Carbohydrate Polymers 250 (2020) 116911

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

An energy efficient production of high moisture barrier nanocellulose/carboxymethyl cellulose films via spray-deposition technique

Humayun Nadeem, Mahdi Naseri, Kirubanandan Shanmugam, Mostafa Dehghani, Christine Browne, Simin Miri, Gil Garnier, Warren Batchelor *

Bioresource Processing Research Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, VIC, 3800, Australia

ARTICLE INFO

Keywords:
Carboxymethyl cellulose
Drying
Embodied energy
Nanocellulose
Packaging
Spray deposition

ABSTRACT

Nanocellulose (NC) films are considered as a prospective alternative to non-sustainable packaging materials, however, their higher embodied energy and limited moisture barrier properties are regarded as a huge constraint regarding their commercialization. This study aims to produce films with relatively low environmental impact and improved barrier performance. For this purpose, carboxymethyl cellulose (CMC) and NC were combined, and this resulted in multidimensional advantages. The mass production of films could be achieved in only 2 h (requiring at least 24 h under ambient conditions) when dried in an oven at 75 °C with enhanced mechanical properties and without compromising their dimensional stability. The moisture barrier properties of the NC/CMC films were improved up to 92 % compared with the NC films alone and the results achieved are comparable with packaging materials such as polyethylene terephthalate (PET), polycarbonates (PC) etc. Finally, the NC/CMC (1:1) films have low environmental impact compared with PET films.

1. Introduction

Escalating greenhouse gas emissions and waste generation are the foremost challenges the modern world is facing in recent years (Nadeem et al., 2017). The situation is alarming and demands the implementation of sustainable approaches for extraction and production of environmentally friendly materials. Plastics exhibit versatile characteristics and remarkable barrier properties, which make them dominant packaging materials in the market (Andrady & Neal, 2009). However, their poor recyclability has raised huge concerns for their future use (Hopewell, Dvorak, & Kosior, 2009). The plastics do not decompose and only 40 % of them are either recycled or incinerated while the rest accumulate in landfills (Geyer, Jambeck, & Law, 2017). Ideally, packaging should consist of materials that are attractive, have no environmental impact, easy to use, show no degradation over time and generate no waste for disposal (Marsh & Bugusu, 2007).

Extracted from natural renewable sources, bio-based raw materials have attracted much attention due to the motivation of environmental protection (Golden et al., 2018). One class of these materials is nanocellulose (NC) which has distinctive features and diversified applications such as being non-toxic, high surface to volume ratio, high abundance, biodegradability, recyclability and extraordinary mechanical, thermal and chemical properties (Onur, Shanmugam, Ng, Garnier, & Batchelor, 2019). Nanocellulose (NC) can be transformed into thin films for use in various applications such as food packaging, energy devices and wound dressings (Herrera, Mathew, & Oksman, 2017; Hollertz, Durán, Larsson, & Wågberg, 2017, Maliha et al., 2019).

Nanocellulose films are either produced via casting or vacuum filtration in laboratory scale (Shanmugam, Varanasi, Garnier, & Batchelor, 2017). Casting has two major limitations such as large production timeframe and lack of the uniformity among the produced films (Shimizu, Saito, Fukuzumi, & Isogai, 2014). Vacuum filtration is a comparatively better process as it produces high strength films in a short time but suffers from the separation and handling constraints (Siró & Plackett, 2010). Owing to its rapidity and simplicity, spray deposition is regarded as a prospective alternative to the conventional methods (Shanmugam et al., 2017). In this process, the NC suspension is sprayed onto a base surface (stainless steel, plastic plates etc.) moving on a conveyer belt and the coat weight can be controlled via the experimental parameters e.g. the suspension concentration and the velocity of conveyor (Shanmugam et al., 2017, Shanmugam, Doosthosseini, Varanasi, Garnier, & Batchelor, 2018).

The NC films possess high strength but there are a number of constraints on their commercialization. Considering the environmental

* Corresponding author.
E-mail address: Warren.Batchelor@monash.edu (W. Batchelor).

https://doi.org/10.1016/j.carbpol.2020.116911
Received 11 May 2020; Received in revised form 31 July 2020; Accepted 4 August 2020
Available online 14 August 2020

aspects, the NC films have high embodied energy which is mainly associated with the production of NC fibres (Li, McGinnis, Sydnor, Wong, & Renneckar, 2013). The incorporation of NC with an environmentally friendly material and forming a composite is one of the viable options to reduce the embodied energy. Another major issue in the production of these spray deposited films is the long drying time. Heat drying can reduce the production time, but it will result in shrinkage in the films due to the deformation of fibres at high temperature (Heggset, Chinga-Carrasco, & Syverud, 2017). Furthermore, while NC films have reasonable oxygen barrier properties, they possess limited moisture barrier performance owing to the hydrophilic nature of NC fibres (Aulin, Gällstedt, & Lindström, 2010). Shanmugam et al. produced the NC films via spray deposition, however, it required 24 h for the films to dry at ambient conditions (Shanmugam et al., 2017). The research was focused on reducing the time of operation for sheet formation without reducing the drying time. A subsequent paper measured the moisture vapour barrier performance, but in the context of the effect of recycling, rather than attempting to match the performance of conventional petroleum-derived polymer packaging materials (Shanmugam, Doosthosseini, Varanasi, Garnier, & Batchelor, 2019). In order to overcome these challenges, combining other materials with NC is an attractive approach. Chemicals can be used with NC to enhance the heat resistivity of the films (Bharimalla, Deshmukh, Vigneshwaran, Patil, & Prasad, 2017). Additionally, the moisture barrier performance of the NC films could also be improved by enhancing the tortuosity of the diffusive path for permeants (Azeredo, 2009, Garusinghe, Varanasi, Raghuwanshi, Garnier, & Batchelor, 2018). Although NC films have the above-mentioned limitations, they are still considered as an attractive substitute for environmentally unfriendly petroleum-derived polymers, especially in packaging, due to their renewability, recyclability and biodegradability. However, uncertainty still exists in producing these films with moisture transmission properties comparable with conventional packaging polymers, such as low-density polyethylene (LDPE). This research focuses on producing low environmental impact, spray deposited composite films with considerably less drying time and improved moisture barrier performance, by substituting part of the NC with CMC.

NC based composites can be produced via chemical modifications or by solvent-exchange procedures in order to improve the compatibility of the mixtures (Siró & Plackett, 2010). However, using organic solvents to disperse NC might cause agglomeration of the fibril structure (Johansson, Tammelin, Campbell, Setälä, & Österberg, 2011). The suspension rheology can be modified by water soluble polysaccharides that have the ability to impart functional groups on the surface of NC (Eronen, Junka, Laine, & Österberg, 2011; Liu, Choi, Gatenholm, & Esker, 2011). Carboxymethyl cellulose (CMC) is a renewable, non-toxic and water soluble polysaccharide that can enhance the heat resistivity Ebnesajjad and Landrock, 2014. CMC is also considered as an environmentally friendly material as it consumes 0.06 MJ per kg of energy for its production (Wernet, 2019). Moreover, due to the high degree of substitution of the carboxylate functional groups, this polymer has the enhanced ability to form composites with other materials in comparison with other polysaccharides (Tongdeesoontorn, Mauer, Wongruong, Sriburi, & Rachtanapun, 2011).

