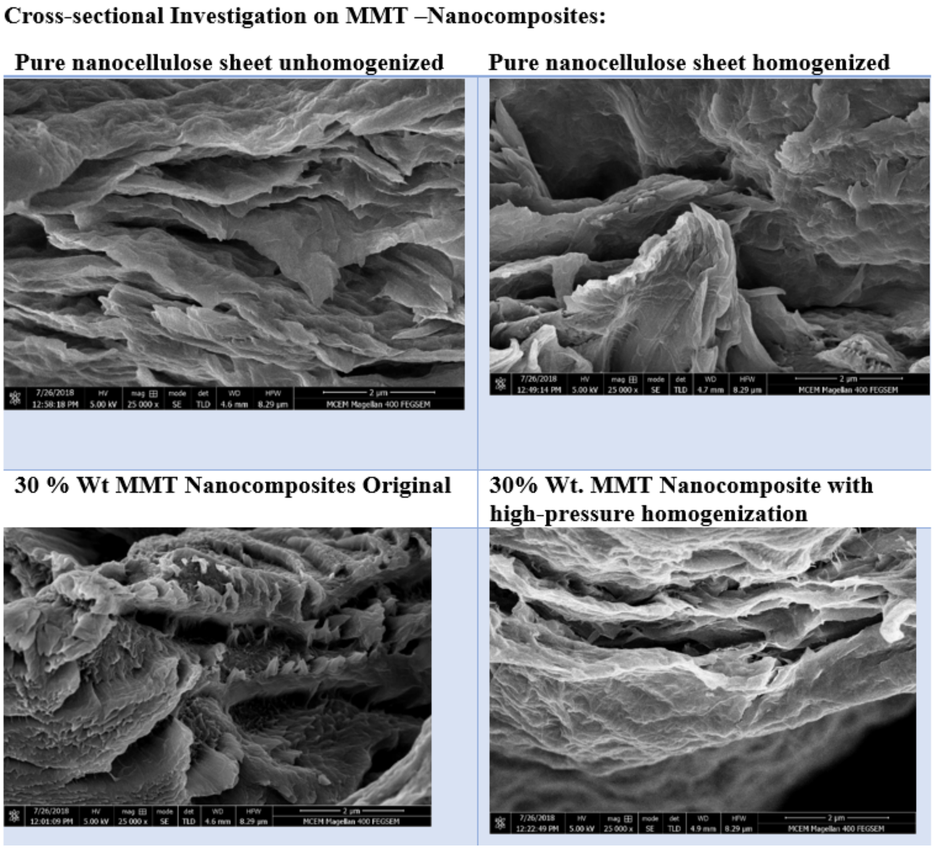


Figure 6. Surface morphology of 30 wt.% original composites and composites with high-pressure homogenization step


Cross-sectional Investigation on MMT –Nanocomposites:

