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An investigation on the ability of Nanofibrillated cellulose to enhance the environmental sustainability of paper product manufacture

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ABSTRACT

There are a number of products which are manufactured at a very large scale globally which are both energy and materials use intensive. In the case of paper and board manufacture, paper pulp (a mixture of cellulose, water and additives such as TiO_2) require large quantities of cellulose, principally from trees and plant sources, with the corresponding addition and subsequent removal of water by mechanical or thermal means.

The objective of the study was to investigate the potential benefit of using a nanofibrillated form of cellulose (NFC) to reduce the total paper pulp quantities used while retaining paper mechanical and printing performance of the paper stock produced. If successfully demonstrated, this would lead to a potential reduction in material usage and a possible pathway to reduce the water evaporative load in the production of paper products.

To investigate the effectiveness of using NFC, we used a conventional 'Top down' approach to create small mass quantities of NFC suspensions generated through high pressure/high shear homogenisation and a microfluidisation recycle loop to break down a refined bleached softwood from a Kraft process feedstock into nanoscalar fibrils. The NFC produced represented 1-3% by weight of the final test paper pulp samples. On completion of nano fibril production, the paper pulp and NFC were combined using an in-line partitioned pipe mixing assembly to ensure homogeneous distribution of the NFC and ensure reproducible composite samples were available for characterisation.

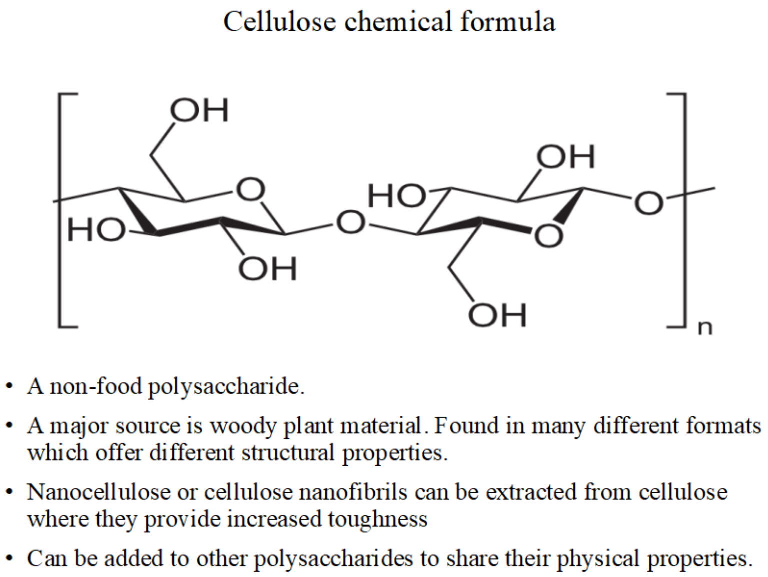
From the measured data, strong evidence indicated that NFC as an added reinforcement aid to bulk paper pulp has an advantageous effect on the ability to create an improved version of paper products with a substantial reduction in the total amount of paper pulp required to maintain both mechanical and printing performance characteristics of NFC enhanced paper products. In addition, the study indicated new opportunities to generate novel functional features for paper and board products using other polysaccharide systems including both chitosan and alginate hydrogels, cellulose acetate and seaweeds as potential mixed hybrid composites to create higher performance paper characteristics.

Keywords

Sugars, polysaccharides, cellulose, nanofibrillated, sustainability, microfluidizer, homogeneous, mechanical testing, hierarchical

INTRODUCTION

Resources that are available for products and product pipelines that provide human centred benefits through cleanliness, hygiene, nutrition, healthcare, intelligent built environments and consumer products need careful consideration in terms of their product lifecycle and their overall sustainability. This has been well documented through the publication ’Cradle to Cradle’ [1] which emphasise why and how we can and must conserve the Earth’s resources for future generations not just through recycling but through reuse and refunctionalisation of materials. This paper describes a Design:STEM Integrated approach that allows consideration of both materials and materials fabrication (making) in new, innovative ways and which can be summarised in general in the following Figure 1. Over the last decade, there has been a very significant increase in the number of useful materials that have been shown to exhibit new and improved performance characteristics in relation to both conventional and new user centred needs [2]. In general, these materials fall into the following classes: Natural, Responsive, Cellular and Structural. Below we will concentrate on Natural materials whose properties are inherently responsive and which can be processed or fabricated to provide beneficial mechanical and interactive behaviours that have both biocompatibility and sustainability through potential reuse and refunctionalisation. The focus of the work presented below therefore centers on how to increase the sustainable production of paper. In particular, the application of abundant polysaccharide materials that are both biocompatible and refunctional [3,4]. The results presented concentrate on the role of cellulosic materials in the form of cellulose and nanoscalar or nanofibrillated cellulose and how best to create more sustainable macroscale paper products manufacture through material property interactions at the macromolecular scale. Fig.1


