Research Article

Effect of Cellulose Nanofiber (CNF)- Montmorillonite (MMT) Composite's Structure on their Water Vapour Barrier Performance

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Abstract

Cellulose Nanofiber (CNF) is one of the emerging nanomaterials for developing high-performance packaging material to replace the synthetic plastics. These materials are renewable, recyclable and biodegradable. The film produced from cellulose nanofiber has very low oxygen permeability, however their water vapour permeability is significantly higher than conventional packaging plastics, such as Low Density and High-Density Polyethylene (LDPE, HDPE). Water Vapor Permeability (WVP) of the spray coated composites was decreased via varying Montmorillonite (MMT) content into CNF suspension and also high-pressure homogenization of CNF-MMT Suspension. The process for spraying Cellulose Nanofiber (CNF)-Montmorillonite (MMT) suspension on the stainless-steel surface was developed to produce 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- ie split up into individual sheets. The water vapour 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 vapour permeability started to increase due to aggregation of the Montmorillonite in homogenized composite. At the optimal addition level, the best performance achieved with spraying was water vapour permeability of 8.3×10^{-12} g/m.s.pa. The air permeability of 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, 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 Nanofibre (CNF); Montmorillonite (MMT); XRD; Water Vapour Permeability; Structure of Nanocomposite

Introduction

Synthetic plastics predominantly occupy as a conventional packaging because of their comfort in processing methods, possess excellent barrier performance against air, water vapour, oxygen, carbon dioxide and liquid water. However, it was mainly expensive in fabrication cost as the feed stock was derived from fossil fuels. When compared with iron, glass and ceramics, synthetic plastics are more flexible and potential for recycling/reprocessing. However, the waste from synthetic packaging is a negative impact on the environment. Plastic debris from these waste causes a contamination of the ecosystem, forming micro/nanoplastics contamination in the oceans and poisoning the wildlife as well the ecosystem [23]. Petroleum-based packaging materials are not biodegradable and also cause severe environmental issues such as landfilling, harmful recycling process 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 find new material from natural sources and is 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 vapours. 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, have good strength and 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, wide availability, 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 [29]. Yet they have poor barrier performance due to the presence of wide pores allowing a significant amount of gas and vapours to pass through. The cellulose susbtrates coating with wax or lamination of these substrates with synthetic platics and substrates extrusion with aluminum were various approach for increase the barrier performance of the substates. These coatings have not any potential for reusability after recyclable.

Utilizing cellulose nanofiber to make nanocomposite allows to enhance the mechanical strength and biocompatibility, and tune barrier potential against water vapour and other gaseous substannces. Cellulose Nanofibre (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 and 2,2,6,6-Tetramethylpiperidine 1-Oxyl Radical (TEMPO) oxidation etc. CNF has good biocompatibility, biodegradability and chemical stability. Recently, the research on the use of CNF in developing barrier materials for packaging applications is increasing 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 Nanofibre (CNF) consists of cellulose fibrils at 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 vapour permeability. The cellulose nanofibrils has a high aspect ratio with a fibril diameter varying from 5 to 100 nm and length of a few microns. As a result, the formed CNF film has a high 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 (Varanasi, 2013), solvent casting, hot pressing and spray coating [12,21,22] are the methods for fabrication of CNF film. Spraying CNF on the polished stainless-steel surface to produce smooth film is a rapid method and the basis weight and thickness of the film could be tailorable with 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 vapour and an alternative to the synthetic packaging material. The cellulose fibrils in the fibrous network produce an outstanding compactness through the interaction between the fibrils via hydrogen bonding and contributes to good barrier performance against gaseous substances (Henriksson, 2008).

Recently, spraying processes were used to fabricate nanocomposites such as graphite carbon black-micro fibrillated cellulose as an electrode [6] and SiO_2-microfibrillated cellulose nanopaper. The operation time for spraying process has an operation time less than 30 mintues to form the MFC-SiO_2 composite. The percentage of SiO_2 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 SiO_2 % in MFC suspension [12].

The oxygen permeability of CNF increased with the relative humidity of the surroundings. Because nanocellulose fibirls plasticize and swelled by adsorption of water molecules under high moisture environment [14]. However, these films have a high-water vapour permeability due to its high polar nature. In brief, the water vapour is absorbed by the cellulose fibre-fibre bond in the fibrous network. There is increased diffusion pathway for enhancing barrier performance [14]. Because of highly polar nature of CNF, fibre- fibre bond was weakened through water sorption. As a consequence, the WVP of the film was increased and increase the swelling of CNF film [30].