The aim of this study is to investigate and optimize the CMC compositions in NC/CMC films in order to upgrade the production characteristics of the composite films. Additionally, the effect of adding CMC on the barrier and mechanical properties of the films were also investigated. Nevertheless, the environmental impact of the composite films produced were also assessed by means of embodied energy.

2. Hypothesis

Optimized addition of CMC can fill up the pores between the fibrous NC, resulting in remarkable barrier and mechanical properties. This composite will lower the environmental impact associated to NC.

3. Materials and methods

3.1. Materials

Different terminologies have been reported for nanocellulose in the literature. Nanocellulose is also named as cellulose nano-fibrils, nanofibrillated cellulose, micro fibrillated cellulose, cellulose micro-fibrils (Shanmugam et al., 2017). However, the generic term that we are using for the cellulose nanomaterial in this paper is nanocellulose (NC). The KY-100S grade NC fibres with 25 wt. % solid content were purchased from DAICEL Chemical Industries Limited (Japan). The commercial grade NC used in this study is speculated to be produced via high pressure homogenization of cotton fibres (Jang, Lee, Endo, & Kim, 2015; Hideno, Abe, Uchimura, & Yano, 2016). The mean diameter of these commercial grade NC fibres was around 73 nm (Varanasi, He, & Batchelor, 2013), while its suspension showed a zeta potential of -22.3 mV (Raj et al., 2017). The average aspect ratio (length to diameter) of the fibres was 142 $\pm$ 28 while the crystallinity index was 78 % (Shanmugam et al., 2018). Carboxymethyl cellulose (CMC; FINNFIX 30 g grade), having a molecular weight of 80,000, a percentage purity of 98 % and a degree of substitution (DS) of 0.8 was purchased from CP Kelco (Finland). The DS is defined as the number of carboxymethyl groups substituted per anhydroglucose unit. The DS range of commercially available CMC is 0.38–1.4, while 0.65–0.85 is more common (Caballero, Trugo, & Finglas, 2003) and typically 0.6−0.95 is used for food applications (Stephen, 1995). The hydro- affinity of CMC increases with increasing DS as this material becomes fully soluble at DS above 0.4, while swelling of the CMC was observed at DS below 0.4. Based on the range for food applications and availability, CMC having a DS of 0.8 was chosen in this study.

3.2. Fabrication procedure

The CMC powder was slowly added into the water and mixed with a Eurostar mixer (Germany) at 600 RPM to prepare solutions with different concentrations of 0.3, 0.9 and 1.5 wt. % of CMC. The solutions were mixed for another 15 min to ensure the complete dissolution of CMC. The NC fibres were added into the CMC solutions to achieve the NC/CMC final weight ratios of 5:1, 5:3, and 1:1 and a total solid content of 1.5 wt. % in the mixtures. The mixtures were disintegrated using a MK IIIC Messmer disintegrator (Netherlands) for 15000 revolutions. The pHs of the suspensions were 6.88, 6.49 and 6.11 for NC/CMC (5:1), NC/CMC (5:3) and NC/CMC (1:1), respectively. The suspensions were then sprayed using a Wagner spray system (Shanmugam et al., 2017, Shanmugam et al., 2018). The sprayed NC/CMC wet films were collected onto circular stainless steel plates (160 mm diameter) and carried away by a moving conveyor belt. The spray nozzle had an orifice of 0.38 mm while the speed of the conveyor belt was set at 0.65 cm/sec. The distance of the nozzle tip was approximately 30 cm from the steel plates. The sprayed plates were then finally transferred to an oven (S.E.M Equipment, Australia) for drying at 75 °C for 2 h. Meanwhile, the NC films were also prepared by adding NC fibres to water (pH = 7.33) making a 1.5 wt. % suspension. After disintegration (15000 revolutions at 3000 RPM) and spraying, the films were dried at 75 °C for 2 h.

Shanmugam et al. produced NC films via spray deposition and found that the operational range for spraying suspensions was in the range of 1.0–2.0 wt% (Shanmugam et al., 2017). Suspension concentrations lower than 1 wt. % were too dilute and could not be removed from the substrate after drying, while above 2 wt. %, the suspension was hard to spray due to the high viscosity. The suspension viscosities were 17.0 $\pm$ 0.6 (1 wt. %) and 32.2 $\pm$ 0.9 (2 wt. %) DIN sec, respectively as measured by Shanmugam et al. From our observations, substituting CMC with the NC fibres improved the ease of spraying, due to thixotropic properties of the CMC. For such materials, the viscosity decreases when its solution is pumped, stirred or sheared by other means (Benchabane & Bekkour, 2008).

3.3. Testing procedure

3.3.1. Basis weight and thickness

The basis weight was measured by dividing the weight of the films to their surface area. The films were kept in an oven for at least 4 h at 105 °C in order to remove any traces of moisture before calculating their basis weight. Additionally, a Lorentzen & Wettre AB (Sweden) Thickness Tester was used to determine the thickness of the films following the Australian/New Zealand standard method 426 (AS/NZS-426, 1994).

3.3.2. Moisture content

The moisture content of the films was determined in accordance with the ASTM D2216 –10 (ASTM, 2010). The weights of the samples were recorded at standard time intervals and the moisture content was calculated as:

$$W = \frac{M_{cws} - M_{cs}}{M_{cs} - M_c} \times 100 \quad (1)$$

Where, W is the moisture or water content (%), M_{cws} is the mass of container plus the wet specimen (g), M_{cs} is mass of container plus the oven dried sample (g) and Mc is the mass of the container (g).

3.3.3. Mechanical properties

Tensile testing was used to evaluate the mechanical properties of the produced films. The strips cut from the films with the dimensions of 100 mm × 15 mm were tested using an Instron universal testing machine (Model 5566, USA). The films were tested following the ASTM D 882-02 at 23 °C and 50 % relative humidity (ASTM, 2002). The tensile index of the films was calculated by the following equation where T′ is the tensile strength (kN/m) and R is the basis weight (g/m^2).

$$\text{Tensile Index (kN. m/g)} = \frac{T'}{R} \quad (2)$$

Additionally, the strips cut from the films were saturated with water and their mechanical properties were determined using an Instron universal testing machine (Model 5566, USA).

3.3.4. Moisture barrier properties

Moisture barrier properties of the films were evaluated by means of water vapour permeability (WVP) following the ASTM E96/E96M-05 (ASTM, 2005). Films were dried at 105 °C for 4 h to remove any traces of moisture prior to the test. At first, for each sample, about 40 g of anhydrous calcium chloride ($CaCl_2$) weighed in 3 non-corroding cups while the two cups were used as blank. The films from each sample were then sealed on the open side of the cups, forming an airtight assembly. The test was conducted at 23 °C and 50 % RH and the assemblies were weighed at regular time intervals. Finally, the water vapour transmission rate (WVTR) was calculated from the slope of the line between the weight and time. The WVTR of NC films were normalized with the thickness of the films and converted into WVP. The WVTR and WVP for the produced films can be calculated as:

$$WVTR = \frac{G}{t \times A} \quad (3)$$

Where, $\frac{G}{t}$ is the slope of the straight line (g. h^{-1}) and A is the film's surface area (m^2). The permeance of the films was determined as:

$$\text{Permeance} = \frac{WVTR}{S(R1 - R2)} \quad (4)$$

In this equation, S is the saturation vapor pressure per mmHg (1.333 × 10^2 Pa) at the tested temperature, R1 and R2 are the relative humidity values of the source and the vapor sink, respectively expressed as a fraction. Finally, the WVP of the films can be determined as:

$$WVP = \text{Permeance} \times \text{Thickness} \quad (5)$$

3.3.5. Characterization

The microscopic morphology of the iridium coated films was determined using scanning electron microscopy (Nova Nano-SEM 450, FEI, USA) at an accelerating voltage of 5 kV and the magnifications ranging from 10,000X to 80,000X. The macroscopic morphology was also determined using an optical profilometer (OLS5000, Olympus, Japan) with a 5X objective.

