Role of Cellulose Nanofibrils in Improving the Strength Properties of Papers: A Review

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Role of Cellulose Nanofibrils in Improving the Strength Properties of Papers: A Review

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ABSTRACT

The pursuit for sustainability in the papermaking industry calls for the elimination or reduction of synthetic additives and the exploration of renewable and biodegradable alternatives. Cellulose nanofibrils (CNFs), due to their inherent morphological and biochemical properties, are an excellent alternative to synthetic additives. These properties enable CNFs to improve the mechanical, functional and barrier properties of different types of paper. The nanosize diameter, micrometre length, semi-crystalline structure, high strength and modulus of CNFs has a direct influence on the mechanical properties of paper such as tensile index, burst index, Scott index, breaking length, tear index, Z-strength, E-modulus, strain at break, and tensile stiffness. This review details the role played by CNFs as an additive to improve strength properties of papers and the factors affecting the improvement in paper quality when CNFs are added as additives. The paper also includes techno-economic aspects of the process and identifies areas that need further research.

Keywords: cellulose nanofibrils, paper additive, mechanical properties.

28 # LIST OF ABBREVIATIONS

Abbreviation	Description
CNFs	Cellulose Nanofibrils
CNC	Cellulose Nanocrystals
TEMPO	Tetramethylpiperidin-1-yl-oxidanyl
TMP	Thermomechanical Pulp
CTMP	Chemo Thermomechanical Pulp
C-PAM-B	Cationic Polyacrylamide Hydrated Bentonite
C-PAM	Cationic Polyacrylamide
PAE	Polyamide Amine Epichlorohydrin
GCC	Ground Calcium Carbonate
PCC	Precipitated Calcium Carbonate
GCC-B	Ground Calcium Carbonate with bentonite
BKP	Bleached Kraft Pulp
DIP	Deinked Recycled Pulp
ONP	Old Newspapers Prints
NaClO	Sodium chlorite
NaBr	Sodium bromide
SSA	Specific Surface Area
UBSWP	Unbleached Softwood Pulp
TEM	Transmission Electron Microscopy
RBA	Relative Bonded Area
RE-CNFs	Refined CNFs
EN-CNFs	Enzymatic CNFs
CM-CNFs	Carboxymethylated CNFs
EKP	*Eucalyptus* Kraft Pulp
BHKP	Bleached Hardwood Kraft Pulp
SBKP	Softwood Kraft Pulp

MPSP	Minimum Product Selling Price

1.0 INTRODUCTION

The growing cognisance of environmental concerns has shifted attention from petroleum-based materials to natural organic materials in various applications. Nanomaterials are becoming popular because of their extraordinary properties attributed to the nanosize dimension (Alagarasi, 2013). In particular, cellulose nanomaterials exhibit high strength and barrier properties (Lee et al., 2017). Cellulose is the main component of plant cell walls responsible for providing protection, strength and support when the cells increase in size. The basic structure of cellulose, represented in Figure 1, shows that cellulose is a long, narrow polymer in which D-glucose units are joined in a 1, 4 β-linkage.

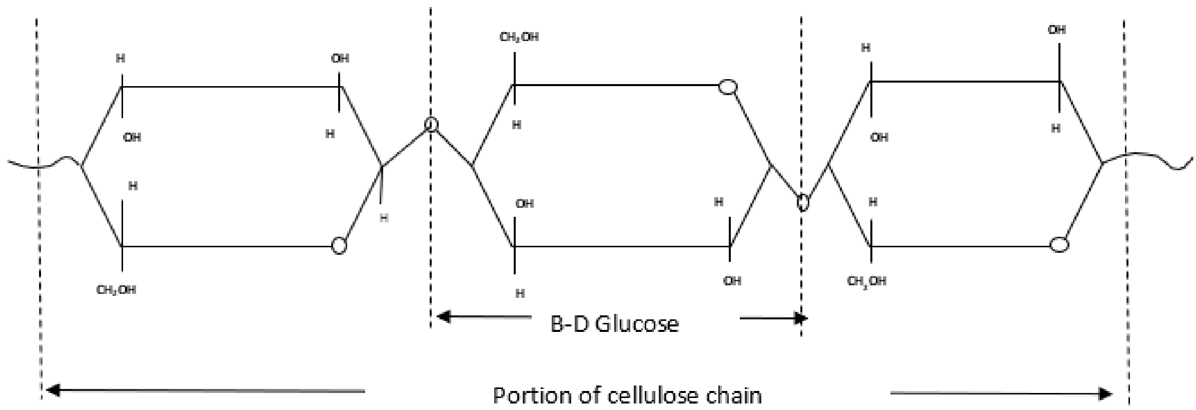

Fig. 1 Basic structure of cellulose redrawn from (Mabee, 2001)