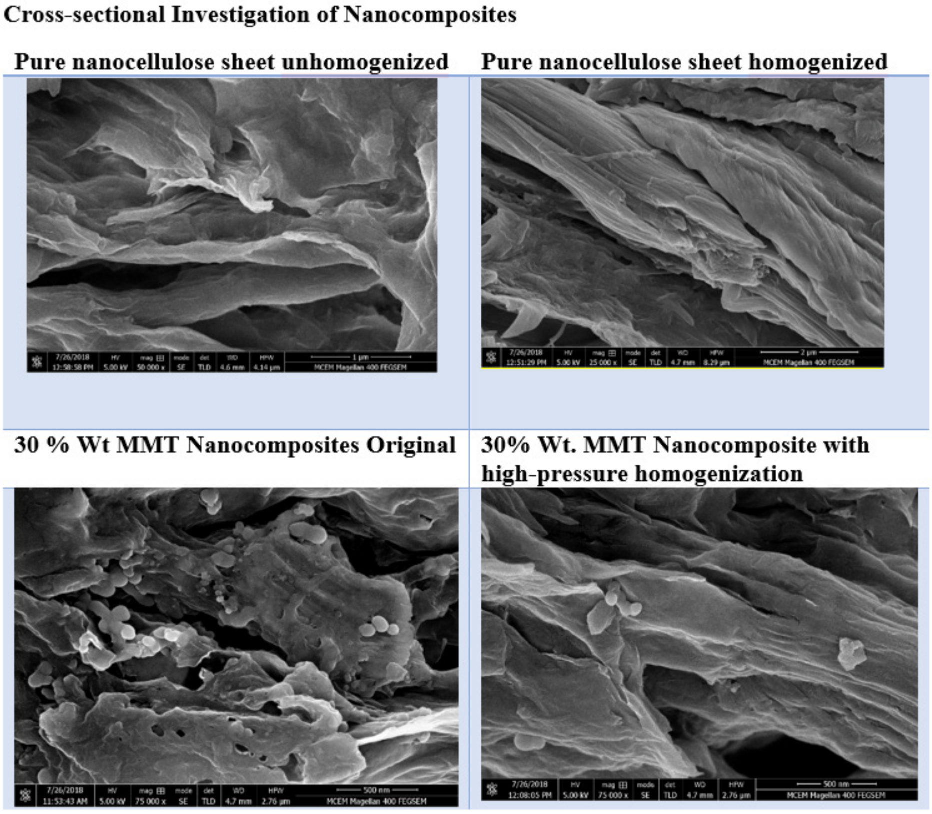
Pure nanocellulose sheet unhomogenized

Pure nanocellulose sheet homogenized

30 % Wt MMT Nanocomposites Original

30% Wt. MMT Nanocomposite with high-pressure homogenization

Figure 7. Cross-sectional view of spray-coated 30 wt.% MMT original composites and composites with high-pressure homogenization step


Cross-sectional Investigation of Nanocomposites

Pure nanocellulose sheet unhomogenized

Pure nanocellulose sheet homogenized

30 % Wt MMT Nanocomposites Original

30% Wt. MMT Nanocomposite with high-pressure homogenization

Figure 8. The cross-sectional investigation of 30 wt.% MMT original composites and composites with high-pressure homogenization step

3.4. EDX investigation on nanocomposites

Energy Dispersive X-ray (EDX) spectroscopy reveals the distribution of MMT on the composite via elemental analysis. It reveals that the distribution of MMT on the surface of the nanocomposites was very uniform. With carbon and oxygen only, the main components of the pure nanocellulose film were observed in both unhomogenized and homogenized plain nanocellulose films. Carbon is in excess when compared with oxygen because the main component of nanocellulose is carbon and oxygen and the molecular formula of cellulose C6H1005 confirms constant carbon/oxygen ratio via estimated from Bruker Esprit 1.9 of EDX analysis. The carbon/oxygen ratio for 10 wt.% and 30 wt.% original spray-coated nanocomposites is evaluated to be 1.9 and constant. **Figure 9** shows the metal ions composition of the composite evaluated via EDX spectra.

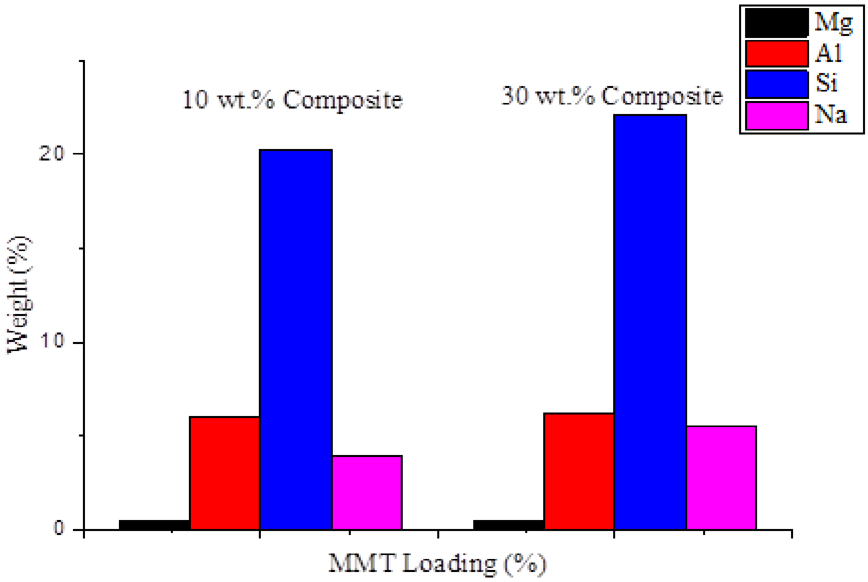


Figure 9. The percentage weights of elements in MMT distributed on the nanocomposite

