Sustainable Materials and Technologies 22 (2019) e00115

Contents lists available at ScienceDirect

Sustainable Materials and Technologies

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

Nanocellulose films as air and water vapour barriers: A recyclable and biodegradable alternative to polyolefin packaging

Kirubanandan Shanmugam, Hamid Doosthosseini, Swambabu Varanasi, Gil Garnier, Warren Batchelor *

Bio resource Processing Research Institute of Australia, Department of Chemical Engineering, Monash University, Melbourne, VIC 3800, Australia

ARTICLE INFO

Article history:
Received 9 May 2018
Received in revised form 19 March 2019
Accepted 1 June 2019

Keywords:
Nanocellulose
Vaccum filtration
Recycling
Water vapour permeability
Uniformity
Tensile index

ABSTRACT

Synthetic polymer packaging is neither reprocessable, renewable nor biodegradable and is difficult to recycle into useful barrier materials. Cellulose fibre based packaging is renewable, easily reprocessable, recyclable and biodegradable, however, it is a poor barrier material both before and after recycling, especially against air and water vapour. Nanocellulose (NC), formed by breaking down cellulose fibres into nanoscale diameter fibres, is a renewable alternative to synthetic polymer packaging barrier layers. This research investigates the recyclability of virgin NC films. Nanocellulose films were recycled and prepared into films, using standard dispersion-based laboratory papermaking techniques through mixing and vacuum filtration of the resultant suspension. The recycled films retained ~70% of the strength of the virgin films. Although the water vapour permeability (WVP) approximately doubled, increasing to 1.29×10^{-10} g.m^{-1}.s^{-1} Pa^{-1}, it is still comparable to synthetic polymer packaging materials such as Polyethylene(PE), Plasticized PVC, Oriented Nylon 6 and Polystyrene (PS). SEM micrographs reveal no fibre agglomeration and no damage to the fibres during the recycling process. The optical uniformity measurements of recycled NC film confirms a drop in uniformity of the film at smaller length scales and an increase in uniformity at larger length scales, compared with virgin NC film. The retained strength and barrier properties combined with easy reprocessability of the product promises a sustainable and recyclable alternative to conventional polyolefin packaging, providing a very attractive alternative for the packaging industry.

1. Introduction

The development of sustainable and recyclable barrier materials for packaging is a critical challenge arising from pressing environmental concerns with the widespread use of non-sustainable petroleum-derived polymers in the food, pharmaceutical, electronics and other industries. Sales of packaging materials is forecasted at US$997 billion by 2020 with a market growth of ~3.5% per year [1]. Presently, glass, aluminium, tin and petroleum-based polymers are extensively used as packaging materials. Throughout the industry, polyolefins have been widely adopted due to their effective barrier properties and simple and cheap processing. Despite these desirable properties, the majority of polyolefin packaging is not re-processable into their original form or into high value products. Petroleum polymers are neither sustainable nor biodegradable; their extensive use has had severe ecological impacts. Consequently, their disposal still raises environmental concerns and recycling requires complex and costly processes. Moreover, the recycle process involving blending the synthetic polymers into a processable melt is very dependent upon the chemical composition and molecular weight of the components; further, volatile organic compounds are emitted which can impact plants, animals and humans. The heat required for thermal recycling of plastics also generates various oxides of carbon that are the most responsible for global warming. Current polyolefin films cannot be reprocessed into the original product, as the recycled product would not yield suitable barrier properties [2–4]. During the recycling process, the mixing of different polymers together leads to a reduction in the quality and properties of the recycled plastic. Moreover, chemical compounds from synthetic packaging materials can affect the quality of food when exposed to post-packaging processes [5] and cause food contamination [6,7].

It is therefore imperative to pursue novel materials for packaging applications to address the ecological and environmental concerns with cost-effective, readily available and sustainable solutions. Bio-based polymers can produce humidity, oxygen and grease barriers for sustainable, biodegradable and compostable packaging [8]. Previously, bio-based materials have been processed into films, significantly enhancing shelf life and quality of foods and reducing waste from packaging. However, such biodegradable polymers have poor barrier performance and are noticeably brittle. As such, complications in processing these materials, such as low heat distortion, render them too expensive for industrial scale use [9].

* Corresponding author at: BioPRIA, Department of Chemical Engineering, 15 Alliance Lane, Monash University, Clayton, Melbourne, VIC 3800, Australia.
E-mail address: warren.batchelor@monash.edu (W. Batchelor).

https://doi.org/10.1016/j.susmat.2019.e00115
2214-9937/

Cellulose fibre-based packaging materials, such as boxes, cartons and paper are renewable, recyclable and biodegradable but are poor barriers to oxygen and water. Laminating with polymers, such as LDPE, can yield products with sufficient barrier performance, but at the expense of recyclability and biodegradability [4].

One solution to improving the sustainability of paper-polymer laminates is to replace the polyolefin layer with a film of nanocellulose (NC). Nanocellulose is directly produced by defibrillating fibres from pulp and wood into their structural constituents [10]. NC can have widths ranging from 5 to 75 nm and lengths exceeding 5 μm. Nanocellulose fibrils show strong nanoscale interaction resulting in a high mechanical strength material with high resistance to diffusion. Nanocellulose and its composites were shown to have outstanding barrier properties against oxygen, air and reasonable barrier properties to water vapour [11]. Nanocellulose can be obtained at relatively low cost from renewable feedstocks, such as wood, rendering it particularly attractive for the development of sustainable barrier materials; the volume of research on NC has grown exponentially over recent years [12,13]. Though often hypothesized to be recyclable, the reprocessability of NC films has never been demonstrated.