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 [13]. The cellulose nanofiber forms a fibre 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 [14]. In the design of barrier materials, water vapour 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 extension of shelf life of the water-sensitive products such as foods and pharmaceuticals [4].

To improve the water vapour permeability of CNF, inorganics fillers have been incorporated into the fibrous matrix producing high-performance nanocomposites. Nanoinorganics provide a relatively larger surface area and favours the nanoclay–matrix interactions elevating the barrier performance and mechanical properties. The layered nanoclay into the polymer suspension enhance the tortuosity of composite for a water vapour/gas molecule diffusion, resulting high barrier performance [5]. "Bentonite" Montmorillonite (MMT) is an alumina-silicate layered clay hydrated and a potential filler at the nanoscale, which provides reinforcement in the nanocomposite and offers a high surface area with a large aspect ratio from 50 to 1000 [26]. MMT is dioctahedral nanoclay with the 2:1 layer linkage and a rigid, impermeable filler. It produces a structure of the maze forcing the transfer of air/oxygen/ water vapours to follow a tortuous path resulting in good barrier performance of the composite. CNF-MMT Nanocomposites via vacuum filtration has low oxygen and water vapour permeability [2] and High-performance composites [30]. However, the time consumption

for production of nanocomposite via vacuum filtration is quite long and sheet formation required 30 mins to 4 days and sometimes some of the nanoparticles will be drained out during dewatering stage of vacuum filtration, affecting the sheet composition and porosity, resulting in poor properties of nanocomposites. The peeling of the composite from 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 [22]. Thus, this is a slow process and very limited in upscaling the process. Spray coating has been used to prepare the composites with cellulose nanofibre with varying content of fillers from 0 to 33% and consumed less than 30 mins for sheet formation. The fillers concentration in CNF suspension does not affect the operation time for spraying process. However, they replaced vacuum filtration with a spray coating but followed the conventional process such transfer of sheet with blotter and vacuum dewatering and then film peeled off after drying [12].

Spraying CNF on the stainless-steel plate is a novel approach for the fabrication of CNF film. This method has minimal operation time less than a minute to form the diameter of film around 15.9 cm [22]. Contour coating and contactless coating with the base surface are notable in spraying process. Mainly, the topography of the base surface does not influence on the coating process. High basis weight and more uniform thickness of the film can be achieved via adjusting the CNF suspension concentration and process parameters in the spray coating process [21,22]. The preparation of CNF-MMT nanocomposite via spraying and functionalization by the addition of specific nanoparticles/nanofillers in the cellulose nanofibre suspension is a novel process and the operation time independent of process variables such as suspension concentration and nanoclay loading in the suspension.

During this process, composite was fabricated and barrier performance of the composite rely 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 effect of CNF-MMT composite structure on the water vapour permeability as one of important barrier properties of the CNF-MMT composite and the structure of the composite evalauted via SAXS.

Materials and Methods

Cellulose Nanofibre

The nomenclature on Cellulose Nanofibre (CNF) was changed frequently in the reported scientific literature. CNF also called as Nanocellulose (NC), Micro-Fibrillated Cellulose (MFC), cellulose nano-fibrils, cellulose microfibrils and Nano-Fibrillated Cellulose (NFC). In present investigation, CNF/NC was considered the term for cellulose nanomaterial. The current investigation for CNF was used as feed stock from DAICEL Chemical Industries Limited (Celish KY-100S) with fibre content varying from 23% to 25%. The cellulose nanofibrils of DAICEL NC (Celish KY-100S) has an average diameter of ~ 70 nm (Raj, 2016 #225) with a mean length of fibre around 8μm. The aspect ratio of KY 100S was evaluated to be 142 ± 28. DAICEL KY-100S. Cellulose pulp as feed stock was micro fibrillated under high pressure of water to produce KY 100S. The crystallinity index of KY100S was reported to be 78 [31]. 2.% wt. CNF suspensions were produced by diluting 25 wt. % fibre content of KY 100S with de-ionized water as per reported in scientific literature and disintegrating for 15,000 revolutions at 3000 rpm in a disintegrator.

Nanoclay

Closite Na++ is a Montmorillonite (MMT) nanoparticle gifted by BYK Additives and Instruments, Germany through IMCD Australia Limited, Mulgrave VIC 3170, Australia. The dry particle size of Closite Na++ is < 25 μm (d_{50}) and packed bulk density of 568 g/li and density of 2.86 g/cm^3 and X-Ray results confirm d_{001} of 1.17 nm.