Cellulose chemical formula

- A non-food polysaccharide.
- A major source is woody plant material. Found in many different formats which offer different structural properties.
- Nanocellulose or cellulose nanofibrils can be extracted from cellulose where they provide increased toughness
- Can be added to other polysaccharides to share their physical properties.

Figure 1: Cellulose chemical formula

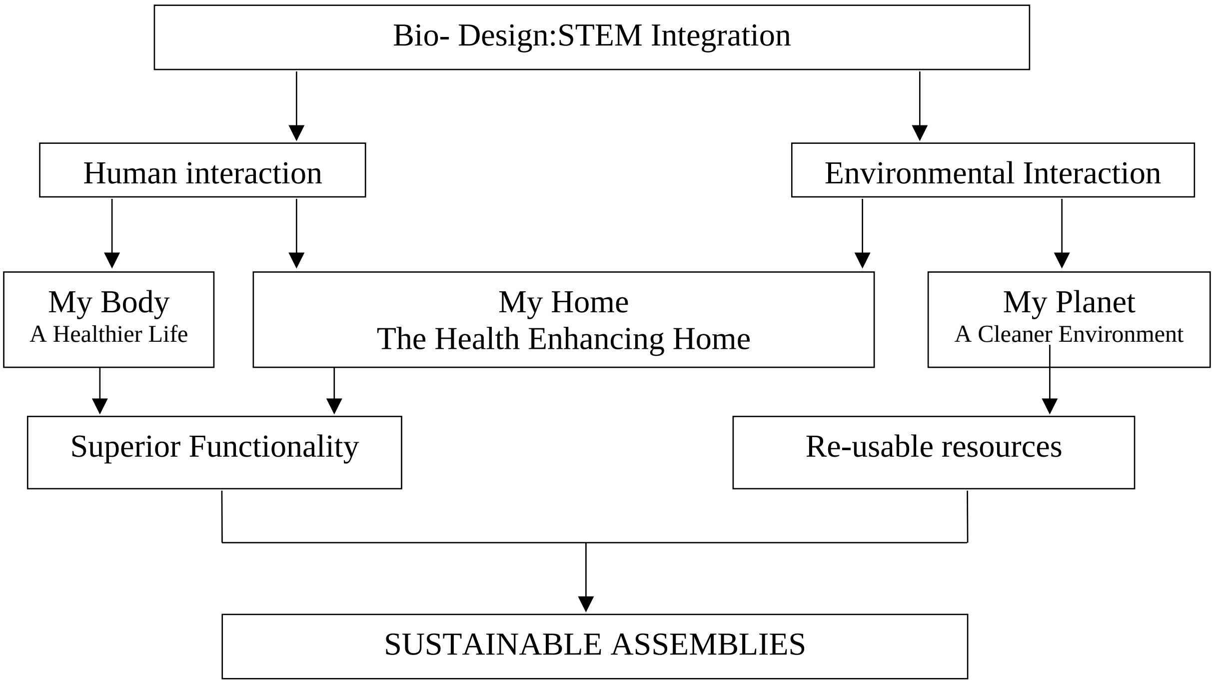


Figure 2: Bio- Design:STEM Integration

LITERATURE REVIEW

The research literature covering natural materials and their fabrication into useful products and relevant enabling technologies is extensive in both insight and application. Our work over the last three years in Design:STEM Integrated Systems has focused on responsive polymers and gels, cellular solids including foams and aerogels and natural materials, in particular the application of abundant polysaccharide materials that are both biocompatible and refunctional due to inherent characteristics that can interact with human centred needs and behaviours.[2-4] This short review concentrates on the role of cellulose based materials as it has been demonstrated to be one of the most versatile and effective ways to create both a sustainable materials technology and a potential 'Effects to Benefits' platform. [5, 6] as highlighted in Fig 2 above and in Fig 3 below.