Cellulose has two nanosize derivatives which are CNCs and CNFs (Nechyporchuk et al., 2016). The nanosized rod-like fibres obtained by cleavage of the amorphous regions while preserving the crystalline regions are termed CNCs (Moon et al., 2011, Khalil et al., 2014, Naz et al., 2019). The nanosized long entangled fibres obtained by mechanical shearing forces are termed CNFs (Nechyporchuk et al., 2016).

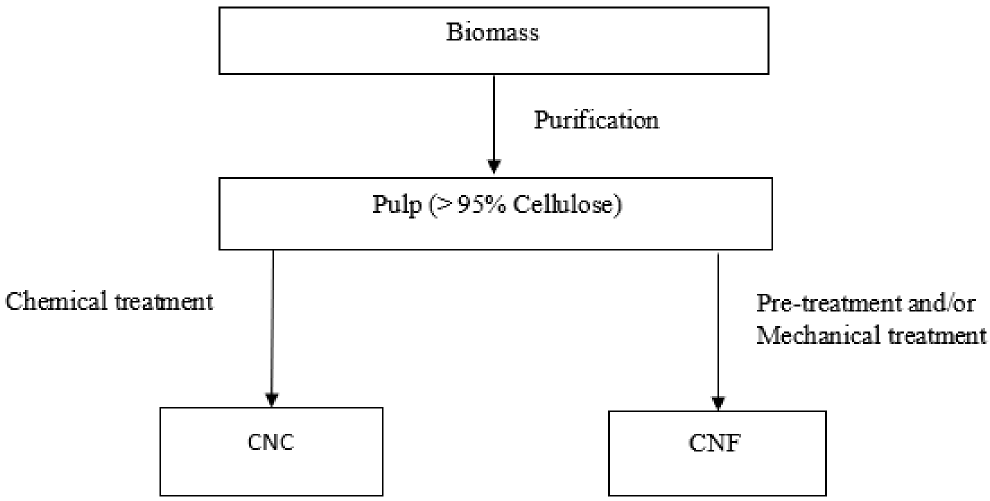

Fig. 2 Production steps of CNF and CNC from biomass redrawn from (de Assis et al., 2017)

CNCs by standard definition (ISO/TS 20477:2017) have an aspect ratio of less than 50 and contains crystalline and paracrystalline regions. CNFs by standard definition have an aspect ratio of more than 10 and contain crystalline and amorphous regions. Its dimensions are typically 3-100 nm in width and up to 100 µm in length (Fotie et al., 2020). The crystalline region is highly ordered and has low flexibility, and is responsible for rigidity and tensile strength. The amorphous region is the less ordered region, which plays a role in extensibility and flexibility (Moon et al., 2011). These properties give CNFs a broad spectrum of applications. Each application has specific demands from the CNF properties (Johansson, 2011). The applications include rheology modifiers, emulsion stabilisers, nanocomposites, papermaking, films, aerogels, bio-medicals, cosmetics, pharmaceuticals, hygiene and absorbent products.