This objective of this study is to evaluate the reprocessability and full recyclability of virgin NC films into a recycled NC film via vacuum filtration. By evaluating the barrier properties of virgin NC film and the effects of recycling on the barrier performance and strength of NC film, we aim to demonstrate that NC film is easily reprocessable and fully recyclable, and a suitable alternative to conventional packaging materials.

2. Materials and methods

The nomenclature for nanocellulose has not been reported consistently in the literature. As well as nanocellulose (NC), it is also called micro-fibrillated cellulose (MFC), cellulose nano-fibrils, cellulose micro-fibrils and nano-fibrillated cellulose (NFC). In this paper, we use NC as the generic term for the cellulose nanomaterials used. The NC used was supplied from DAICEL Chemical Industries Limited (Celish KY-100S) at 25% solids content. DAICEL NC (Celish KY-100S) has cellulose fibrils with an average diameter of ~ 73 nm with a wide distribution of fibre diameter, a mean length of fibre around 8 μm and an average aspect ratio of 142 ± 28 [14]. DAICEL KY-100S is prepared by micro fibrillation of cellulose with high-pressure water. The crystallinity index of DAICEL nanocellulose was measured to be 78% [15]. NC suspensions were prepared using by diluting the original concentration of 25 wt% to 1.5 wt% with de-ionized water and disintegrating for 15,000 revolutions at 3000 rpm in a disintegrator.

2.1. Preparation of nanocellulose film by vacuum filtration

The Virgin NC films were prepared using the conventional vacuum filtration method using British Handsheet Maker (BHM) as reported in the literature [16]. 600 ml of NC suspension with 0.2 wt% concentration was poured into a cylindrical container having a 150 mesh filter at the bottom and filtered to form a wet film on the mesh. The wet film was carefully separated using blotting papers and subsequently dried at 105 °C in a drum drier for around 10 min.

2.2. Recycling of nanocellulose film

Recently, a spray coating method to produce NC films on a smooth and polished stainless steel surface was developed and this method is capable of spraying a high solids NC suspension [17]. To make the large quantity of films required for recycling, we prepared 40 films according to this method [17,18] by spraying each film onto a smooth stainless steel plate on a moving conveyor at a fixed velocity 0.32 cm/s using a Professional Wagner spray system (Model number 117) at a pressure of 200 bar. The type 517 spray tip used in the spray system produce an elliptical spray jet and the spray jet angle and beam width are 50° and 22.5 cm, respectively. The spray distance is 30.0 ± 1.0 cm from the spray nozzle to the circular steel plate. After spraying, the film on the plate was dried under restraint at the edges for at least 24 h.

After drying, the nanocellulose films were dispersed and suspended in water following TAPPI standard T205 SP-02, where the films were torn into pieces of 1 cm × 1 cm dimensions and soaked in de-ionized water for 24 h. The soaked films were disintegrated for 75,000 revolutions at 3000 rpm in a disintegrator Model MK III C. The obtained suspension was then made into films according to the vacuum filtration method explained above. Fig. 1 shows the method of recycling of spray coated NC films.

2.3. Evaluating NC fibre diameter

A drop of 0.2 Wt% of recycled or virgin nanocellulose suspension was cast on the silicon chip and then dried in a controlled laboratory environment. The dried suspension on the silicon chip is coated with an iridium layer. Its surface was studied using secondary electron mode-II with FEI Magellan 400 FEGSEM for NC film at a voltage of 5 KV. The diameter distribution of the raw nanocellulose fibres and recycled NC fibres were measured with Image J. The data are reported as average diameter of NC with 95% confidence interval. The supplementary information gives the micrographs and the diameter distribution histograms of virgin and recycled nanocellulose fibres.

2.4. Evaluating NC film properties

All prepared virgin and recycled NC films prepared were stored at 23 °C and 50% RH for 24 h prior to further testing.

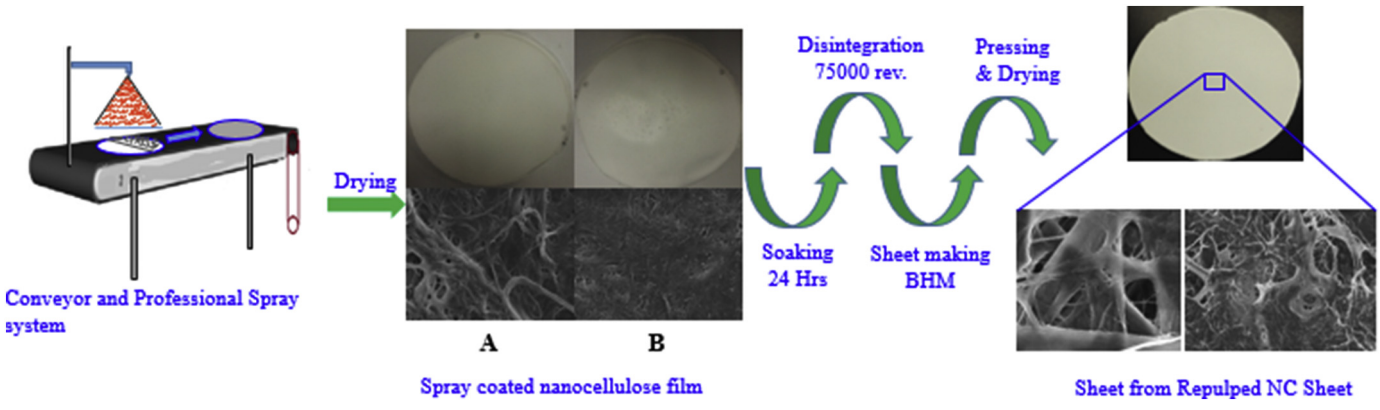

Fig. 1. Method on recyling of spray coated virgin nanocellulose films.

2.5. Basis weight

The basis weight (g/m^2) of each nanocellulose film was calculated by dividing the weight of the film, after 4 h drying in the oven at a temperature of 105 °C, by the film area.