Natural materials are a product of the forest (cellulose), the sea (chitin and Chitosan), from crops (starch biomaterials) and from bacteria. Cellulose along with lignin, another product extracted from wood form the two most abundant and relatively low cost natural materials that have been studied in detail in order to understand how best to utilise them for human, economic and environmental benefit [1,7-10]. The physico-chemical properties of NFC and its incorporation into bulk paper pulp (BPP) formulations indicate that NFC lends itself to a very wide applications space that incorporates potentially favourable fabrication choices and novel manufacturing routes through 0,1,2,3,4D manipulation. i.e. 'dots', 'lines', 'surfaces', 'structures' and spatiotemporal constructs due to the rheology and malleable nature of cellulose often in the form of a super molecular polymer, hydrogel or as an organic aerogel assembly. [5, 11-22]. Nanocellulose introduction into paper formulations therefore provides a very wide ranging set of application opportunities from use in regenerative medicine [15,16] to structural applications in lightweight architectural structures [17] to automotive , aerospace and Space [18,19,20] to fashion and consumer goods [21,22] incorporating , for instance, new paper and board constructs in new ways that are attractive through their interactive attributes as well as their sustainability through reuse and refunction. [23-32]. We can summarise the key requirements of research and development through Fig. 3 below which follows the evolution of the polysaccharide platform from the bulk material (cellulose) through to the synthesis of NFC's to its incorporation for implementable manufacture of nano composite based paper. Figs. 4

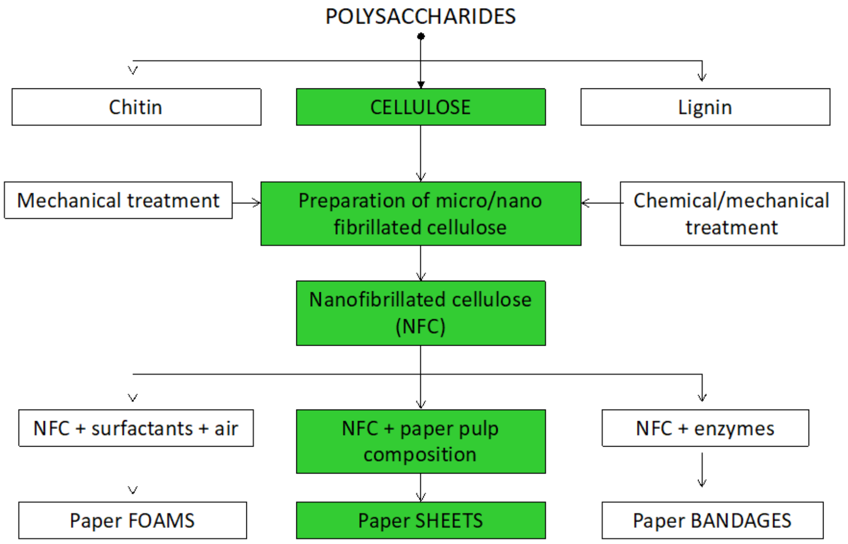


Figure 3: Polysaccharides and the future of paper products

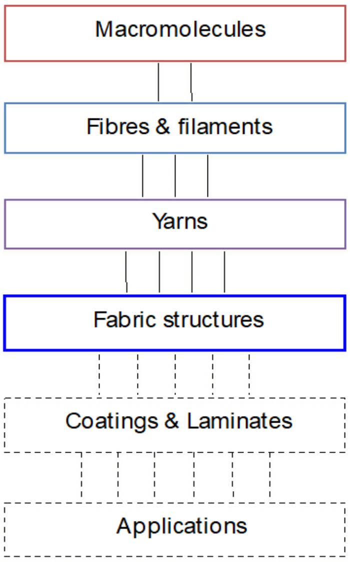


Figure 4: Textile 'DNA'