Preparation of Nanoclay-Cellulose Nanofibre Suspension

The 2 wt. % of CNF suspension was prepared and disintegrated as per reported procedure in scientific literature. The nanoclay addition is based on fibre (solid content) in the nanocellulose and varies 5 wt%, 10 wt%, 20 wt.%, 30wt.%, 50wt.% and 75wt.% into 960g 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.%, 30wt.% , 50wt.% and 75wt.% of Closite Na++.

Homogenization

Homogenization of CNF-MMT suspension is implemented to process the nanocomposite with the 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 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 homogeniser. The 2 wt. % suspension with MMT underwent 2 passes at 1000 bar pressure. The homogenised suspension was then used for spraying on the polished metal surface to make as a nanocomposite.

Spraying of Nanoclay Montmorillonite (MMT) –Cellulose Nanofibre Suspension

The CNF-MMT composite was prepared through spray coating as reported for 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 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 200 bar. In the spray system, an elliptical spray jet with an angle of 50° from the spray nozzle 517 was able to develop a 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 set up 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 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.

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 were reported. The Technical Association of the Pulp and

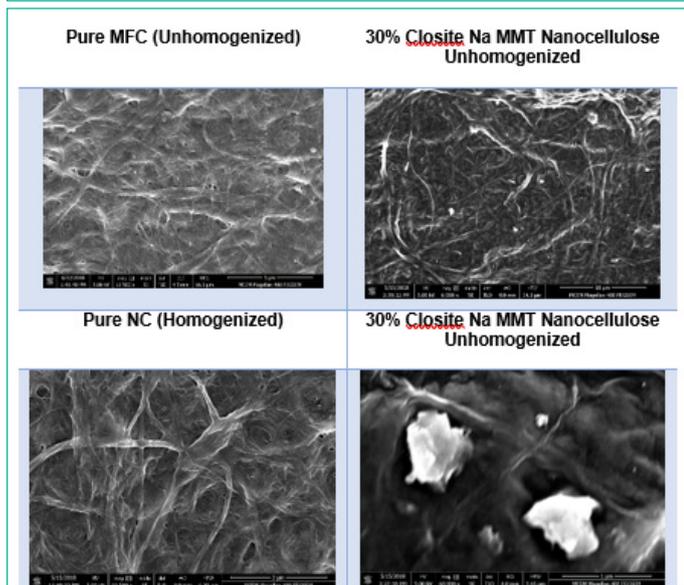**Figure 1:** An experimental set up for spraying of nanocellulose suspension with MMT.

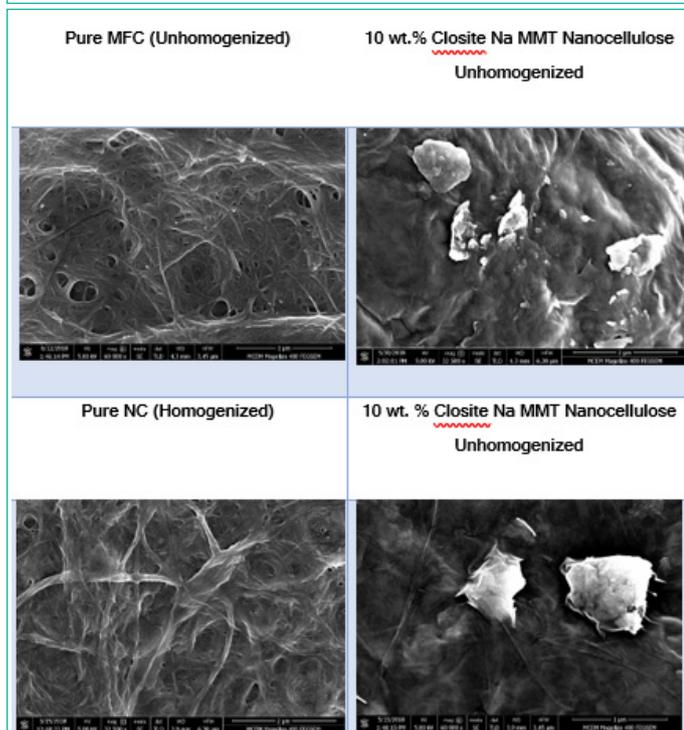**Figure 2:** Surface appearance of spray coated 30 wt.% nanocomposites.

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

Paper Industry (TAPPI) standard T 460-om-2 has been used to measure the air permeance of the composite.