2.6. Thickness of NC films

The thickness of the virgin and recycled NC films was determined using a Thickness Tester Type 21 from Lorentzen & Wettre AB, Stockholm, Sweden. The thickness of each NC film was evaluated at fifteen points and averaged. The thickness of NC film was measured according to TAPPI T 411, 2015.

2.7. Apparent density

The apparent density of the NC films was evaluated through dividing basis weight by mean thickness of the film.

2.8. Air permeability

The air permeance of dried NC films was measured with a L&W air permeance tester with an operating range from 0.003 to 100 μm/Pa·S. The mean value of air permeance evaluated from 3 different areas of each NC film was reported. The Technical Association of the Pulp and Paper Industry (TAPPI) standard T 460 is used to measure the air permeance of the films.

2.9. Water vapour permeability

Water vapour permeability (WVP) was evaluated according to the American Society of Testing and Materials (ASTM) standard (E96/E96M-05) method using anhydrous Calcium Chloride ($CaCl_2$). In this method, NC film was dried for 24 h at a temperature of 105 °C in an air oven. ~40 g of dried anhydrous $CaCl_2$ was added into the cups and covered by the NC films. The increase in weight of the cups is caused by the absorption of water vapour by $CaCl_2$ in the cups through NC film. Test sample was weighed at standard time intervals. The variation in weight of the cups with time was noted and the WVTR calculated from the slope of the line between weight and time. The water vapour transmission rate were carried out at 23 °C and 50% Relative Humidity (RH). The water vapour transmission rate (WVTR) of NC film are normalised with thickness of the NC film and converted into WVP. The mean value of three replicates of each virgin NC film was reported. The value of four different recycled NC films were reported.

2.10. ***Film uniformity analysis***

The uniformity of the NC films were evaluated using the Paper Perfect Formation (PPF) Tester (OpTest Equipment Inc., Canada) which measures the optical uniformity of light transmitted through the sample. In brief, the PPF consists of a black and white camera based image analyser and uses a CCD camera interfaced with 256 Gy levels, 65 μm/pixel resolution. The analyser uses a diffuse quartz halogen light source with IR filters and automatic intensity control. The PPF classifies formation quality over 10 length scales ranging from 0.5 mm to 60 mm. The data reported here is the Relative Formation Value (RFV) of each component relative to one of the films made by vacuum filtration, which was used as a reference film. Three films were measured for each condition, with the results averaged. RFV value less than 1 means that the optical uniformity of the NC film tested is worse than the reference film at that length scale.

2.11. Surface properties

The surface roughness of the NC films was evaluated by Parker surface instrument and optical profiler (Bruker Contour GT-I). The raw image from Optical profilometry is processed with the Gwyddion 2.49 software to accurately evaluate RMS of each film. Surface topography of the film was studied using secondary electron mode-II with FEI Magellan 400 for virgin and recycled NC film.

2.12. Mechanical properties

The strength of both virgin and recycled NC films were evaluated by an Instron model 5566 using test specimens of 100 mm length and 15 mm width, conditioned for 24 h at 23 °C and 50% RH before dry tensile testing based on the Australian/New Zealand Standard AS/NZS 1301.448S-2007. All thickness and tensile tests were done at 23 °C and 50% RH. The samples were tested at a constant rate of elongation of 10 mm/min. The Tensile Index (TI of the samples was calculated from the tensile strength (expressed in Nm^{-1}) divided by basis weight (gm^{-2}). The mean value was obtained from six to seven valid tests and the error bars in the plots indicate standard deviation.

The zero span tensile index of the films were evaluated with a Pulmac Troubleshooter using six samples 1.5 cm wide and 0.5 cm long for each test [19]. In brief, six samples of NC film were required for an individual investigation. A specimen of NC film was placed in the central clamping area of the tester and two other samples were kept under the two back steps of the clamping jaws to ensure proper jaw alignment under pressure. After each test, the samples were removed and replaced. Before the zero-span testing, optimum clamping pressures were determined. An optimum clamping pressure of 70 psi was used for nanocellulose film samples.

3. Results

3.1. Air permeability

The air permeability of the virgin NC film was less than 0.003 μm/Pa·S, which is the detection limit of the instrument, confirming the film is highly impermeable for packaging application. The air permeance of the recycled NC film was 0.0045 μm/Pa.S, which still provides a good impermeable film for packaging.

3.2. NC film density

The relationship between film density and basis weight is shown in Fig. 2, for all the sheets made in this study. The effects of reprocessing can be seen in a change in apparent density as shown in Fig. 2. The apparent density of NC films from virgin fibres is higher, demonstrating that a less compact structure is formed after recycling. It is noteworthy that the same process was used to make both the recycled film and virgin film by vacuum filtration, therefore, the decrease in apparent density after recycling is attributed to fibre properties and not to process.

The density of the NC film is approximately the same and independent of the NC film basis weight for both the recycled and virgin NC film, but it is statistically lower for the recycled NC film. The reason for the reduced density of recycled NC film is probably the formation of larger aggregates in the nanocellulose fibrous network that has hindered the compaction of the fibre network. As a result, recycled NC films have formed larger pores, which has caused an increase in permeation of water vapour and air through the pores. Drying of recycled cellulose fibres and fibre hornification may also have reduced the fibre swelling capacity and decreased the conformability of recycled fibres, which will also reduce the compaction of the fibre web as the film forms. This will also reduce the film density.