MATERIALS AND METHODS

Cellulose and Nanofibrillated Cellulose (NFC) materials

Cellulose has many excellent physico chemical characteristics. It is the most abundant natural and renewable materials on Earth and has been the subject of thorough investigation as to the use and novel application. It is the main constituent of wood & bamboo and contributes to the hierarchical structure of nearly all plant cell walls which, in turn, allows them to be disintegrated, providing native cellulose nanoscale fibres with good mechanical properties within crystalline and amorphous domains. It is an excellent example of Nature's way of creating a sustainable biopolymer that is constructed from the bottom up from CO_2 and water catalysed by chlorophyll. [33-36]. An essential characteristic is the formation of its macromolecular structure controlled by hydrogen bonding that links and dictates the positioning of glucose molecules through an energetically favourable condensation reaction pathway. Fig.5

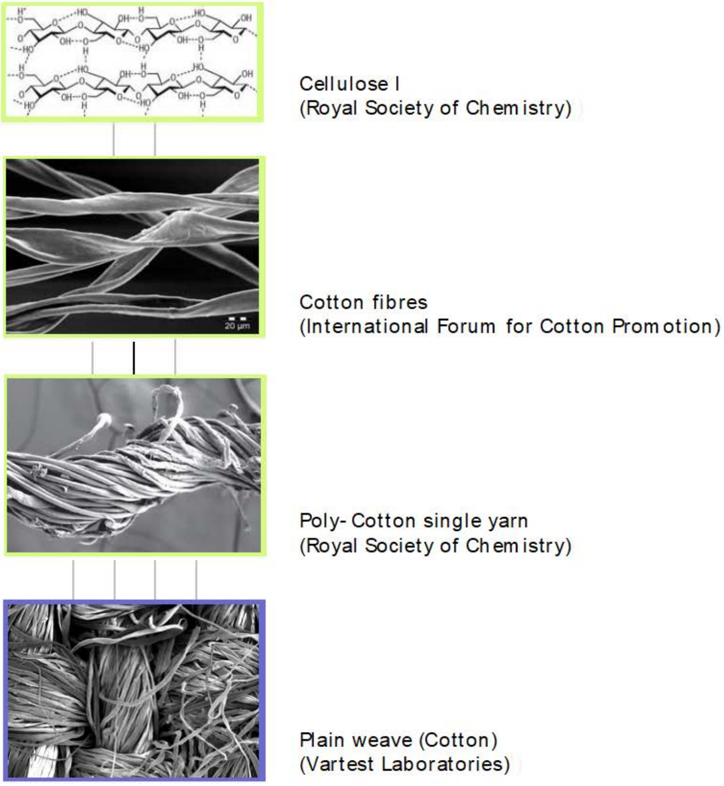


Figure 5: Textile visual 'DNA'

The nano-micro-meso-macro scale characteristic of cellulosic growth can be exploited to generate a reverse breakdown of macro cellulose to micro and nano cellulose. In the case of nanoscalar material, the formation of nanocrystalline and nanofibrillated forms are possible. In top down energetically intense processing, nanofibrillated cellulose (NFC) is obtained with an average fibril diameter between 3 and 30 nanometres and an overall fibril length of 1-5 microns. For typical NFC cylindrical dimensions, the specific surface area S_gSA is O(100m^2/gm), making nanofibrillated cellulose extremely reactive. In addition, individual NFC fibrils are very strong (37-40) which makes the combination of a nanoscalar network of strong entangled fibrils ideal for the creation of fibril based reinforcement. When combined with cellulose bulk paper pulp (BPP), provides the hypothesis that we can create a new paper product that is mechanically robust and potentially requires a reduced BPP content in order to yield a more sustainable product outcome.

Processing technologies:

There are numerous routes to the creation of NFC. The most common techniques for NFC preparation feature a number of energy intensive mechanical 'Top Down' approaches, and chemical and biological 'Bottom up' methodologies well documented in the literature [38-42]. They can be summarized for selection purposes as follows:

a) Mechanical – energy intensive but relatively uncomplicated
b) Chemical – complex pathways, higher cost but good control
c) Biological – the subject of the most active research in order to explore the concept of living material systems for a sustainable bio-economy

For our purposes, a mechanical route was chosen to create NFC that allowed us to minimize the use of additional chemicals. Once the dispersed phase NFC was acceptable in terms of nanoscalar attributes, the NFC was then mixed with bulk paper pulp (BPP) using customised in-line partitioned pipe mixing to create homogeneous composite mixtures. The reproducible composite feed material was pressed into 10cm x 10cm test samples of final paper sheets for mechanical property evaluation. The experimental set-up is shown diagrammatically in Fig. 6 below and biological 'Bottom up' methodologies well documented in the literature [43-47]. They can be summarized for selection purposes.