The effects of different levels of CMC addition on the optical properties was determined by transmission spectra of the heat dried composite films using an Agilent Cary 60 UV–vis Spectrophotometer in the wavelength ranging between 200–800 nm. A Dataphysics Contact Angle Measurement System (Germany) was used to determine the static contact angles of deionized water on the films. A helium gas pycnometer (Micromeritics AccuPyc 1330) was used to measure bulk density, ρ_{bulk} and skeletal density, $\rho_{skeletal}$ of the NC and NC/CMC composite films. The porosity ε *(%)* was calculated as follows:

$$\varepsilon\ (\%) = 1 - \frac{\rho_{bulk}}{\rho_{skeletal}} \quad (6)$$

Additionally, the specific surface areas of the NC/CMC (5:1) and NC/CMC (1:1) samples were analysed using Micromeritics 3FLEX via (Brunauer–Emmett–Teller) BET model. The samples were degassed for 24 h at 105 °C prior to the experiment, while Krypton was used as adsorptive analysis.

3.3.6. Embodied energy

Embodied energy was determined and compared with the conventional packaging materials to evaluate the environmental characteristics of the products. Assumptions made to assess the embodied energy are listed in Table 1. Embodied energy was calculated using the Ecoinvent 3.5 (Switzerland) (Wernet, 2019). The values for the recycled films were calculated considering the disintegration and spraying as the only contributors to the energy consumptions.

4. Results and discussion

4.1. Film production

4.1.1. Environmental aspects

The excessive energy waste in the production of materials is a serious environmental concern that needs to be addressed. Environmental aspects of NC and NC composite films were determined by means of determining the embodied energy. Embodied energy comparisons of virgin and recycled PET, NC and NC/CMC (1:1) films is illustrated in Fig. 1. Calculations of the embodied energy of these films are included in the supplementary data.

The energy consumption of the Daicel NC fibres used in this study were not supplied by the manufacturer. Instead we have used values for what we believe are a comparable material, produced via high pressure homogenization with a very high energy consumption of 30,000 kWh/tonne (108 MJ/kg) to fibrillate the cellulose via mechanical treatment

Table 1
Assumptions in determining embodied energy.

Process	Assumptions
Materials	1. The pulp used to produce NC fibres has an embodied energy of 50−70 MJ/kg (Arvidsson, Nguyen, & Svanström, 2015). 2. The NC fibres produced from pulp has an overall embodied energy of 108 MJ/kg (Li et al., 2013). 3. The overall embodied energy requirements of CMC production was 0.06 MJ/kg (Wernet, 2019).
Production	1. Approximately 300 films were produced via spray depositing in 1 h. 2. Approximately 12 films could be produced with 1 l of suspension. 3. A large oven (2 kWh) was utilized for heat drying that can accommodate for about 100 films in one batch. 4. All films i.e. NC, NC/CMC (1:1) and PET weigh 2 g.

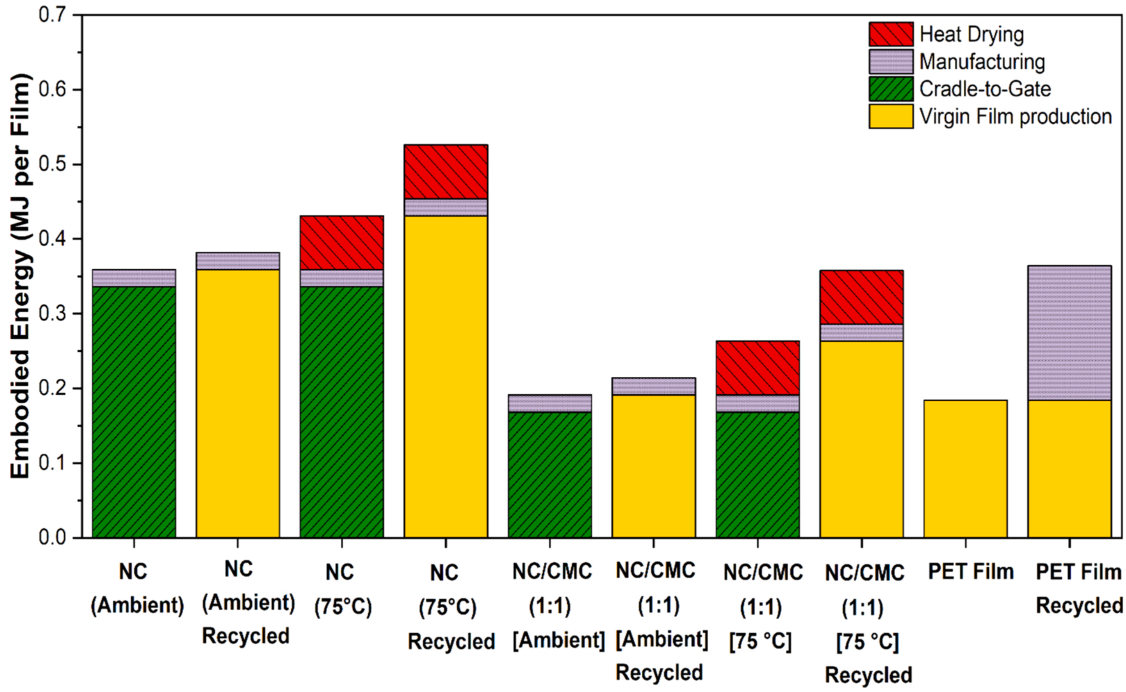

Fig. 1. Embodied energy comparison for NC, NC/CMC (1:1) composite and PET films.

(Nakagaito & Yano, 2004). Pre-treatment methods (enzymatic hydrolysis, carboxymethylation, and TEMPO-mediated oxidation etc.) can reduce the energy consumptions to a significant extent, but all have a number of limitations such as corrosiveness, toxicity and cost (Isogai, Saito, & Fukuzumi, 2011; Lavoine, Desloges, Dufresne, & Bras, 2012). Alternatively, the high energy consumption (associated with the production of NC) can be overcome by producing NC via an energy efficient way, recycling or forming the composites with environmentally friendly materials.

The embodied energy of virgin NC film was significantly higher than that of the conventional PET films. The high embodied energy of NC is mainly associated with the production of NC fibres (Li et al., 2013), which indicates that the NC itself is an energy inefficient material. However, the recyclability and biodegradability are the distinguishing features inherent to NC, which combining with its life cycle indicates that it can be considered as an environmentally friendly material compared to PET. Shanmugam et al. (Shanmugam et al., 2019) showed that NC films could be recycled while retaining much of its barrier and mechanical properties. In contrast, the PET films are either difficult to recycle or require a high energy consumption (Jackson, 2006). The one-time recycling of NC films had lower impact on its overall embodied energy compared with that of PET films (Fig. 1). Recently, it has been reported that the production of NC fibres via a vegetable source could be a more energy efficient method with a reduced energy consumption of approximately 8500 kWh/tonne (Varanasi, Henzel, Sharman, Batchelor, & Garnier, 2018). The production of NC via this method required 4 times lower energy consumption as compared with the conventional mechanical fibrillation (Lavoine et al., 2012). The composite films produced using plant-based NC fibres would have a lower embodied energy as compared with the PET film even prior to recycling.