3.3. Water vapour permeability (WVP)

The Water Vapour Permeability (WVP) was measured in triplicate for all samples. The results are compared in Fig. 3 as a function of film basis weight. Fig. 3 shows that recycled cellulose films show higher

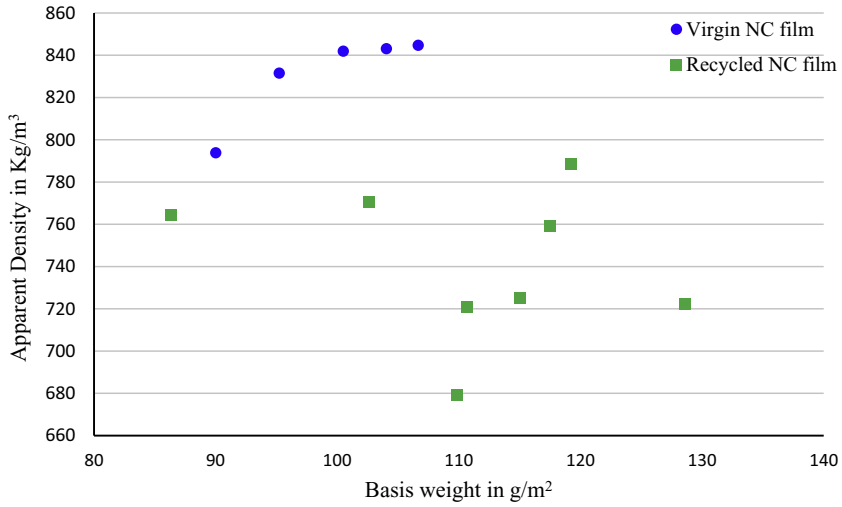

Fig. 2. Effect of recycling on the density of the NC films.

WVP than the virgin NC films, with an average increase of approximately 7.5×10^{-11} g.m^{-1}.s^{-1} Pa^{-1}.

Agglomerates from the incomplete breakdown of recycled films into separated nanofibers, produce non-uniformity in the film and will increase the size of both the surface and bulk pores elevating water vapour permeability and air permeance over than that of virgin NC film. These floc aggregates will also have a poorer bond to the separated cellulose fibrils resulting in a weaker recycled NC film. Additionally, the presence of agglomerates reduces the total surface area available for bonding thereby limiting film density, uniformity and compactness of the fibril network.

3.4. ***Film uniformity analysis***

The formation test concludes the good uniformity of recycled NC films compared to the virgin NC film. Fig. 4 also shows that the recycled film is less uniform than that of the virgin NC film at lower inspection tiles of 15 mm and more uniform for areas greater than 15 mm.

3.5. *Mechanical properties of the recycled film*

The tensile strength of the virgin and recycled NC films was measured at both standard 100 mm test spans, in an Instron, and at zero-span. The zero span tensile index is a measure of the nanofibre film strength over a very short span [19]. Fig. 5 showed that the tensile index, at both long and short spans has decreased by 30% and ~ 28%, respectively, for the recycled film compared to the virgin film.

A loss in mechanical strength is expected in recycling of conventional cellulose fibres due to poorer hydrogen bonding between fibres and their hornification. The tensile index of the recycled film is affected by weaker inter-fibre bonds due to reduced conformability of the cellulose fibres [20].

3.6. *Effect of recycling on cellulose fibrils and cellulose film uniformity*

The effect of recycling on the nanocellulose fibres was evaluated with surface morphology, topography and diameter of the fibres measured with SEM micrographs. Fig. 6 shows SEM micrographs of the NC fibres before and after recycling, showing a wide distribution of fibre size in each sample. The average diameter of the nanocellulose was 69.8 ± 11.3 nm before recycling and 69.6 ± 12.6 nm after, showing no evidence of agglomeration at this smaller inspection area. SEM micrographs show a more compact structure after recycling, but no increase in average fibre diameter.

The surface topography and morphology of recycled films were evaluated by SEM micrographs and compared with virgin NC films in Fig. 7.

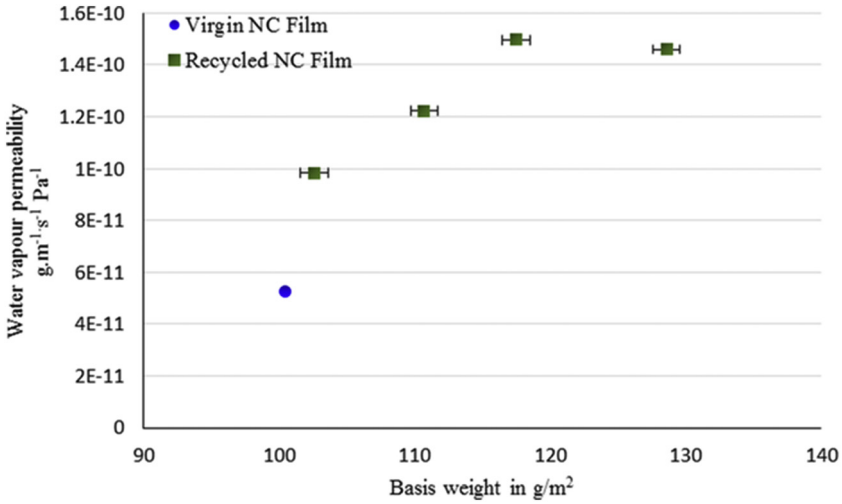

Fig. 3. Water Vapour permeability of Virgin and Recycled NC Film against basis weight of the film.