The EDX analysis performed on the 10 Wt % and 30 Wt % MMT original composite film confirms the presence of MMT distributed on the rough surface of the nanocomposites. The elements in the nanocomposite were quantified with the support of software and the elemental ratio was increased with MMT loading in the original and composite via high-pressure homogenization of nanocellulose with MMT.

3.5. Water vapor permeability of nanocomposites

Water vapor permeability (WVP) for spray-coated nanocomposites with different amounts addition of MMT was explored in the previous report. The performance of water vapor transmittance of spray-coated nanocomposite was compared with the data from composites via vacuum filtration. The WVP of spray-coated composite increased with MMT content. The WVP of 30 wt.% MMT composite reaches 3.3×10^{-11} g/Pa.s.m from 2.5×10^{-11} g/Pa.s.m of pure CNF film. For sprayed films, the WVP of the original nanocomposite decreased for 5 wt.% loading compared to pure nanocellulose films and beyond this loading it was observed to increase with the increase in MMT loading. On the other hand, with additional high-pressure homogenization before spraying, the films obtained showed a reduction in WVP up to 20 wt.%, after which a slight rise in the WVP was observed. In homogenized composites, the MMT stacks and aggregates are broken and are uniformly distributed in the interior of the nanocomposite. This was evidenced by the cross-section SEM micrographs. As a result, the composite produces a tortuous pathway for the permeance of water vapor. However, the WVP of both the original and homogenized MMT nanocomposites showed higher WVP when produced by this method, when compared with similar films made by the vacuum filtration method. MMT stacks and their aggregates formed in the cellulose nanofiber matrix cause elevation of WVP at higher loading MMT for original nanocomposites. In the case of composite with a high-pressure homogenization step, the stacked MMT in nanocellulose suspension was delaminated and broken down during high-pressure homogenization and platelets well intercalated with cellulose nanofibrils creating a tortuous pathway for water vapor penetration. As a result, the WVP of these composites decreased as MMT loading increased, a minimum value of $8.28 \pm 0.012 \times 10^{-12}$ g/Pa.s.m at 20 wt. % of MMT loading and increased then again at 30 wt. % loading.

3.6. SAXS investigation of original composites

Figure 10 (left) shows the SAXS curves for 5 and 10 % MMT loading in the cellulose nanofibrils network. **Figure 10** (right) shows the SAXS curves for higher MMT loadings of 10%, 30%, and 50 % MMT in the cellulose nanofibrils network. The sample with the 5% loading shows a hump between q = 0.1-0.25, which is coming from the stacks arrangements. Increasing the MMT loading to 10 % and higher, the peak at q = 0.16 becomes broader and disappears completely for 50 % loading.