The CNF market or application can be divided into a low volume, high volume and novel (Li et al., 2013). Papermaking is an example of a high volume application where the fibrous form of cellulose is of paramount importance than the crystalline form (Cowie et al., 2014). Even though CNFs were identified many years back as a paper additive, the major challenge impeding its commercial use has been high production cost, low yields from feedstocks, its negative impact on drying, pressing due to poor drainage properties, and poor retention of CNFs within pulp (Bardet and Bras, 2014, Hubbe, 2014). The production cost is attributed to the high energy requirements in processing CNFs. The main raw material in papermaking is wood. The general processes in papermaking are feedstock preparation (debarking and chipping), pulping (chemical and mechanical), and sheet preparation (forming, pressing and drying) (Gullichsen et al., 2000). In addition to pulp, additives, such as fillers, fixatives, flocculants, sizing and retention agents, are used to facilitate handling and improve end-use properties such as opacity and wet or dry strength properties of paper (Ankerfors et al., 2014, Diab et al., 2015). CNFs can be added at various stages of the papermaking process. For instance, it can be added directly into pulp. This increases the pulp total surface area, which also causes water retention by hydrogen bonding, thereby causing drainage problems. Externally, CNFs can be used as a coating on the finished paper to improve barrier, printing and functional properties (viz., antimicrobial, hydrophobic, conductive, etc.) (Bardet and Bras, 2014). It is well known that CNFs improves the physical and mechanical properties of paper, diminishes drainability and creates runnability problems (Ahola et al., 2008). For instance, 130% increase in tensile index was reported for paper produced using bleached softwood pulp, Polyamide amine epichlorohydrin (PAE) and 10 wt% carboxymethylated CNFs. Alcalá et al. (2013) reported 169% increase in tensile index for paper produced using unbleached hardwood kraft pulp combined with cationic starch and 12 wt% 2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl (TEMPO)-oxidised CNFs. Low dosages of CNF and/or absence of retention aides and additives led to little improvements in the mechanical strength of CNF reinforced paper. As an example, 4 wt% of mechanically produced CNF resulted in only 21% increase in the tensile index for thermomechanical pulp (TMP) paper (Eriksen et al., 2008). Mashkour et al. (2015) produced paper using 10 wt% of mechanically produced and acetylated CNFs combined with softwood pulp in the presence of C-PAM as a retention aid. A 17% increase in the tensile index was reported. However, some authors have reported a negative effect of CNFs on the tensile strength of paper. Therefore, it is important to understand the mechanisms of paper strengthening, effects of dosage, source, production method and grade of CNFs (Ämmälä et al., 2013, Diab et al., 2015). Reviews have been compiled which detail the strategies in which CNFs can be incorporated in papermaking, the interaction of CNFs with other additives, the impact of CNFs on paper properties, the best CNF grades, and the optimum amounts of CNFs obtained (Bardet and Bras, 2014, Brodin et al., 2014, Osong et al., 2016, Boufi et al., 2017, Jawaid et al., 2017, Balea et al., 2020). A summary of studies is listed in Table 1, which includes the source of CNF, production method, type of pulp for papermaking, additive or retention aid, CNFs dosage, mechanical properties, and references arranged in ascending order of the publication year. This review addresses the role played by CNFs as an additive to improve strength properties of papers and the factors affecting the improvement in paper quality when CNFs are added as additives.

Table 1 A review of studies published on the impact of CNF on paper properties

CNFs Source	**CNFs production method**	**Type of pulp for papermaking**	**Additive or retention aid**	**CNFs (wt%)**	**Mechanical properties of sheets**	**Reference**
Bleached sulphite pulp	Carboxymethylation Microfluidisation	Bleached pine kraft pulp	PAE	5	Dry tensile index = 65 $N \cdot m \cdot g^{-1}$	(Ahola et al., 2008)
Bleached sulphate kraft pulp	Grinding	TMP	None	4	Tensile index = 48 $kN \cdot m \cdot kg^{-1}$	(Eriksen et al., 2008)
Unrefined bleached softwood kraft fibres	Grinding	TMP	Clay	2.9	Tensile index ~ 60 $N \cdot m \cdot g^{-1}$ Z-strength ~ 425 kPa	(Mörseburg and Chinga-Carrasco, 2009)
Bleached spruce sulphite pulp	Homogenisation Grinding	TMP	-	-	Tensile index = 136 ± 14 $N \cdot m \cdot g^{-1}$ Tensile strength= 145 ± 12 Mpa Elongation = 8.0 ± 0.8% E modulus = 16.5 ± 0.2 GPa	(Syverud et al., 2009)
Bleached hardwood kraft pulp	Refining Carboxymethylation Micro fluidisation	Bleached softwood kraft pulp.	High and medium molar mass cationic Polyelectrolytes	10	Tensile index = 110 $N \cdot m \cdot g^{-1}$	(Taipale et al., 2010)
Bleached chemical birch pulp.	Grinding	Bleached chemical softwood pulp (pine)	Starch	5	Tensile strength = 90 $N \cdot m \cdot g^{-1}$	(Manninen et al., 2011)