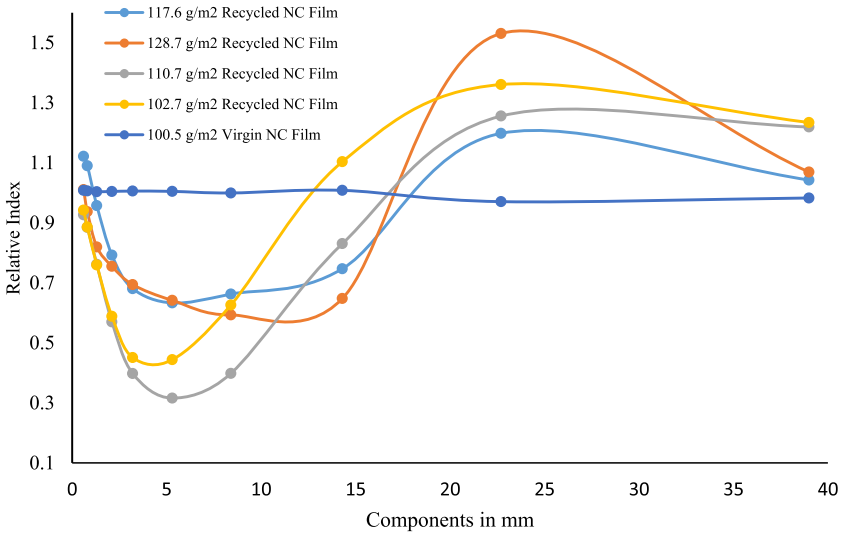

Fig. 4. Formation of Recycled NC film and its comparison with Virgin NC film.

The recycled films retained fibre morphology and topography, showing no significant damage to fibres. Cellulose fibrils were randomly distributed and orientated. In the recycled film, some larger pores were observed and might be a reason for increased air permeance and water vapour transmission. Additional micrographs of both virgin and recycled NC fibres and NC film from virgin and recycled NC fibres from 1 to 100 μm are in the supplementary information.

3.7. Surface roughness investigation

Fig. 8 shows the surface roughness of the recycled and virgin NC films measured using optical profilometry. For an inspection area of 125.7 μm × 94.2 μm, the RMS roughness of the recycled film was found to be 2624 nm and 3116 nm on filter side and free side, respectively, showing a similar roughness to the values of 2445 nm on filter side and 3113 nm on free side after recycling. Previously published data shows RMS roughness at 2673 nm and 3751 nm for NC film via vacuum filtration [17]. Additional optical profilometry images (5× magnification) for virgin and recycled NC are in the supplementary information, and also show similar surface roughness for virgin and recycled NC films.

4. Discussion

The effect of recycling on the NC fibres and NC films was tested at a range of length scales, and is summarised in Table 1. The effect of recycling on virgin NC fibres is predominantly observed at larger inspection areas affecting its properties such as zero-span strength, strength, WVP, air permeability and optical uniformity.

The change in the properties of recycled NC fibres cannot be explained by the traditional model of fibre hornification on recycling, which impacts the bonding between fibres and mostly reduces the strength of NC film. Our best explanation is that some of the agglomeration in initial film preparation has not been fully broken down, leaving small flakes. These flakes of material are probably at the 100 μm or so scale. If the structure is partly composed of flakes of materials connected with NC fibres, then this will not pack together as well as individual fibres, thus lowering density, reducing uniformity, and lowering strength at multiple length scales, while at the same time increasing permeability, with only a moderate decrease in density.

However, these effects are limited and recycling does not undermine the applicability of the reprocessed product, which is still both strong, with reasonable barrier performance. It should be noted that the properties of the recycled film might be further improved by optimising

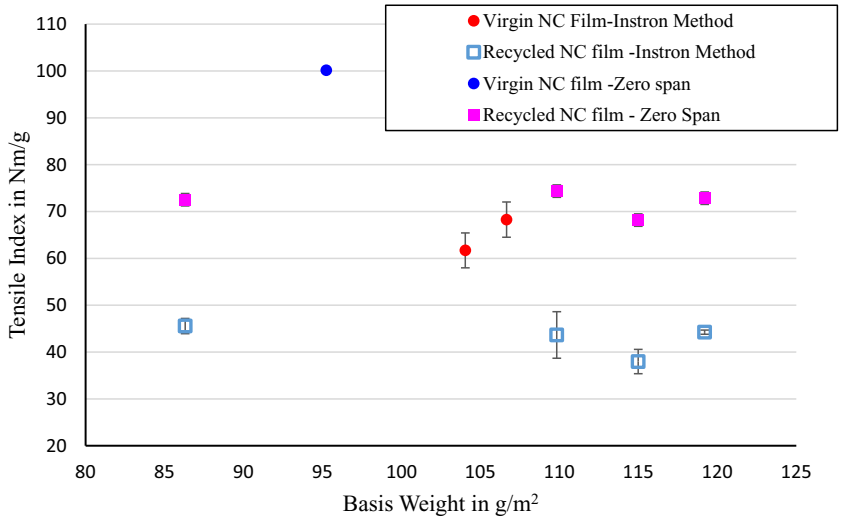

Fig. 5. Effect of basis weight and preparation process on Tensile Index and Zero Span Tensile Index of NC Film via Vacuum Filtration and recycled film.

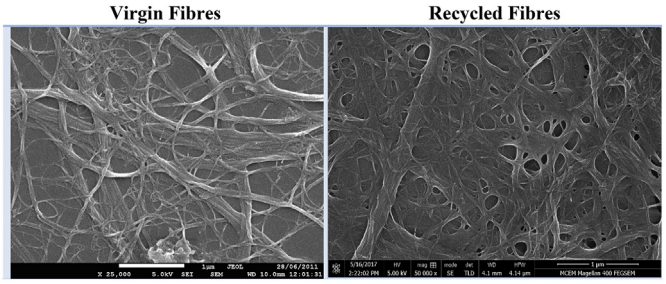

Fig. 6. Scanning Electron Micrograph of nanocellulose before and after recycling.

the recycling conditions and processing. Possible strategies could be to increase the disintegration time or to use well established chemistry from the paper recycling process to improve the separation of the fibrils [21]. Homogenisation of the disintegrated fibres could also be used; this was an effective technology to break down clay agglomerates within a cellulose nanofiber suspension [22]. These additional processes could also reverse the effects of larger aggregates formation. Mixing recycled and virgin NC fibres could also produce films with enhanced barrier performance due to substantial increase of narrow pores in the films. From this investigation, it has been determined that fibrils are not impacted in the micro scale by recycling, retaining their structure and size. A limited negative impact on WVP and air permeability is observed and is likely due to the formation of small agglomerates. These may also have reduced the strength, although other factors such as hornification may be playing a role.