CMC is a biodegradable water-soluble cellulose based polymer, making it a very environmentally friendly material. CMC has significantly lower embodied energy (0.06 MJ/kg) as compared with the NC (108 MJ/kg) (Wernet, 2019), since mechanical fibrillation via high pressure homogenization, which consumes a very high amount of energy, is not required for CMC production. Substituting 50 % of the NC with CMC lowered the overall embodied energy by 40 % for the composites dried at 75 °C (Fig. 1). After recycling the heat-dried NC/CMC (1:1) film one time, the environmental impact of the composite was lower as compared with the PET film.

4.1.2. *Drying characteristics*

It was observed that most of the NC films dried at 75 °C or higher temperature showed a level of shrinkage after drying (Fig. 2A). 50 °C was found to be the optimal temperature to dry the NC films with no visible shrinkage. However, the drying time was long (~ 5 h) which makes it infeasible for commercialization. Hence, forming the composites of NC with additives that could enhance its heat resistivity and considerably decrease its drying time could be ideal (Bharimalla et al., 2017). For this purpose, we decided to add CMC to NC and dry the composites at 75 °C. The moisture content of the composite films (NC/CMC) measured at several time intervals is represented in Fig. 2C. As expected, the drying time at 75 °C (~2.5 h) was considerably shorter than 50 °C. 2.5 h is an acceptable time-frame for large scale production. The inclusion of CMC has improved the drying characteristics of films without comprising their dimensional stability. It was also observed that the drying time did not change to a considerable extent at various CMC concentrations, as the total solid contents remained the same (Fig. S1). It also had negligible shrinkage (Fig. 2B) compared with the NC film dried at 75 °C (Fig. 2A). Moreover, as the CMC content increases, the composite films become smoother and improved optical transparency can be seen. The NC/CMC (1:1) showed an approximately 15 times lower roughness values compared with the NC films. This demonstrates the addition of CMC drops the surface roughness by decreasing the friction among the network of fibres and consequently results in the formation of a smoother and more optically transparent film (Shanmugam, Nadeem, Browne, Garnier, & Batchelor, 2020).

4.2. *Film properties*

4.2.1. *Mechanical characteristics*

Mechanical characteristics were determined in terms of the tensile index and strain at break (Fig. 3). These are the important characteristics as conventional packaging films have usually high strength and high strain at break. The tensile index of the NC film was 52 ± 5 Nm/g, which is almost similar to what was observed previously by Shanmugam et al.

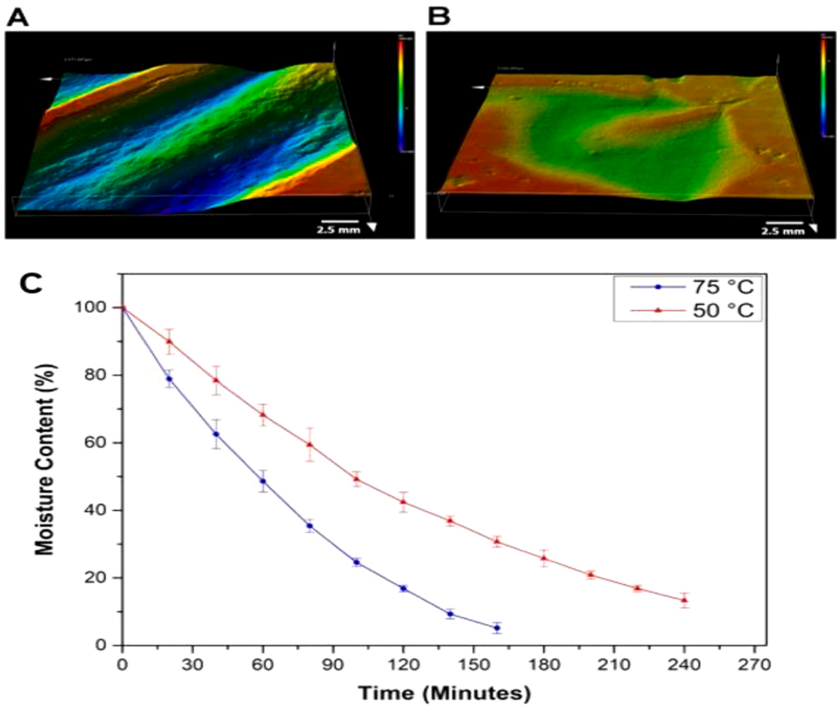

Fig. 2. (**A**) The optical profilometric image of the NC film (2.5 cm × 2.5 cm) dried at 75 °C (average roughness ~ 370 μm), (**B**) The optical profilometric image of the NC/CMC film (2.5 cm × 2.5 cm) dried at 75 °C (average roughness ~ 24 μm), (**C**) Moisture content vs time for the NC/CMC films dried at 50 °C and 75 °C.

(Shanmugam et al., 2017, Shanmugam et al., 2018) at the basis weight of 45 g/m^2 to 100 g/m^2. Addition of CMC to NC significantly enhanced the tensile strength of the films. As Fig. 3 shows, when the CMC content increased, the tensile index of the composite films increased up to 65 % compared with the NC film. The tensile index greater than 80 Nm/g was achieved with the NC/CMC (1:1) at the basis weight of 41 ± 4 g/m^2. This increase in strength is due to the CMC having functional groups of carboxyl and free hydroxyl producing strong intermolecular interactions with the NC (Mandal & Chakrabarty, 2018). The inherent hydrogen bonds (intramolecular or intermolecular) specifically existing in NC are substituted with new hydrogen bonds on addition of CMC. The chains of CMC contains a large number of hydroxyl groups, which provide suitable conditions for the formation of intermolecular hydrogen bonding

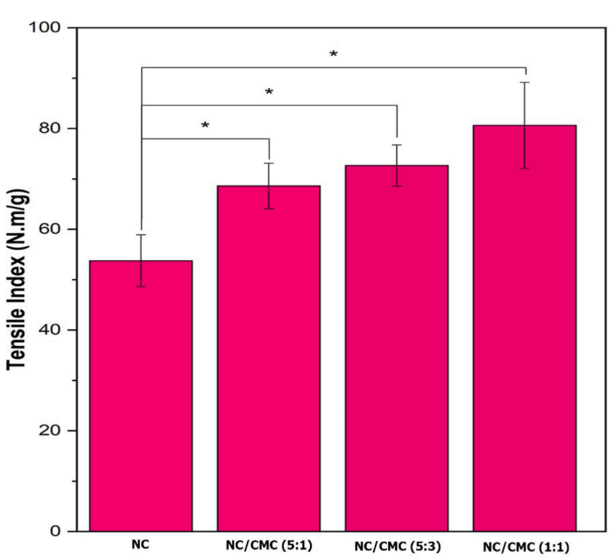

Fig. 3. Tensile index of the films produced at 75 °C. Values represent the mean ± SD, n = 3, *$P < 0.05$ (obtained by Student's *t*-test).

and consequently increasing the intermolecular forces (Lan, He, & Liu, 2018). The increase in intermolecular hydrogen bonds resists molecular slip, which increases the tensile index of the NC/CMC films (Mandal & Chakrabarty, 2018; Youssef et al., 2015).