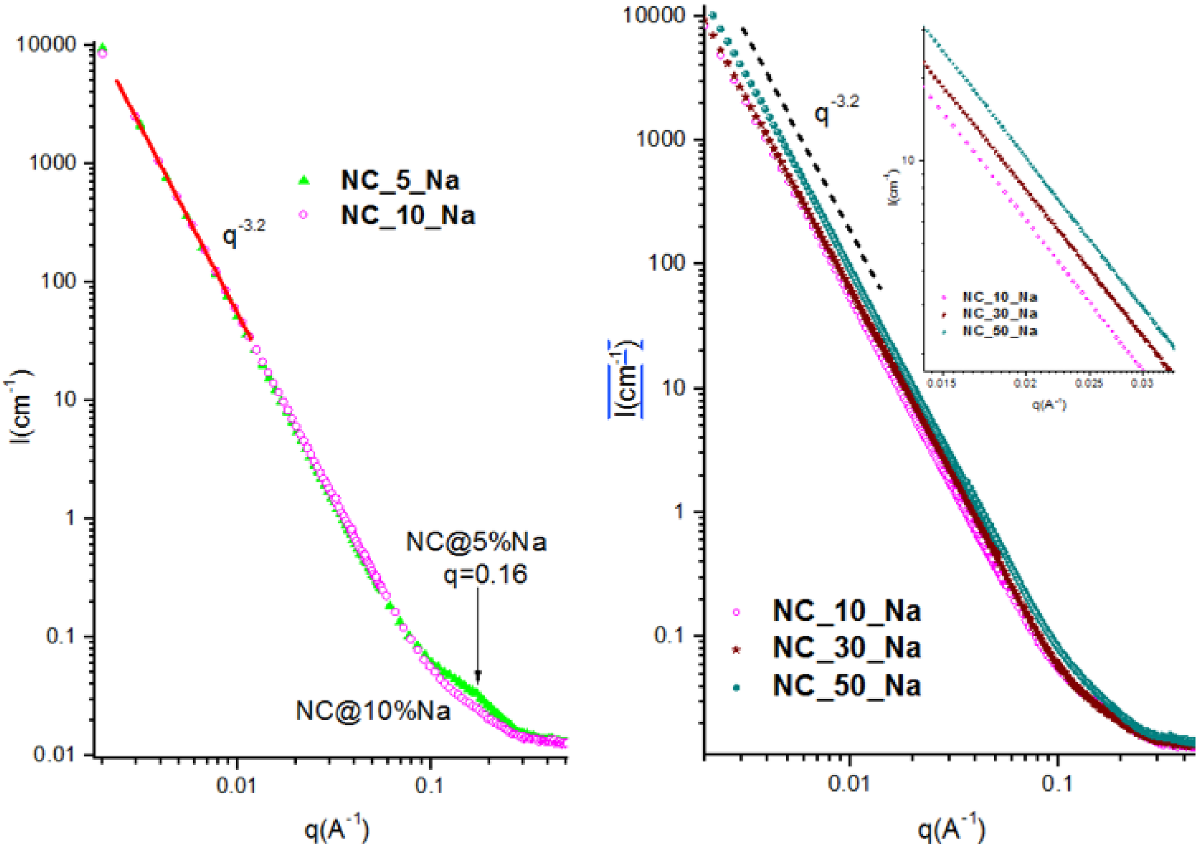


Figure 10. SAXS studies on the CNF-MMT composites

The boarding and disappearance of the peak for higher MMT loading (>10%) might be due to the exfoliation of the clay stacks. These exfoliated MMT become more disordered and randomly oriented in the cellulose nanofibrils (CNF) network. In the lower q values ($q < 0.1\ A^{-1}$), no structure appeared and the scattering curve slope follows the $q^{-3.2}$ variation. This indicates that at the larger length scales ($q < 0.1\ A^{-1}$) no assemblies/orientations of the MMT were observed and the scattering is coming only from the surface of the larger randomly oriented MMT structures. Furthermore, the intensity of scattering curves increases with an increase in the clay loadings, which hints at higher MMT incorporation amounts or increased MMT concentrations in the cellulose nanofiber network. It is concluded that the higher loading (>10%) of MMT creates MMT stack exfoliations which results in random distributions of exfoliated clay. The open and random NC distribution in cellulose nanofiber composites might affect a tortuous path for diffusing the water vapor molecules to transmit through and show poor barrier performance.

3.7. Role of composite structure in water vapor barrier performance

Spray-coating is a flexible process to tailor the properties of the nanocomposite as their operation time is independent of MMT concentration and CNF solids content in the suspension. The suspension of 2 wt.% CNF with MMT formed fine droplets from the spray jet and the uniform composite film was fabricated on the stainless-steel plate, so various ranges of MMT-loading can be concluded to be within sprayable limits. Compared with vacuum filtration, spray coating provides simplicity in sheet formation, rapidity, and achieving the tailorable properties of composites and very minimal operation time.