Water Vapour Permeability

ASTM standard (E96/E96M-05) method was used to evaluate the Water Vapour Permeability (WVP) of the composites. This test was normally carried out 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 for every 4 hours. The Water Vapour 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 were normalised with thickness of the composites and converted into Water Vapour Permeability (WVP). The mean value of three parallel tests of each NC-MMT composites were reported. Simultaneously, the test without $CaCl_2$ in the cups as blank was carried out.

Cross-Sectional Investigation of Nanocomposite

The SEM FEI Magellan 400 was utilised 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 iridium. After that, the coated specimen was subjected to SEM imaging.

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 sample 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 be172 um x 172 um. The curve from scattered data was processed after the data reduction and radial averaging by the in-house beamline software Scatter Brain. Silver behenate and glassy carbon were used to calibrate the q scale and normalizing scattering curves to an absolute scattering cross section.

Result and Discussion

Spraying CNF-MMT suspension on the polished stainless steel is a novel approach for 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 on 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 the vacuum filtration vary from 30 minutes to 24 hours. The spray coated CNF -MMT composite has two unique surfaces namely rough surface which exposed to air (also called as free surface) and smooth surface which exposed to polished metal side. The roughness of smooth surface was lower than that of rough surface. The smooth surface of the composite film has glossy and shiny which can be used for further development for various functional materials such as printed electronics and flexible electronics.

The MMT-nanocellulose composites were prepared via spray coating and engineering its barrier performance and tailoring their bulk properties by adding the percentage of MMT from 0% to 30 wt.%. The air and Water Vapour Permeability (WVP) properties of nanocomposites via spraying were evaluated
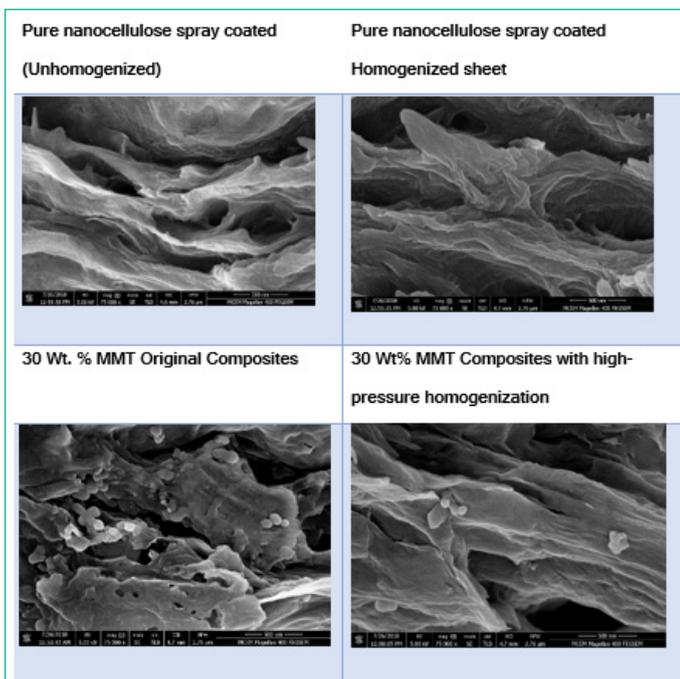
Figure 4: Cross-sectional view of Original composite and Composite with High-Pressure Homogenization.
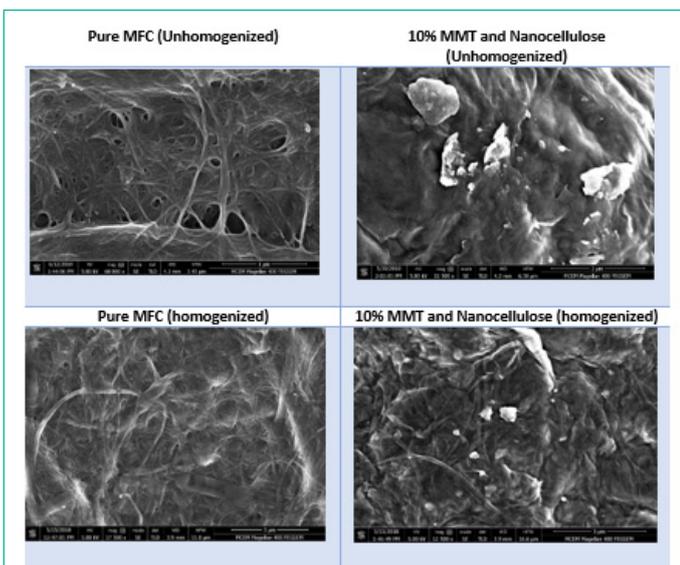