EXPERIMENTAL STUDIES

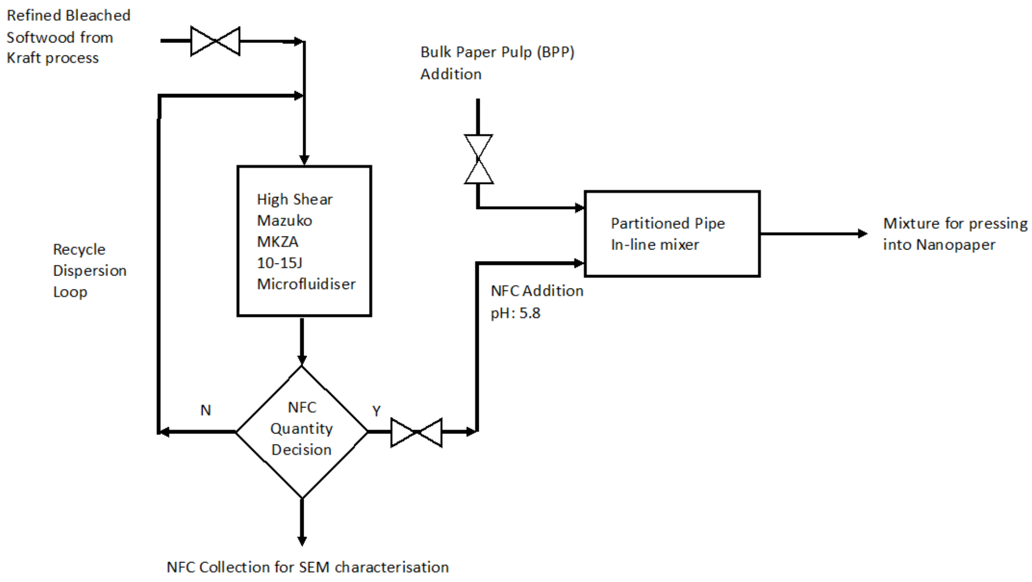


Figure 6: Materials processing flowsheet

To test our hypothesis that NFC addition to BPP feedstock can lead to sustainable paper products we had the following materials and processing objectives:

i) To prepare and disperse NFC suspensions and incorporate them homogeneously into BPP suspensions
ii) To prepare the resulting nanopaper sheets and test the effect of added quantities of NFC on the mechanical properties of the prepared nanopaper in the form of pressed test sheets. (modulus, strength, breaking/tearing load and air permeability)
iii) Establish the conditions of NFC addition that provides a significant reduction in the amount of BPP required to equal or exceed the characteristics of base BPP paper production

To quantify and characterize the effect of incorporating NFC into BPP and to measure the effect on fabricated paper sample mechanical properties and surface features while systematically reducing the mass of the paper pulp used in each sample, the following materials, process equipment and characterization apparatus were used.

1 Basic paper pulp feedstock was gently bleached softwood from the Industrial Kraft process and supplied by VTT
2 NFC material samples were obtained using mechanical nano fibrillation carried out in a Masuko MKZA 10-15J apparatus to generate high shear breakage conditions followed by a 5 pass recycle loop through a micro-fluidisation zone.
3 The NFC Suspensions were then added into a partitioned pipe mixer with a BPP feed to generate reproducible samples for paper sheet testing.
4 NFC rheological characterization was carried out using a Brookfield Viscometer RVDV 111 with a V73 vane spindle at 23^0C. The results are shown in Table A below.
5 Mechanical property measurements were carried out using a bench scale Instron mechanical tester
6 The NFC suspensions were incorporated into BPP at a range of concentrations frpm 1-4% by weight in a series of experimental trials in which the basic weight of the BPP content was reduced from 100 to 70 wt%. The experimental design pattern is shown in Table B below:

Experimental results

Table A. NFC suspension rheology

Yield Stress (Pa)	Viscosity mPa sec @ 0.5rpm	Viscosity mPa sec @ 10rpm	
49	208971	25701	Mean
4	6460	654	Standard Deviation