Additionally, the incorporation of CMC, had reduced the fibrillar interactions that might be due to the ionic repulsion between fibrils resulting in the orientation of fibres with moderate shearing (Lasseuguette, 2008).

The strain at break (%) and young modulus for NC and NC/CMC films are shown in Table 2. For pure NC, the strain at break was approximately 8.75 %. The addition of CMC to NC and forming a composite film enhanced the flexibility considerably and for NC/CMC (1:1) the strain at break achieved was up to 35 %. These results are indicative of the plasticising effect caused by the addition of CMC groups. The huge improvement in mechanical properties is due to the interaction of NC and CMC, possibly owing to the incorporation of carboxyl and hydroxyl groups on the NC surface (Mandal & Chakrabarty, 2018). Additionally, the fibres reduced the overall stresses on the composite which improved the overall interfacial adhesion and increased the strength and strain at break (Morán, Vázquez, & Cyras, 2013). The increase in tensile index and strain at break is indicative that the addition of CMC has imparted an increased toughness to the films.

As expected, NC films have limited wet strength due to the hydrophilic nature of cellulose (Aulin et al., 2010). Moreover, the NC/CMC

Table 2
Mechanical characteristics of dry and wet NC and NC/CMC films.

	Characteristics	NC	NC/CMC (5:1)	NC/CMC (5:3)	NC/CMC (1:1)
Dry	**Young's Modulus (MPa)**	3334.3 ± 145.0	4805.3 ± 230.9	6766.9 ± 125.4	2308.7 ± 143.9
	Strain at Break (%)	8.75 ± 1.58	12.22 ± 1.03	17.79 ± 3.4	34.86 ± 2.90
Wet	**Young's Modulus (MPa)**	112 ± 22	105 ± 18	96 ± 18	N/A
	Strain at Break (%)	2.8 ± 1.2	2.1 ± 0.8	1.9 ± 1.2	N/A

composite films have shown a significant reduction in mechanical characteristics when saturated with water due to polar nature of CMC. The NC/CMC (1:1) and NC/CMC (5:3) films were very soft and disintegrated in the wet state and therefore, could not undergo testing. However, the mechanical properties of the wet films could be improved by different techniques such as ionic crosslinking or modifying the cellulosic surface with cationic surfactants (Blomstedt & Vuorinen, 2007; Hubbe, 2006).

4.2.2. Moisture barrier properties

The moisture barrier properties of the produced films were determined by means of WVP and the results are shown in Fig. 4. The average WVP of NC films was measured to be 8.21 $\times 10^{-11}$ g/Pa.s.m, which is similar to the values of 6.18 $\times 10^{-11}$ g/Pa.s.m and 7.5 $\times 10^{-11}$ g/Pa.s.m as reported by Rodionova et al. and Shanmugam et al., respectively (Rodionova, Lenes, Eriksen, & Gregersen, 2011, Shanmugam et al., 2019). The WVP values were reduced significantly by incorporating the CMC with NC to 3.50 $\times 10^{-11}$ g/Pa.s.m for NC/CMC (5:1) and 2.90 $\times 10^{-11}$ g/Pa.s.m for NC/CMC (5:3) films. Mandal and Chakrabarty (Mandal & Chakrabarty, 2018) reported a similar value (4.32 $\times 10^{-11}$ g/Pa.s.m) for the NC/CMC composite films produced via casting followed by drying at 75 °C for 24 h. The NC/CMC (1:1) film showed the lowest WVP with the value of 2.5 $\times 10^{-12}$ g/Pa.s.m which is comparable with the WVP of conventional packaging materials (Rosato, 2016). Addition of a polymer such as CMC into NC may have reduced the internal pore size and enhanced the tortuosity of the path in the films and thus caused a slower diffusion which consequently led to a lower permeance (Ray, Quek Siew, Easteal, & Chen Xiao, 2006). The free carboxyl groups present in CMC tend to form hydrogen bonds with themselves and the NC fibres which results as a resistance to the transmission of moisture.

The contact angle values for the NC and NC composite films are shown in Fig. 5. As expected, NC films had high wettability owing to the hydrophilic nature of porous cellulose fibre film (Aulin et al., 2010). Adding CMC and forming composites with the NC reduced the hydrophilicity of the films. The largest contact angle (≈80°) was achieved for the NC/CMC (1:1) films. The hydrogen bonding between polysaccharide chains decreased the polar groups available to react with water and consequently, the hydrophilicity of the composite films is reduced (de Britto, de Rizzo, & Assis, 2012). The contact angle was almost doubled for the film with a 1:1 NC/CMC concentration over the film with NC alone, indicating the significant improvement in reducing the wettability of the films, however, the films were not completely hydrophobic

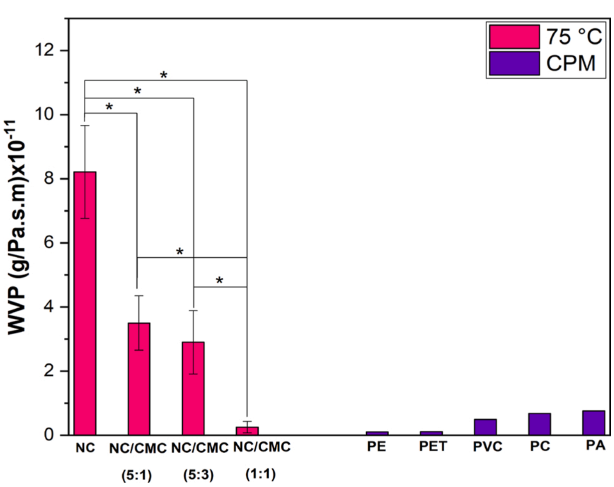

Fig. 4. The WVP of the NC and NC composite films dried at 75 °C. The numbers for conventional packaging materials (CPM) were found in the literature (Bhunia, Sablani, Tang, & Rasco, 2013; Steven & Hotchkiss, 2002). Values represent the mean ± SD, n = 3, *$P < 0.05$ (obtained by Student's *t*-test).

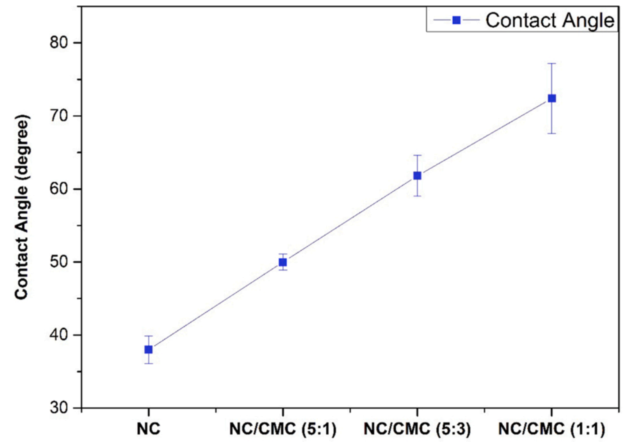

Fig. 5. The contact angle values of the NC and NC composite films dried at 75 °C.

(Ismail, Rahman, Othman, & Matsuura, 2018).