The potential of the recycled NC film as a packaging material can be evaluated through comparing with numerous synthetic and other cellulose polymers. The WVP of virgin NC films and recycled films of approximately 100 g/m^2 are 4.97 $\times$ 10^{-11} and 9.83 $\times$ 10^{-11} g/m.s.Pa, respectively. This is somewhat above WVPs for plastic packaging materials. For example, Ethylene-vinyl acetate (EVA), Polyamide (PA), Polycarbonate (PC), Low Density Poly-Ethylene (LDPE) and Poly Propylene (PP) have been reported at 3.41 $\times$ 10^{-12}, 7.54 $\times$ 10^{-12}, 6.78 $\times$ 10^{-12}, 8.75*10^{-13} and 2.94 *10^{-13} g/m.s.Pa respectively [[5], Data taken http://usa.dupontteijinfilms.com]. However, this difference can be overcome by using NC films of higher thickness. The standard thickness of plastics reported falls between 15 and 25 μm, whereas the thickness of standard 100 g/m^2 films prepared in this work are approximately 100 μm, which then attains WVTRs lower than that of PA and PC and almost equal to that of EVA. This demonstrates the applicability of recycled

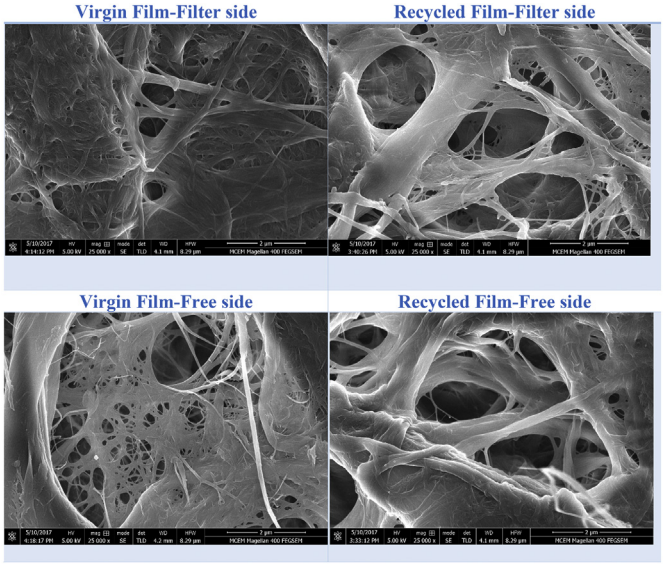

Fig. 7. SEM Micrographs of Virgin and Recycled NC films 2 μm scale bar.

products and the suitability of the recycling process. The recycled NC films also have comparable WVP with the virgin NC films of cellulose nanofibrils (CNF) of 8.12 $\times$ 10^{-11} and acetylated CNF of 6.35*10^{-11} g/m.s.Pa previously reported in Rodionova, 2011 [23]. The full set of data is given in a table in supplementary information. Recycled NC film can be promised as a suitable alternative for synthetic packaging.

The strength of the recycled films is also impacted by the effects of recycling on fibres, however the recycling process retained 70% of film tensile strength. This, too, could possibly be further enhanced by procedures discussed above. The micrographs of recycled films confirm the presence of intact fibres. The roughness of the recycled film is similar to a film prepared via vacuum filtration and that of the rough side of the vacuum filtered NC Film. This is critical as the surface roughness and network of pores in NC films are controlling parameters in barrier performance and a change in roughness can cause differing behaviour in wettability of the NC surfaces [24].

Moreover, the recycling process used here is an eco-friendly and chemical free process and the simplicity and efficiency of reprocessing, i.e. soaking and disintegration, and ease of upscaling for recycling processes demonstrate the unique advantages obtained herein. Recycled NC film obtained can serve as an alternative to synthetic polymers where recycling and reprocessing is not possible or very difficult.

While plastics, such as LDPE are low cost and easy to fabricate into a desired form, they are produced from by-products of fossil fuel. Such plastics are neither renewable nor biodegradable and are a serious threat to the ecosystem. 322 million tonnes of plastics are produced every year and a substantial fraction of accumulates as waste in the environment as it is not biodegradable [25]. Recently the European Union has introduced new rules to reduce the amount of single-use plastics in applications such as packaging, which will reduce the cost advantages of plastic packaging [26,27]. Biopolymers are a potential choice to replace fossil-fuel derived plastics. However, biopolymers such as starch or chitosan have neither good enough strength nor appreciable barrier performance. Therefore, NC fibres, with better strength and barrier performance are being actively developed as barrier layer alternatives to conventional plastics [28].

Preliminary energy consumption analysis on a comparison of spray coating with vacuum filtration concludes that spray coating consumes 0.15 MJ for spraying 1 kg of dry NC film, compared with vacuum filtration which requires 0.56 MJ/Kg. The energy required for spraying the film is similar to that required to form a conventional film of Low-Density Polyethylene (LDPE).