Figure 5: Surface Morphology of 10 wt.% MMT Original Composites and Composites with High-Pressure Homogenization Step.
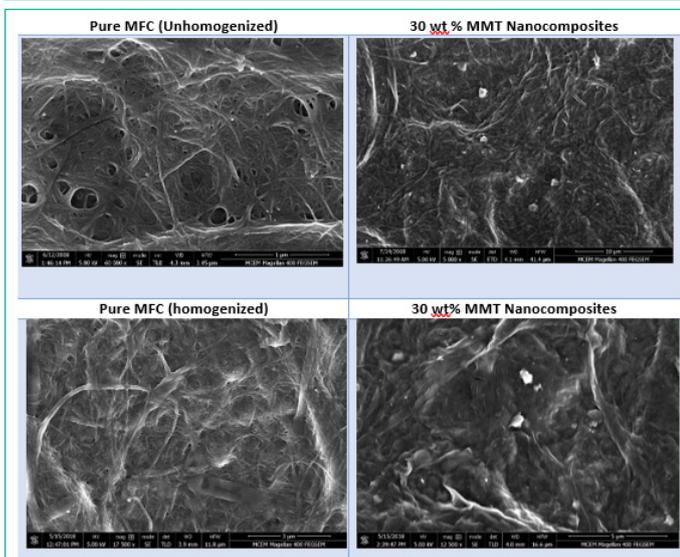

Figure 6: Surface Morphology of 30 wt.% Original Composites and Composites with High-Pressure Homogenization Step.

for each type of composites. Spray coated nanocomposites were flexible and foldable, more uniform in thickness. The nanocomposites are yellowish in colour due to the increased MMT content in the nanocomposites. The reason for yellowing of the surface of nanocomposites is due to absorption spectra of MMT in the nanocomposites and similar observations were reported in the previous literature [9,27]. The coloured nanocomposite as a finishing quality could be produced by spray coating and simply adjust MMT loading in the nanocellulose suspension.

Surface Appearance of Nanocomposites

Figure 02 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 cellulose nanofibrils network. MMT nano clay particle's size varies from 20 nm to 50 nm and capacity 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 vapour barrier performance. The 10 μm and 100μm of SEM micrographs of these spray coated nanocomposites confirms the distribution of MMT in the nanocomposites at various magnification. 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, Na along with carbon and oxygen from cellulose molecule.

Figure 03 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 neighbour fibres 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 formation of a good compact fibrous network.

Cross section Investigation on Nanocomposite

Figure 4 reveals the SEM micrograph on the cross-sectional view of both composites prepared via spraying. The aggregation of MMT as clumps were 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 fibre around 8μm and an average aspect ratio of 142 ± 28. The size of Bentonite MMT (nano clay) particles varied from 20 to 50 nm in length. In original composites, MMT platelets were not intercalated between nanocellulose fibrils due to its large aspect ratio. As a consequence, the spray coated original composites retains an exfoliated structure where MMT platelets are concentred 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 high-pressure homogenization step, MMT platelets are well distributed in the interior nanocomposites and MMT platelets were intercalated uniformly in between the cellulose
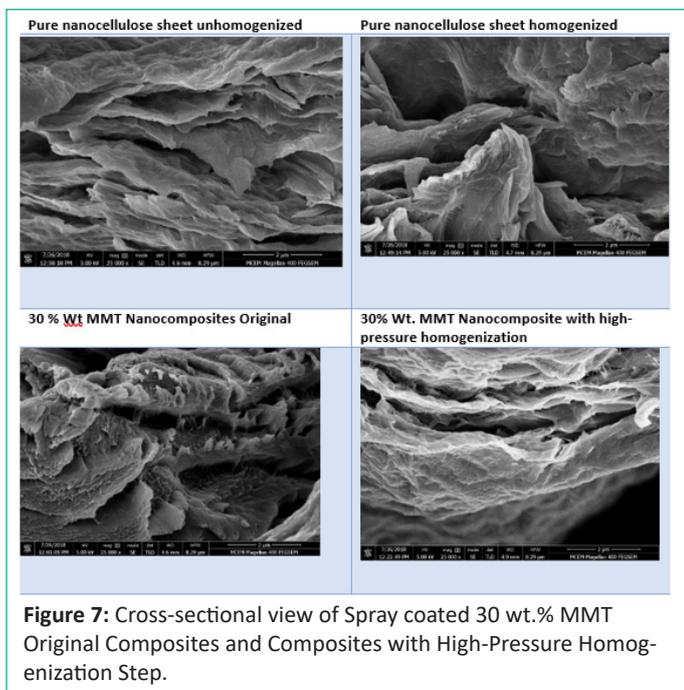
Figure 7: Cross-sectional view of Spray coated 30 wt.% MMT Original Composites and Composites with High-Pressure Homogenization Step.
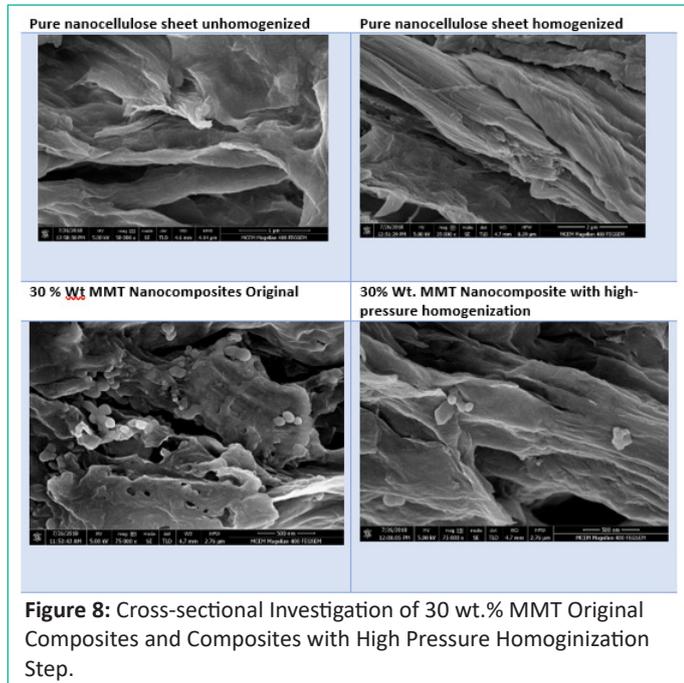