4.2.3. Morphology

The morphological changes of CMC addition to NC was determined using a scanning electron microscopy (SEM) and the results are shown in Fig. 6. The NC film dried at 75 °C mainly exhibited a porous structure made of cellulose nano and micro fibres having a random distribution. The CMC addition resulted in filling the pores between the NC fibres, with decreasing porosity from the NC/CMC (5:1) to NC/CMC (1:1). The reduced porosity due to CMC addition is considered as the main reason behind the decrease of moisture barrier performance and improved tensile strength from the NC film to NC/CMC (1:1).

The porosity results of the NC and NC/CMC composite films dried at 75 °C are illustrated in Table 3. Increasing the amount of CMC to a 1:1 ratio, increased the density by 0.22 g/cm^3, as the CMC filled the pores between the fibres. This finding agrees with the moisture barrier results, which showed that WVP of films was reduced with increasing CMC content.

The NC films showed a high specific area of approximately 1.0247 m^2/g, however, it reduced to a significant extent with the addition of CMC. For instance, the NC/CMC (1:1) films had a lower specific surface area (0.09 m^2/g) as compared with the NC/CMC (5:3) composite films (0.22 m^2/g), referring to a reduction in porosity with the increasing concentration of CMC. This suggests that the addition of CMC filled the pores among the fibres and led to smaller specific surface area.

4.2.4. Transmittance

The transparency of NC and NC/CMC films was investigated using UV–vis spectrophotometry and the results are displayed in Fig. 7 while the images at the top of this figure are the films used to conduct the transmittance experiment. As expected, the NC films formedwere opaque due to the reason that nanofibers are densely packed and have the ability to suppress light scattering (Ray et al., 2006). The addition of CMC resulted in improved transparency of the films and made them translucent. As the CMC concentration increased, the transparency of the composite film was also enhanced as shown in the images overlayed at the top of Fig. 7. The NC/CMC (1:1) showed more than 500 % increase in transparency (in the visible spectrum range of 400 nm–700 nm) compared with the NC films. As CMC has a slightly lower refractive index than NC, the improvement in transparency of the NC/CMC composite might be due to reduced mean refractive index difference between the NC and CMC as compared with air (Kim et al., 2015). This is an indication that the transparency can be increased further if the difference in refractive index of the materials used to form a composite is further minimized.

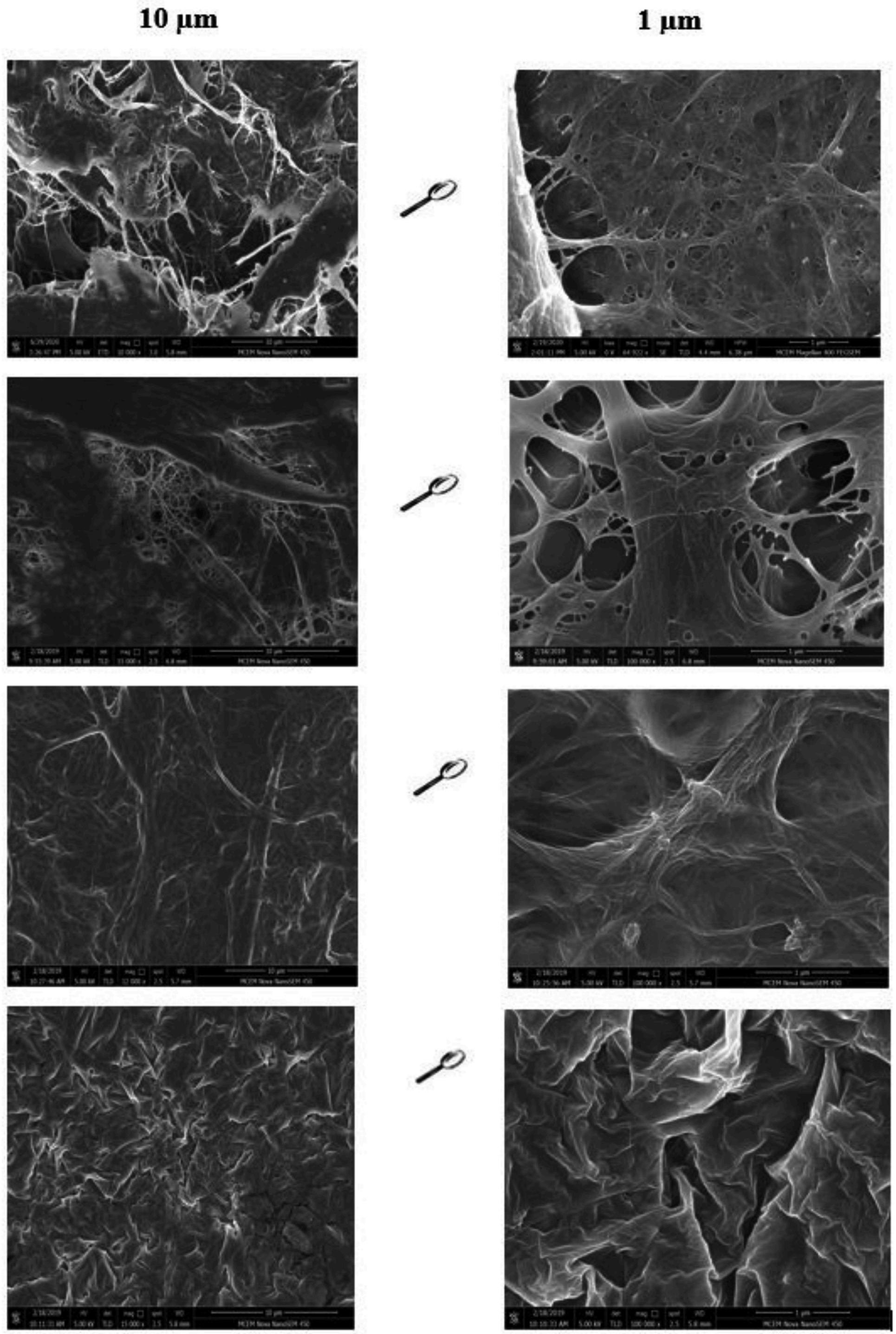

Fig. 6. SEM images of the NC and NC/CMC films dried at 75 °C.

Table 3
Bulk and skeletal densities and porosities of NC and NC/CMC films.

Sample	ρ_{bulk} (g/cm^3)	$\rho_{skeletal}$ (g/cm^3)	Porosity ε (%)
NC	0.72	1.573	54.2
NC/CMC (5:1)	0.82	1.568	47.7
NC/CMC (5:3)	0.85	1.53	44.4
NC/CMC (1:1)	0.94	1.47	36

5. Conclusion

This research investigates the incorporation of CMC with NC to produce composite films using the spray deposition technique as an alternative for petroleum-based packaging materials. Addition of CMC improved the heat resistivity of the NC and the composite films could be dried in 2 h at 75 °C (at least 10 times faster than drying at ambient condition) without compromising the dimensional stability. The CMC addition has also boosted the moisture barrier performance of the NC and the results were comparable with the plastic packaging materials such as PET, polycarbonates (PC) etc. Moreover, the NC/CMC composite