Table B. NFC – Paper pulp sample plan

Trial no.	Name	Grammage (g/m^2	Thickness 9microns)	Density (kg/m^3)	Base Weight	NFC Con^n (wt%)
1	Reference	99.3	137	723	100	0
2	90 NFC 1	87.0	120	726	90	1
3	90 NFC 3	88.1	120	738	90	3
4	80 NFC 1	75.9	108	705	80	1
5	80 NFC 3	78.2	111	703	80	3
6	70 NFC 1	66.5	97	684	70	1
7	70 NFC 3	67.6	98	688	70	3

For each formulation, mildly dried sheets of treated paper (0.14m x 0.14m) were prepared. Each of the 7 experiments were repeated 5 times and the grammage, paper sheet thickness, tensile strength, strain at breaking point, Elastic modulus and sheet stiffness were measured and recorded in Tables C and D and in Fig,7 below.

Table C. Mechanical property characteristics (mean of 5 measurement cycles) for NFC bulk paper pulp reinforced nano-composites

Sample code	Tensile strength N/m^2	Textile index N/m^2	Breakage energy J/m^2	Breakage energy index J/m^{2}gm	Strain @ breakage %	Modulus of elasticity N/mm^2	Tensile stiffness N/m
REF	7000	70.4	215	2.17	4.5	4298	589
90 NFC 1	6370	73.2	188	2.16	4.4	4440	533
90 NFC 3	6790	72.1	200	2.27	4.4	4623	555
80 NFC 1	5550	73.2	160	2.11	4.3	4507	497
80 NFC 3	6110	78.2	180	2.44	4.6	4649	516
70 NFC 1	4830	72.7	141	2.12	4.3	4525	439
70 NFC 3	5170	76.5	149	2.20	4.3	4446	436

Table D. Mechanical property characteristics (standard deviation of 5 measurement cycles) for the above nano-composites

Sample code	Tensile strength N/m^2	Textile index N/m^2	Breakage energy J/m^2	Breakage energy index J/m^{2}gm	Strain @ breakage %	Modulus of elasticity N/mm^2	Tensile stiffness N/m
REF	490	4.93	32.5	0.328	0.40	236	32.4
90 NFC 1	363	4.17	12.9	0.206	0.22	204	24.5
90 NFC 3	455	5.17	26.3	0.298	0.34	221	26.5
80 NFC 1	359	4.74	23.6	0.312	0.42	271	29.3
80 NFC 3	226	2.90	13.7	0.175	0.21	168	18.7
70 NFC 1	271	4.07	18.2	0.274	0.38	280	27.1
70 NFC 3	203	3.01	13.5	0.199	0.26	311	30.5

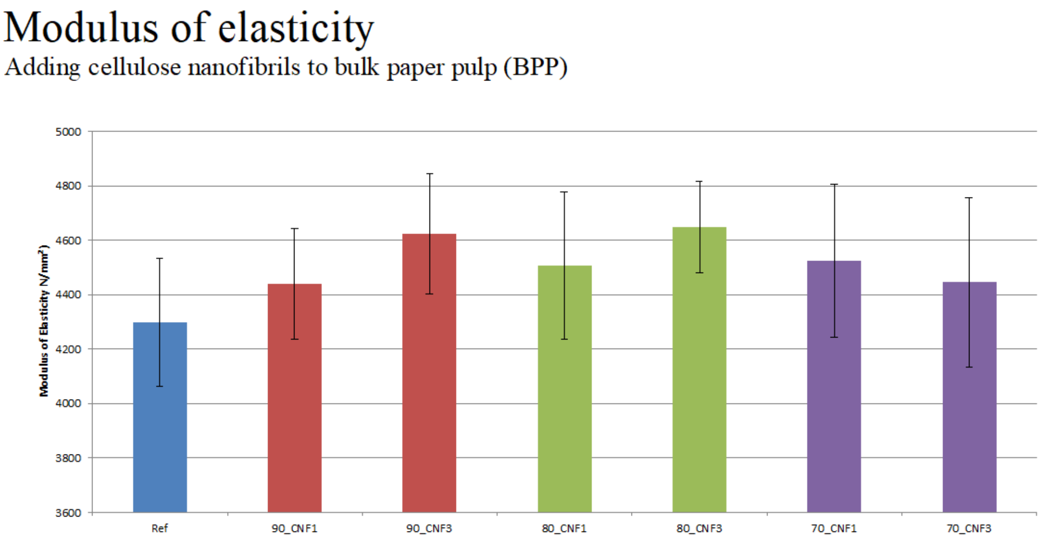


Figure 7: Histogram representation of the BPP modulus at a range of bulk paper solids content