3.8. Barrier performance of spray-coated nanocomposites

The air permeance of the spray-coated CNF-MMT composite was evaluated to be less than 0.003 μm/Pa.S, confirming the sheet was highly impermeable. It shows good barrier performance against moist air and oxygen transfer across the composites. This value was evaluated within the limitation of the instrument. The effect of MMT addition into cellulose nanofiber suspension on air permeance is not able to be predicted by the instrument measuring limits.

The water vapor barrier performance of the nanocomposites was decided by the composite's structure, MMT's content, and its orientation in the composite. MMT nanoparticles on the surface and interior of nanocomposites produce a tortuous path, resulting in lower permeation of water vapor. The SEM micrographs of nanocomposite confirm that there is no aggregation or clumps of MMT on the surface of nanocomposites. The WVP was elevated in the original composite beyond 5 wt.% MMT load due to MMT stacks and aggregates in fibrous matrix. In high-pressure homogenization, MMT stacks were broken into individual particles in the fibrous matrix, producing a tortuous pathway for permeating water vapor. As a consequence, the WVP of homogenized nanocomposite decreased with MMT loading up to 20 wt % MMT. However, it elevated WVP after 30% MMT loading due to the aggregation of MMT and the hydrophilic nature of clays. Compared with composite via vacuum filtration, WVP of spray-coated nanocomposites shows similar behaviors with MMT loading. In the case of homogenized composite via vacuum filtration, WVP decreased with MMT loading up to 20% and elevated in 30% MMT loading, similar to the observation for spray-coated homogenized composites.

3.9. Structure of spray-coated nanocomposite

The structure of nanocomposites can be classified into, phase-separated, intercalated, and exfoliated [17]. A phase-separated structure forms the agglomeration of the clay particles in the fibrous matrix resulting in poor properties of the composites [18]. The reason for structuring the composite was the layer formation between clay particles and polymers and the homogeneity between particles and polymers. The intercalated structure consists of intercalation of layered clays between polymers. The exfoliated composites consist of well-delaminated clay layers randomly distributed and dispersed into the fibrous or polymer matrix [18].

3.10. Elevation of WVP in original composites

WVP of the spray-coated composite decreased at 5 wt% MMT loading in the CNF suspension. The reason for the elevation of WVP was the absorption of water vapor at higher loading of MMT and aggregation of MMT platelets into the nanocomposites allowing the opening of new pores into the structure of original composites. Permeability is one of the predominant mechanisms of transport of WVP into the nanocomposites. **Figure 11** reveals the conceptualized understanding of the structure of the CNF-MMT composites.