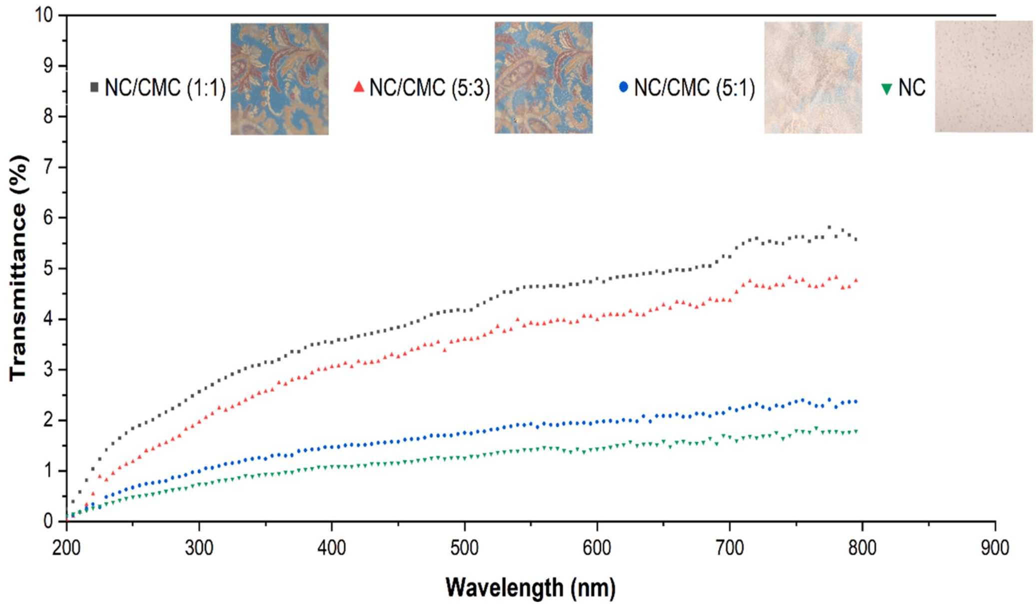

Fig. 7. The transmittance of the NC and NC/CMC composite films dried at 75 °C.

material has high strength and reasonable toughness as indicated by its mechanical properties. Considering the energy consumption factor, the NC/CMC films had an overall low environmental impact due to their ease of recyclability.

CRediT authorship contribution statement

Humayun Nadeem: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing. **Mahdi Naseri:** Investigation, Writing - review & editing. **Kirubanandan Shanmugam:** Investigation, Methodology. **Mostafa Dehghani:** Investigation. **Christine Browne:** Investigation, Methodology, Writing - review & editing. **Simin Miri:** Investigation. **Gil Garnier:** Writing - review & editing, Supervision, Funding acquisition. **Warren Batchelor:** Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Acknowledgments

The authors would like to express their gratitude to the Australian Research Council and the ARC Research Hub for Processing Lignocellulosics into High Value Products (PALS) for their financial support through the Industry Transformation Research Hub grant No IH170100020. The authors are also grateful to the Monash Centre for Electron Microscopy (MCEM) for availing their facilities. H. Nadeem is also grateful to Monash University, Bioprocessing Research Institute of Australia (BioPRIA) and Faculty of Engineering for providing financial support for his doctoral studies.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.26180/5f0f94f8963df.

References

Andrady, A. L., & Neal, M. A. (2009). Applications and societal benefits of plastics. *Philosophical Transactions of the Royal Society of London Series B, Biological Sciences, 364*(1526), 1977–1984.

Arvidsson, R., Nguyen, D., & Svanström, M. (2015). Life cycle assessment of cellulose nanofibrils production by mechanical treatment and two different pretreatment processes. *Environmental Science & Technology, 49*(11), 6881–6890.

AS/NZS-426. (1994). *Determination of thickness and apparent bulk density or apparent sheet density*.

ASTM, D., 882-02. (2002). *Standard Test Method for tensile properties of thin plastic sheeting*. West Conshohocken, PA.

ASTM, D., 2216-10. (2010). *Standard test methods for laboratory determination of water (moisture) content of soil and rock by mass*. West Conshohocken, PA.

ASTM, E., 96/96M-05. (2005). *Standard test methods for water vapor transmission of materials*. West Conshohocken, PA.

Aulin, C., Gällstedt, M., & Lindström, T. (2010). Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. *Cellulose, 17*(3), 559–574.

Azeredo, H. M. C.d. (2009). Nanocomposites for food packaging applications. *Food Research International, 42*(9), 1240–1253.

Benchabane, A., & Bekkour, K. (2008). Rheological properties of carboxymethyl cellulose (CMC) solutions. *Colloid and Polymer Science, 286*(10), 1173.

Bharimalla, A. K., Deshmukh, S. P., Vigneshwaran, N., Patil, P. G., & Prasad, V. (2017). Nanocellulose-polymer composites for applications in food packaging: Current status, future prospects and challenges. *Polymer-Plastics Technology and Engineering, 56*(8), 805–823.

Bhunia, K., Sablani, S. S., Tang, J., & Rasco, B. (2013). Migration of chemical compounds from packaging polymers during microwave, conventional heat treatment, and storage. *Comprehensive Reviews in Food Science and Food Safety, 12*(5), 523–545.

Blomstedt, M., & Vuorinen, T. (2007). Modification of softwood kraft pulp with carboxymethyl cellulose and cationic surfactants. *Journal of Wood Science, 53*(3), 223–228.

Caballero, B., Trugo, L. C., & Finglas, P. M. (2003). *Encyclopedia of food sciences and nutrition*. Academic.

de Britto, D., de Rizzo, J. S., & Assis, O. B. G. (2012). Effect of carboxymethylcellulose and plasticizer concentration on wetting and mechanical properties of cashew tree gum–based films. *International Journal of Polymer Analysis and Characterization, 17*(4), 302–311.

Ebnesajjad, Sina, & Landrock, Arthur H. (2014). Chapter 5 – Characteristics of adhesive materials. *Adhesives technology handbook* (pp. 63–135). Norwich, NY: William Andrew.

Eronen, P., Junka, K., Laine, J., & Österberg, M. (2011). Interaction between water soluble polysaccharides and native nanofibrillar cellulose thin films. *BioResources, 6*(4), 4200–4217.

Garusinghe, U. M., Varanasi, S., Raghuwanshi, V. S., Garnier, G., & Batchelor, W. (2018). Nanocellulose-montmorillonite composites of low water vapour permeability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 540*, 233–241.

Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances, 3*(7), Article e1700782.

Golden, J. S., Handfield, R., Pascual-Gonzalez, J., Agsten, B., Brennan, T., Khan, L., et al. (2018). *Indicators of the U.S. biobased economy*. U.S. Department of Agriculture, Office of Energy Policy.

Heggset, E. B., Chinga-Carrasco, G., & Syverud, K. (2017). Temperature stability of nanocellulose dispersions. *Carbohydrate Polymers, 157*, 114–121.

Herrera, M. A., Mathew, A. P., & Oksman, K. (2017). Barrier and mechanical properties of plasticized and cross-linked nanocellulose coatings for paper packaging applications. *Cellulose, 24*(9), 3969–3980.

Hideno, A., Abe, K., Uchimura, H., & Yano, H. (2016). Preparation by combined enzymatic and mechanical treatment and characterization of nanofibrillated cotton fibers. *Cellulose, 23*(6), 3639–3651.