Figure 8: Cross-sectional Investigation of 30 wt.% MMT Original Composites and Composites with High Pressure Homoginization Step.

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 5μm in length of cellulose fibres, the aspect ratio of homogenized nanocellulose is evaluated to be 286 [30]. Due to the reduction of nanocellulose fibres via high-pressure homogenization, cellulose nanofibrils are easily penetrated into MMT platelets layers resulting nanocomposite with an intercalated structure.

Flexible Spray Coating Process for Preparation of Nanocomposite

Figure 05 reveals the surface and topography pf 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 particle were aggregated and shows large clumps on the surface of the composite. This aggregation of MMT cause the exfoliation of MMT particles in cellulose nanofibrils. As a result, WVP of the composite is not much decreased. In composite prepared via spraying of high-

pressure homogenised CNF-MMT suspension, CNF are well fibrillated and reduced the fibre 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 and allowing reduce the WVP of the composite.

Figure 06 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, Increase MMT concentration in composite could be elevated the WVP of the composite. Generally, Bentonite MMT was highly hygroscopic and increase the quantity of MMT in the composite leading to more water absorption. This phenomenon was observed in the plot of WVP versus MMT percentage.

Cross-Sectional Investigation on MMT –Nanocomposites

Cross-Sectional Investigation of Nanocomposites

Figure 07 and 08 reveals the cross-sectional images of the composite and pure CNF film. In the cross section of the composite. In original composites, the MMT stacks was observed in the interior of cellulose nanofibrils network and causes the exfoliation of the MMT in the composite. In homogenised composites, the MMT stacks are broken into MMT layer particles and mixed well with cellulose nanofibrils matrix resulting intercalated composites. The WVP of the homogenized composite has lowest value than that of original composites.

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. 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 $C_6H_{10}O_5$ confirming 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 nanocomposite is evaluated to be 1.9 and constant.
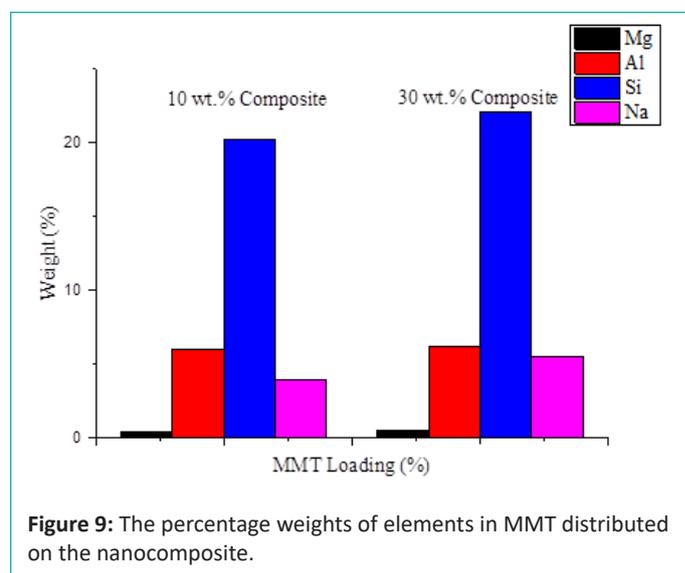

Figure 9: The percentage weights of elements in MMT distributed on the nanocomposite.