DISCUSSION

The drivers behind this study are based on the continuing need to reduce material use while maintaining material performance. At the same time, asking the question from the point of view of alternative value adding applications that increase the versatility of paper. Nanocomposites have been a feature of material applications from the 1950's onwards and with the accelerated study of nanoscience and technology, much has been learned about the new uses and functions that can be attributed to nanoscalar objects that can enhance mechanical and physico-chemical reactivity.

Nanocomposites by adding nanoscale reinforcements to tune or tailor mechanical properties have now become regarded as an advantageous way to provide dispersed phase additions of small nanoscalar material quantities, usually < 5% by weight to minimize excess cost, into a bulk commodity material to reinforce the mechanical characteristics of the ensuing bulk material. In the case of paper production, creating a homogeneous mixture of bulk paper pulp (BPP) and nanofibrillated cellulose (NFC) [7,8,32-38].

Perhaps the key characteristic feature of nanoscalar additives lies in their extremely high surface/volume ratio and so the properties of the nanocomposite material greatly depends on the engineering of the interface interactions and subsequent properties. However, nanoscalar materials nearly always tend to want to agglomerate and so homogeneous mixing is a key part of generating a successful outcome, in this case BPP reinforcement. (41). In general, nanocomposites allow a better method of adjusting the balance of mechanical properties (strength v's toughness), lighter structures, improved thermal properties and scratch or tare resistance for example. In addition, nanofibrils can provide new or enhanced functionalities, such as electrical conductivity. Optical effects and importantly, gas barrier property improvements (O_2 and H_2O). NFC has a length / diameter ratio >>10 which gives rise to entangled nanofibril networks and, when coupled to the fact that the NFC surfaces are easy to modify due to high degree of reactivity, allows good dispersibility in aqueous environments and therefore the NFC can be admixed with several types of matrix polymeric bulk materials to allow bonding with various surfaces.

The results of the exploration on the role of nanoscalar cellulose have shown, through reproducible experiments, that the mechanical and surface properties of basic paper production can be maintained while at the same time reducing the total bulk paper pulp usage. Both the physico-chemical nature of nano fibrillated cellulose and the ability to homogeneously incorporate the NFC into bulk paper pulp are key to the final paper performance and stem from nanoscalar fibrils with dimensions of 5-50 nanometres (fibril width) and 1-5 microns (fibril length). Measured values of individual fibril mechanical properties, for example Young's Modulus (E) have been measured in the range 60-150G Pa with the spread dependent on the raw material type. The modulus and strength of NFC/paper nanocomposites are estimated from measurements taken on nanocomposite paper sheets (NCP) as shown in the previous section, where it was important to test the reproducibility of the data as shown in Tables (C) and (D) above. From the experimental data, we can make the following conclusions from the experimental investigation concerning the influence of nano-fibrillated cellulose (NFC) content on the quality and performance of bulk paper containing (NFC) as a nanocomposite reinforcement agent and its effect on the ability to 'tune' the paper product mechanical properties as follows:

i. As base weight of NCP decreased, the thickness and density of prepared NCP films decreased.
ii. The addition of NFC influenced the bulk modulus of NCP with the modulus value increasing as the NFC concentration increased.
iii. Surface roughness remained constant across all of the NCP samples produced.
iv. The specific tensile strength or tensile index was maintained despite the significant reduction in base weight by up to 30%

Overall, the results indicate that the grammage of the NCP can be reduced by at least 10-15% without compromising the tensile strength when as NFC concentration of 3wt% is introduced into the bulk paper pulp. This is significant in terms of the potential to reduce total paper pulp and the associated water evaporative load. In addition, elastic modulus was also maintained as well as strain energy required to break the NCP paper films. Since the nanofibrillated cellulose has a very high specific surface area O[100m^2/gm], the reactivity of surface sites is key in developing a physico-chemical network when homogeneously introduced into bulk paper pulp, especially in terms of ease of hydroxyl group interaction. In the experiments undertaken, the ability to ensure homogeneity was vital to ensure any scale up process would be both reliable and reproducible. Given the rheological character of both the NFC and the bulk paper pulp, the use of laminar flow stretching and folding mechanism could be an effective processing technology to carry out such scale up. Further work to establish the most effective fabrication technology for manufacture is essential, the literature has some clear guidance on which process technology would be most beneficial, sustainable and cost effective.