The production of nanocellulose consumes ten times more energy than conventional packaging films [29,30], although significant research is being conducted to lower the energy consumption. In addition, it should be noted that the full scale production of NC is still in the early stages of development and that estimates of energy consumption have often been derived using laboratory scale production. Recent analysis has suggested that substantial savings in energy could be expected as production facilities are scaled up [31]. Growing biomass for nanocellulose will also have significantly higher land-use and water consumption, than is required to produce polyolefin products. From this particular comparison, it could easily conclude that conventional packaging films are more sustainable and the sustainability trade-off between petroleum-derived and bio-based derived packaging may only conserve the non-renewable resources. However, when it comes to recycling, only two third of the packaging films could be recycled and rest ends up in landfill or released to the environment [32]. Waste from packaging materials will overburden the landfills in the near future and poses significant environmental concerns. Work to include the impacts of plastic waste in life-cycle analysis is still in the very early stages of development [32]. It is also interesting to note that the recycling of polyolefin films such as LDPE consumes more than half of the energy in comparison to the energy required to produce these virgin films [33]. In contrast, the energy consumption for recycling

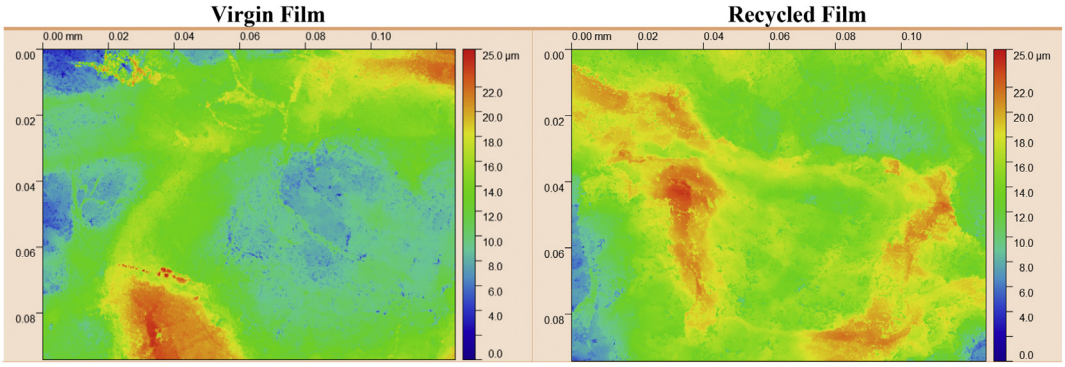

Fig. 8. Optical Profilometry of Free side of NC Film and Recycled NC Film (50 X Magnification).

nanocellulose is negligible in contrast to the energy emission from its production [29]. Thus, considered the end of life analysis, nanocellulose could be more sustainable and greener owing to its ease of recycling when compared to conventional packaging films, and certainly is worthy of active development.

5. Conclusion

Virgin NC films of low permeability and high uniformity were manufactured by standard approch. Virgin NC films were recycled using standard paper testing techniques and formed into films again. Results confirm that some of the agglomeration in initial film formation has not been fully broken down, leaving small flakes. The flakes did not pack together as well as individual fibres, thus lowering density, reducing uniformity, and lowering strength. However, the recycled NC barrier materials retained ~70% of the tensile strength and showed limited reductions in barrier performance and was still able to perform acceptably for most synthetic packaging applications. Nanocellulose films can now provide an alternative to conventional packaging, and readily recycled and reprocessed into a potential barrier material. This process leads to global sustainability by replacing non-renewable polluting synthetic plastic packaging and laminates with a product that can be recycled directly into a barrier material or could be used in the conventional paper recycling process.

Table 1
Effect of recycling on properties of NC fibres.

Measurement Technique	Area examined	Effect of Recyling compared to virgin fibres
SEM Measurement of Fibre diameter	1 µm scale bar	None
SEM Measurement of Film Surface	2 µm scale bar	Nothing conclusive
SEM Measurement of Film Surface	10 µm scale bar	None
Optical Profilometry roughness	100 × 90 µm	None
SEM Measurement of Film Surface	100 µm scale bar	None
Film thickness	159 mm diameter of film	Higher thickness at the same basis weight (g/m^2)
Zero-span strength	Estimated 300 µm span length	30% Less
PPF tester of optical uniformity	1–15 mm inspection areas 16–39 mm inspection areas	Decrease in uniformity at lower areas of Inspection Increase in uniformity at higher areas of Inspection
Water vapour permeability	63.5 mm diameter circle of film	Higher permeability ~ Doubled WVP
Air permeability	50 cm^2 sample	Higher permeability: permeability increased above the detection limit of the instrument.
Tensile strength via Instron Method	100 mm test span	30% less strength

Acknowledgments

The financial support from the Australian Research Council, Australian Paper, Carter Holt Harvey, Circa, Norske Skog and Visy through the Industry Transformation Research Hub grant IH130100016 are acknowledged. The use of the facilities of Monash Centre for Electron Microscopy is acknowledged. Thanks to Dr. Xi-Ya Fang for SEM and Dr. Hemayet Uddin, Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.susmat.2019.e00115.