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 a 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.

Water Vapour Permeability of Nanocomposites

Water Vapour Permeability (WVP) for spray coated nanocomposites with different amount addition of MMT is shown in Figure -10. The performance of water vapour transmittance of spray coated nanocomposite was compared with the data from composites via vaccum filtration [9].

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 increase in MMT loading. On the other hand, with additional high-pressure homogenization prior to spraying, the films obtained showed reduction in WVP upto 20 wt.%, after which a slight rise in the WVP was observed. In homogenised 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 vapour. However, the WVP of both the original and homogenised MMT nanocomposites showed higher WVP when produced by this method, when compared with similar films made by vacuum filtration method [30]. MMT stacks and its aggregates formed in the cellulose nanofiber matrix cause elevation of WVP at higher loading MMT for original nanocomposites. In the case of composite with 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 nanofibirls creating a tortuous pathway for water vapour penetration. As a result, 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.

SAXS Investigation of Original Composites

Figure 11a (left) shows the SAXS curves for 5 and 10 % MMT loading in the cellulose nanofibrils network. Figure 11b (right) shows the SAXS curves for higher MMT loadings of 10, 30 and 50 % MMT in the cellulose nanofibrils network. Sample with the 5% loading shows a hump between q=0.1-0.25, which is coming from the stack's arrangements. Increasing the MMT loading to 10 % and higher, the peak at q=0.16 becomes broader and more disappeared completely for 50 % loading.

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}) show no structure appeared and the scattering curve slope follows $q^{-3.2}$ 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 increasing
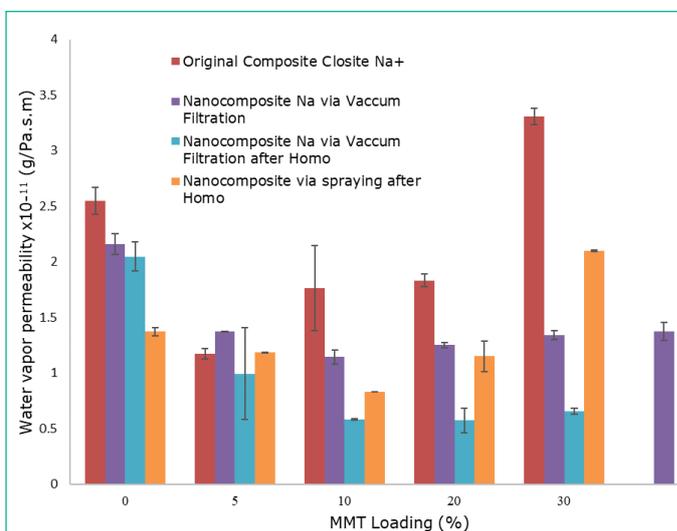

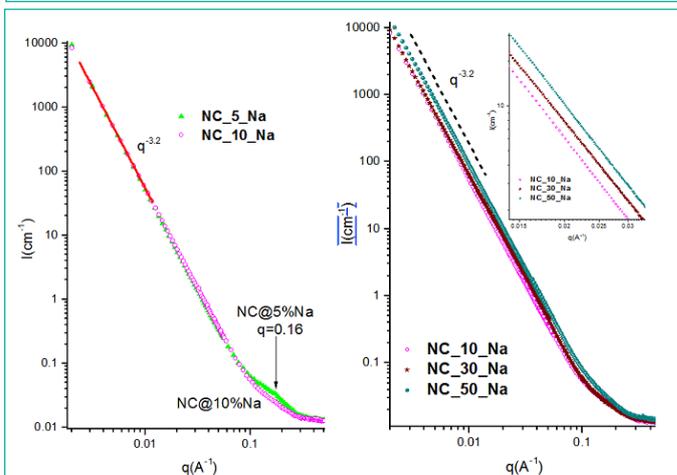**Figure 10:** Watervapor permeability of spray coated nanocomposites [36].