From Fig.7, it is shown that the ability of NFC through it's high surface/volume ratio and its ability to create entangled networks and are well documented in the literature of nanoscalar use of additives incorporated into polysaccharide matrices [42-50]. The most significant consequence from our studies indicate that overall paper quality is at least maintained but with a significant reduction in total paper pulp usage by upto 30% by wt.

It is important to recognise compelling environmental and human centred needs and challenges as identified earlier in the introduction. Creative design when coupled to innovative materials and materials fabrication led to the final choice of experimental design strategy employed. Finally, therefore, it is possible to design and demonstrate better environmental outcomes through novel materials and new fabrications related to nanoscale material characteristics and biotechnology as key enablers for smart manufacturing with applications such as alternatives to synthetic plastics for consumer goods and food packaging. Future follow on work can provide an answer to the tenet that BioNano technology can provide an extensive 'innovation toolkit' that enables tailoring of material systems at the supramolecular and microscale level that can reduce depletion of material use in products used by people every day with no reduction in performance but with the possibility of an increase in new application spaces. Fig. 8, 9, 10

Figure 8: Casting a bio-nanocomposite packaging film

Figure 9: Sample showing laser cut NFC film

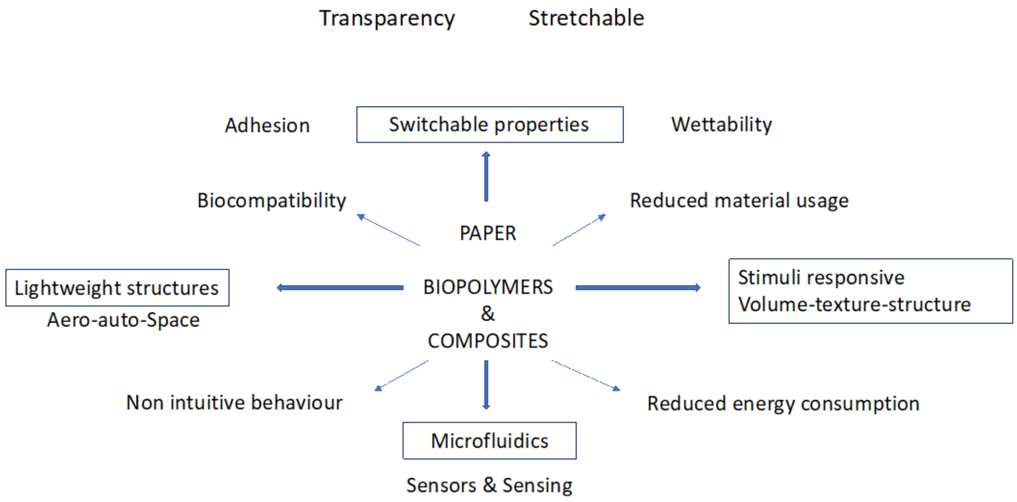


Figure 10: Paper and biopolymers as metamaterial

CONCLUSIONS

Nanofibrillated cellulose (NFC) was found to act as a reproducible reinforcement agent as shown in the measurement of the mechanical property characteristics of fabricated nanocellulose paper (NCP).

In addition, even with additive NFC concentrations of 1-3% by weight, the base paper pulp can be reduced substantially without degradation in mechanical properties and visual appearance of NCP product samples.

The potential reduction in bulk paper pulp content by 20-30 wt% indicated no measurable detrimental effect on NCP quality, however, it does yield the prospect of reduced bulk paper and water use, increasing the possibility of a ‘More for Less’ sustainable and economic production manufacturing route.

It is important to create not only the optimal NFC concentration and nanoscalar size control but it is vital also to achieve homogeneously distributed NFC for optimum benefit in bulk paper pulp manufacture.

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