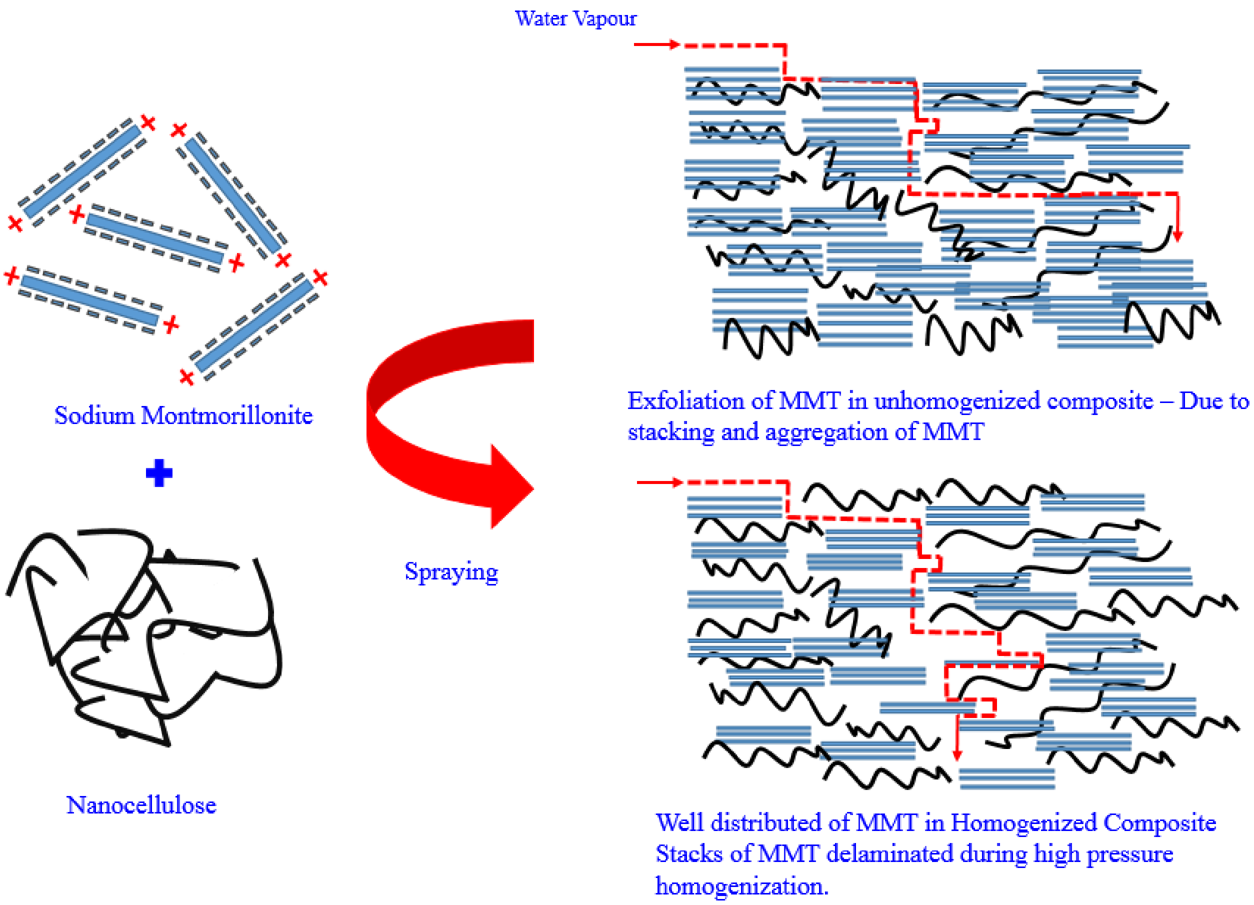


Figure 11. Structure of CNF-MMT composite

The MMT stacks in the composites are a common problem and breaking MMT stacks is a challenging task in engineering the water vapor permeability of the nanocomposites. The dispersion of MMT in the cellulose nanofiber suspension was performed by high-pressure homogenization. In this process, the cellulose nanofiber suspension with MMT was mixed with higher intensity before spraying. Moreover, high-pressure homogenization provides the reduction of microfibrils into cellulose nanofibrils at very reduced dimensions and so clay platelets are integrated into the fibrils to form an intercalated structure of composite.

Aggregation or stacking of MMT platelets is a serious problem in the fabrication of composite and processing of suspension with a high load of MMT into a nanocomposite would effectively affect their barrier performance and strength of nanocomposites. The critical parameters to fabricate the MMT-CNF suspensions are shear rate and mixing time. A high load of MMTs in the CNF suspension causes stacking of MMT resulting in the formation of large aggregates via electrostatic and Van der Waals forces [19–20]. **Figure 11** reveals the structure of the original composite and composite from the homogenized suspension of CNF-MMT and their effect on water vapor transfer.

4. Conclusion

Spraying Cellulose nanofiber (CNF)-nano-MMT suspension on the polished stainless-steel plate rapidly produces nanocomposite. It is a flexible process for the fabrication of CNF-MMT composite with two surfaces, namely a rough surface and a smooth surface. The smoothness of the composite was replicated from the surface of the stainless-steel plate. The operation time for forming the composite which has a diameter of 15.9 cm was less than a minute. The increase of MMT in CNF suspension has no effect on the operation time for spraying to fabricate the composites. The MMT in the spray-coated original composite was exfoliated and aggregated resulting in poor water barrier performance. The composite derived from spraying of homogenized CNF–MMT was excellent in the water vapor barrier via MMT stacks broken into MMT particles in cellulose nanofiber matrix through high-pressure homogenization. Given this correspondence, the structure of the composite has a strong influence on the barrier performance of the composite and can be altered via spraying and a high-pressure homogenization process.

Disclosure statement

The author declares no conflict of interest.

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