Hollertz, R., Durán, V. L., Larsson, P. A., & Wågberg, L. (2017). Chemically modified cellulose micro- and nanofibrils as paper-strength additives. *Cellulose, 24*(9), 3883–3899.
Hopewell, J., Dvorak, R., & Kosior, E. (2009). Plastics recycling: challenges and opportunities. *Philosophical Transactions of the Royal Society of London Series B, Biological Sciences, 364*(1526), 2115–2126.
Hubbe, M. A. (2006). Bonding between cellulosic fibers in the absence and presence of dry-strength agents–A review. *BioResources, 1*(2), 281–318.
Ismail, A. F., Rahman, M. A., Othman, M. H. D., & Matsuura, T. (2018). *Membrane separation principles and applications: From material selection to mechanisms and industrial uses*. Elsevier.
Isogai, A., Saito, T., & Fukuzumi, H. (2011). TEMPO-oxidized cellulose nanofibers. *Nanoscale, 3*(1), 71–85.
Jackson. (2006). *Recycling of plastics* (p. 3). UK: University of Cambridge.
Jang, J.-H., Lee, S.-H., Endo, T., & Kim, N.-H. (2015). Dimension change in microfibrillated cellulose from different cellulose sources by wet disk milling and its effect on the properties of PVA nanocomposite. *Wood Science and Technology, 49*(3), 495–506.
Johansson, L.-S., Tammelin, T., Campbell, J. M., Setälä, H., & Österberg, M. (2011). Experimental evidence on medium driven cellulose surface adaptation demonstrated using nanofibrillated cellulose. *Soft Matter, 7*(22), 10917–10924.
Kim, H.-J., Kwon, H.-J., Jeon, S., Park, J.-W., Sunthornvarabhas, J., & Sriroth, K. (2015). Electrical and optical properties of nanocellulose films and its nanocomposites. *Handbook of polymer nanocomposites. Processing, performance and application* (pp. 395–432). Springer.
Lan, W., He, L., & Liu, Y. (2018). Preparation and properties of sodium carboxymethyl cellulose/sodium alginate/chitosan composite film. *Coatings, 8*(8), 291.
Lasseuguette, E. (2008). Grafting onto microfibrils of native cellulose. *Cellulose, 15*(4), 571–580.
Lavoine, N., Desloges, I., Dufresne, A., & Bras, J. (2012). Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review. *Carbohydrate Polymers, 90*(2), 735–764.
Li, Q., McGinnis, S., Sydnor, C., Wong, A., & Renneckar, S. (2013). Nanocellulose Life Cycle Assessment. *ACS Sustainable Chemistry & Engineering, 1*(8), 919–928.
Liu, Z., Choi, H., Gatenholm, P., & Esker, A. R. (2011). Quartz crystal microbalance with dissipation monitoring and surface plasmon resonance studies of carboxymethyl cellulose adsorption onto regenerated cellulose surfaces. *Langmuir, 27*(14), 8718–8728.
Maliha, M., Herdman, M., Brammananth, R., McDonald, M., Coppel, R., Werrett, M., Andrews, P., & Batchelor, W. (2019). Bismuth phosphinate incorporated nanocellulose sheets with antimicrobial and barrier properties for packaging applications. *Journal of Cleaner Production*, Article 119016.
Mandal, A., & Chakrabarty, D. (2018). Studies on mechanical, thermal, and barrier properties of carboxymethyl cellulose film highly filled with nanocellulose. *Journal of Thermoplastic Composite Materials, 32*(7), 995–1014.
Marsh, K., & Bugusu, B. (2007). Food packaging—Roles, materials, and environmental issues. *Journal of Food Science, 72*(3), R39–R55.
Morán, J. I., Vázquez, A., & Cyras, V. P. (2013). Bio-nanocomposites based on derivatized potato starch and cellulose, preparation and characterization. *Journal of Materials Science, 48*(20), 7196–7203.
Nadeem, H., Habib, N. Z., Ng, C. A., Zoorob, S. E., Mustaffa, Z., Chee, S. Y., et al. (2017). Utilization of catalyzed waste vegetable oil as a binder for the production of environmentally friendly roofing tiles. *Journal of Cleaner Production, 145*, 250–261.
Nakagaito, A. N., & Yano, H. (2004). The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Applied Physics A, 78*(4), 547–552.
Onur, A., Shanmugam, K., Ng, A., Garnier, G., & Batchelor, W. (2019). Cellulose fibre-perlite depth filters with cellulose nanofibre top coating for improved filtration performance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 583*, Article 123997.
Raj, P., Blanco, A., de la Fuente, E., Batchelor, W., Negro, C., & Garnier, G. (2017). Microfibrilated cellulose as a model for soft colloid flocculation with polyelectrolytes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 516*, 325–335.
Ray, S., Quek Siew, Y., Easteal, A., & Chen Xiao, D. (2006). The potential use of polymer-clay nanocomposites in food packaging. *International Journal of Food Engineering, 2*.
Rodionova, G., Lenes, M., Eriksen, Ø., & Gregersen, Ø. (2011). Surface chemical modification of microfibrillated cellulose: improvement of barrier properties for packaging applications. *Cellulose, 18*(1), 127–134.
Rosato, D. (2016). *Novel medical plastics packaging material and process advances*. from http://exclusive.multibriefs.com/content/novel-medical-plastics-packaging-material-and-process-advances/engineering.
Shanmugam, K., Doosthosseini, H., Varanasi, S., Garnier, G., & Batchelor, W. (2018). Flexible spray coating process for smooth nanocellulose film production. *Cellulose, 25*(3), 1725–1741.
Shanmugam, K., Doosthosseini, H., Varanasi, S., Garnier, G., & Batchelor, W. (2019). Recycled nanocellulose films as air and water vapour barriers: A recyclable and biodegradable to polyolefin packaging. *Sustainable Materials and Technologies*, Article e00115.
Shanmugam, K., Nadeem, H., Browne, C., Garnier, G., & Batchelor, W. (2020). Engineering surface roughness of nanocellulose film via spraying to produce smooth substrates. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 589*, Article 124396.
Shanmugam, K., Varanasi, S., Garnier, G., & Batchelor, W. (2017). Rapid preparation of smooth nanocellulose films using spray coating. *Cellulose, 24*(7), 2669–2676.
Shimizu, M., Saito, T., Fukuzumi, H., & Isogai, A. (2014). Hydrophobic, ductile, and transparent nanocellulose films with quaternary alkylammonium carboxylates on nanofibril surfaces. *Biomacromolecules, 15*(11), 4320–4325.
Siró, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose, 17*(3), 459–494.
Stephen, A. M. (1995). *Food polysaccharides and their applications*. CRC press.
Steven, M. D., & Hotchkiss, J. H. (2002). Comparison of flat film to total package water vapour transmission rates for several commercial food wraps. *Packaging Technology and Science, 15*(1), 17–27.
Tongdeesoontorn, W., Mauer, L. J., Wongruong, S., Sriburi, P., & Rachtanapun, P. (2011). Effect of carboxymethyl cellulose concentration on physical properties of biodegradable cassava starch-based films. *Chemistry Central Journal, 5*(1), 6.
Varanasi, S., He, R., & Batchelor, W. (2013). Estimation of cellulose nanofibre aspect ratio from measurements of fibre suspension gel point. *Cellulose, 20*(4), 1885–1896.
Varanasi, S., Henzel, L., Sharman, S., Batchelor, W., & Garnier, G. (2018). Producing nanofibres from carrots with a chemical-free process. *Carbohydrate Polymers, 184*, 307–314.
Wernet, G. (2019). *Ecoinvent 3.5*.
Youssef, B., Soumia, A., Mounir, E. A., Omar, C., Abdelaziz, L., Mehdi, E. B., et al. (2015). Preparation and properties of bionanocomposite films reinforced with nanocellulose isolated from moroccan alfa fibres. *Autex Research Journal, 15*(3), 164.