References

[1] Smithers Pira, The Future of Global Packaging to 2020, (14 December 2015; Available from) http://www.smitherspira.com/industry-market-reports/packaging/the-future-of-global-packaging-markets-to-2020 2015.
[2] G. Davis, J.H. Song, Biodegradable packaging based on raw materials from crops and their impact on waste management, Ind. Crop. Prod. 23 (2) (2006) 147–161.
[3] A. Tukker, Plastic waste-feedstock recycling, chemical recycling and incineration, Rapra. Rev. Rep. 13 (4) (2002) 1–10.
[4] E. Bugnicourt, et al., Processing and validation of whey-protein-coated films and laminates at semi-industrial scale as novel recyclable food packaging materials with excellent barrier properties, Adv. Mater. Sci. Eng. 2013 (2013) 10.
[5] K. Bhunia, et al., Migration of chemical compounds from packaging polymers during microwave, conventional heat treatment, and storage, Compr. Rev. Food Sci. Food Saf. 12 (5) (2013) 523–545.
[6] O.-W. Lau, S.-K. Wong, Contamination in food from packaging material, J. Chromatogr. A 882 (1–2) (2000) 255–270.
[7] T.D. Lickly, K.M. Lehr, G.C. Welsh, Migration of styrene from polystyrene foam food-contact articles, Food Chem. Toxicol. 33 (6) (1995) 475–481.
[8] M.A. Hubbe, et al., Nanocellulose in thin films, coatings, and plies for packaging applications: a review, BioResources 12 (1) (2017) 2143–2233.
[9] R.N. Tharanathan, Biodegradable films and composite coatings: past, present and future, Trends Food Sci. Technol. 14 (3) (2003) 71–78.
[10] H.M.C. Azeredo, M.F. Rosa, L.H.C. Mattoso, Nanocellulose in bio-based food packaging applications, Ind. Crop. Prod. 97 (2017) 664–671.
[11] C. Aulin, M. Gällstedt, T. Lindström, Oxygen and oil barrier properties of microfibrillated cellulose films and coatings, Cellulose 17 (3) (2010) 559–574.
[12] J. Bras, S. Saini, 8 - nanocellulose in functional packaging A2 - Jawaid, Mohammad, in: S. Boufi, A.K. H.P.S (Eds.), Cellulose-Reinforced Nanofibre Composites, Woodhead Publishing 2017, pp. 175–213.
[13] H.P.S. Abdul Khalil, et al., A review on nanocellulosic fibres as new material for sustainable packaging: process and applications, Renew. Sust. Energ. Rev. 64 (2016) 823–836.

[14] S. Varanasi, R. He, W.J. Batchelor, Estimation of cellulose nanofibre aspect ratio from measurements of fibre suspension gel point, Cellulose 20 (4) (2013) 1885–1896.
[15] P. Raj, et al., Gel point as a measure of cellulose nanofibre quality and feedstock development with mechanical energy, Cellulose 23 (5) (2016) 3051–3064.
[16] S. Varanasi, W.J. Batchelor, Rapid preparation of cellulose nanofibre sheet, Cellulose 20 (1) (2013) 211–215.
[17] K. Shanmugam, et al., Rapid preparation of smooth nanocellulose films using spray coating, Cellulose 24 (7) (2017) 2669–2676.
[18] K. Shanmugam, et al., Flexible spray coating process for smooth nanocellulose film production, Cellulose 25 (3) (2018) 1725–1741.
[19] S. Varanasi, H.H. Chiam, W. Batchelor, Application and interpretation of zero and short-span testing on nanofibre sheet materials, Nordic Pulp Paper Res. J. 27 (2) (2012) 343.
[20] M. Delgado-Aguilar, et al., Are cellulose nanofibers a solution for a more circular economy of paper products? Environ. Sci. Technol. 49 (20) (2015) 12206–12213.
[21] M. Hietala, K. Varrio, L. Berglund, J. Soini, K. Oksman, Potential of municipal solid waste paper as raw material for production of cellulose nanofibres, Waste Manag. 80 (2018) 319–326 2018/10/01/.
[22] U. Garusinghe, S. Varanasi, V.S. Raghuwanshi, G. Garnier, W.J. Batchelor, Nanocellulose-montmorillonite composites of low water vapour permeability, Coll. Surf. A Physicochem. Eng. Aspects 540 (2018) 233–241.
[23] G. Rodionova, M. Lenes, Ø. Eriksen, Ø. Gregersen, Surface chemical modification of microfibrillated cellulose: improvement of barrier properties for packaging applications, Cellulose 18 (1) (2011) 127–134.
[24] Pieter Samyn, Wetting and hydrophobic modification of cellulose surfaces for paper applications, J. Mater. Sci. 48 (19) (2013) 6455–6498.
[25] Leonidas Milios, Aida Esmailzadeh Davani, Yi Yu, Sustainability impact assessment of increased plastic recycling and future pathways of plastic waste management in Sweden, Recycling 3 (3) (2018) 33.
[26] European Commission, Single use of Plastics, 28 May 2018; Available from: https://ec.europa.eu/commission/news/single-use-plastics-2018-may-28 2018.
[27] European Commision, Technical report on " A european strategy for plastics in a circular economy", 2018 , Available from http://ec.europa.eu/environment/circular-economy/pdf/plastics-strategy-brochure.pdf.
[28] Joo-Hyung Kim, et al., Review of nanocellulose for sustainable future materials, Int. J. Precision Eng. Manuf. Green Technol. 2 (2) (2015) 197–213.
[29] Qingqing Li, Sean McGinnis, Cutter Sydnor, Anthony Wong, Scott Renneckar, Nanocellulose life cycle assessment, ACS Sustain. Chem. Eng. 1 (8) (2013) 919–928.
[30] Sue Jackson, T. Bertényi, Recycling of plastics, ImpEE Project, Department of Engineering, University of Cambridge, 2006 , Available from; http://www-g.eng.cam.ac.uk/impee/topics/RecyclePlastics/files/Recycling%20Plastic%20v3%20PDF.pdf.
[31] F. Piccinno, R. Hischier, S. Seeger, C. Som, Predicting the environmental impact of a future nanocellulose production at industrial scale: application of the life cycle assessment scale-up framework, J. Clean. Prod. 174 (2018) 283–295, https://doi.org/10.1016/j.jclepro.2017.10.226.
[32] J. Rydz, M. Musioł, B. Zawidlak-Węgrzyńska, W. Sikorska, Present and future of biodegradable polymers for food packaging applications, Biopolymers for Food Design 2018, pp. 431–467.
[33] Bulim Choi, Seungwoo Yoo, Su-il Park, Carbon footprint of packaging films made from LDPE, PLA, and PLA/PBAT blends in South Korea, Sustainability 10 (7) (2018) 2369.