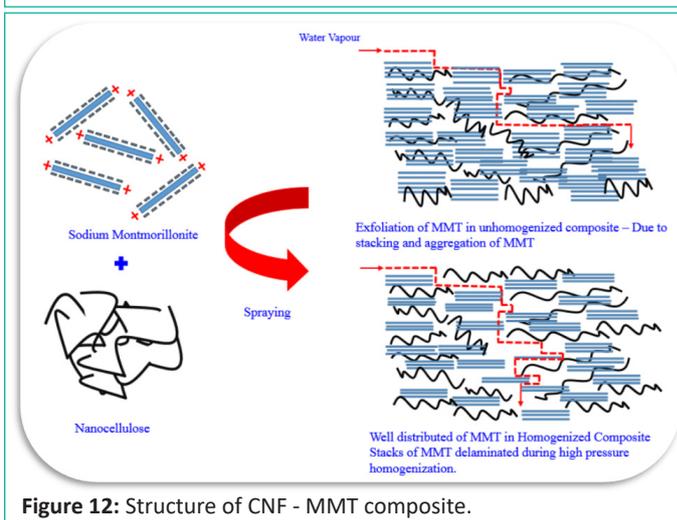**Figure 11:** SAXS studies on the CNF-MMT Composites.

Figure 12: Structure of CNF - MMT composite.

with increase in the clay loadings, which hints of higher MMT incorporation amounts or increased MMT concentrations in the cellulose nanofiber network. It is concluded that the higher loading (>10%) of MMT create MMT stacks exfoliations which results in random distributions of exfoliated clay. The open and random NC distribution in cellulose nanofibre composites might affect a tortuous path for diffusing the water vapour molecules to transmit through and show poor barrier performance.

Role of Composite Structure in Water Vapour 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 were formed fine droplets from the spray jet and the uniform composite film was fabricated on the stainless-steel plate and so various range of MMT-loading can be concluded to be in sprayable limits. Comparing with vacuum filtration, spray coating provides its simplicity in sheet formation, rapidity and achieving the tailorable properties of composites and very minimal operation time.

Barrier Performance of Spray Coated Nanocomposites

The air permeance of 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 vapour barrier performance of the nanocomposites was decided by composite's structure and 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 vapour. 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 and produces a tortuous pathway for permeating water vapour. As a consequence, WVP of homogenized nanocomposite decreased with MMT loading upto 20 wt % MMT. However, it was elevated WVP after 30% MMT loading due to aggregation of MMT and hydrophilic nature of clays. Comparing with composite via vaccum filtration, WVP of spray coated nanocomposites shows similar behaviours with MMT loading. In the case of homogenised composite via vaccum filtration, WVP decreased with MMT loading upto 20% and elevated in 30% MMT loading, similar to the observation for spray coated homoginized composites.

Structure of Spray Coated Nanocomposite

The structure of nanocomposites can be classified inot (1) a phase separated (Kalia et al.) (2) Intercalated and (Kalia et al.) and (3) Exfoliated. A phase separated structure forms the agglomeration of the clay particles in the fibrous matrix resulting poor properties of the composites [3]. The reason for structuring the composite was the layer formation between clay particles and polymers and inhomogeneity between particles and polymers. Intercalated structure consists of intercalation of layered clays between polymers. The exfoliated composites consist of the well-delaminated clay layers randomly distributed and dispersed into the fibrous or polymer matrix [5].

Elevation of WVP in Original Composites

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

The MMT stacks in the composites is a common problem and breaking MMT stacks is a challenging task in engineering the water vapour 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 together with higher intensity before spraying. Moreover, high pressure homogenization provides the reduction of micro fibril into cellulose nanofibrils at very reduced dimension and so clay platelets 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 high load of MMT into a nanocomposite would effectively affect their barrier performance and strength of nanocomposites. The critical parameter to fabricate the MMT-CNF suspensions are shear rate and mixing time. High load of MMTs in the CNF suspension cause stacking of MMT resulting in the formation of large aggregates [20] via electrostatic and Vanderwall forces [8]. Figure 12 revels the structure of original composite and composite from homogenized suspension of CNF- MMT and their effect on water vapour transfer.

Conclusion

Spraying Cellulose nanofiber (CNF) – nano-MMT suspension on the polished stainless-steel plate produce nanocomposite in a rapid manner. It is a flexible process for fabrication of CNF-MMT composite which two surfaces namely rough surface and 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 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 poor water barrier performance. The composite derived from spraying of homogenized CNF – MMT was excellence in water vapor barrier via MMT stacks broken into MMT particles in cellulose nanofiber matrix through high pressure homogenization. Given this correspondence, the structure of composite's is strong influence on the barrier performance of the composite and can be altered via spraying and high-pressure homogenization process.

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