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Table 1 A review of studies published on the impact of CNF on paper properties (continued)

CNFs Source	**CNFs production method**	**Type of pulp for papermaking**	**Additive or retention aid**	**CNFs (wt%)**	**Mechanical properties of sheets**	**Reference**
Bleached sulphite softwood pulp fibres from spruce	Mechanical beating Enzymatic treatment Homogenisation process Microfluidization	Sulphite softwood pulp fibres from spruce	None	10	Tensile index = 69 $N \cdot m \cdot g^{-1}$ Tensile energy absorption = 67 $J \cdot m^{-2}$	(Sehaqui et al., 2011)
Commercial dried, bleached eucalyptus pulp	TEMPO-mediated oxidation High pressure homogenisation	Enzyme-treated Pulp	Cationic starch Silica colloidal	9	Tensile index =50.02 $N \cdot m \cdot g^{-1}$ Breaking length = 5,103 ± 296 m Burst Index = 2.60 ± 0.26 $kPa \cdot m^2 \cdot g^{-1}$	(González et al., 2012)
Never-dried Pinus radiata kraft pulp	Homogenisation	Unbeaten newsprint grade TMP	Ground calcium carbonate (GCC) Cationic polymer	5	-	(Hii et al., 2012)
Pulp	Pre-refining Fibrillation	Chemical hardwood and softwood machine pulp mixture	1% of cationic Starch	2	Tensile index = 4.1 $kN \cdot m^{-1}$	(Kajanto and Kosonen, 2012)

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Table 1 A review of studies published on the impact of CNF on paper properties (continued)

CNFs Source	**CNFs production method**	**Type of pulp for papermaking**	**Additive or retention aid**	**CNFs (wt%)**	**Mechanical properties of sheets**	**Reference**
Unbleached kraft pulp of Kenaf and Scotch Pine	PFI mill refining Enzymic pre-treatment Homogenisation	Unbleached softwood kraft pulp	C-PAM	10	Tensile index increase = 32% Strain at break = 3.9% Tensile strength = 61.5 ± 0.8 $N \cdot m \cdot g^{-1}$ Tensile energy absorption index = 1.5 ± 0.3 $kJ \cdot g^{-1}$ Tensile strength = 43.1 ± 0.5 MPa elasticity modulus = 4.60 ± 0.09 GPa Tensile stiffness = 6.5 ± 0.1 $N \cdot m \cdot g^{-1}$ Burst index = 6.9 ± 0.2 $kPa \cdot m^2 \cdot g^{-1}$	(Charani et al., 2013)
Softwood	Grinding	Softwood pulp	None	20	Tensile strength = 5621 ± 336 $N \cdot m^{-1}$ Tear Strength=500-600 mN	(Afra et al., 2013)
		Bagasse pulp	None	20	Tensile strength = 4000 to 5000 $N \cdot m^{-1}$ Tear Strength = 400 to 580 mN	
Bleached birch chemical wood pulp	TEMPO-mediated oxidation Periodate-chlorite oxidation	Kraft pulp	GCC	4	Tensile index = 60 $kN \cdot m \cdot kg^{-1}$ Tear index =12 $N \cdot m^2 \cdot kg^{-1}$	(Ämmälä et al., 2013)

	Homogenisation					

Table 1 A review of studies published on the impact of CNF on paper properties (continued)

CNFs Source	CNFs production method	Type of pulp for papermaking	Additive or retention aid	CNFs (wt%)	Mechanical properties of sheets	Reference
Commercial bleached hardwood eucalyptus pulp	TEMPO mediated oxidation (neutral PH) Homogenisation	Bio-beaten bleached hardwood eucalyptus pulp	Cationic starch and silica colloidal	6	Tensile index = 50.9 to 60.2 $N{\cdot}m{\cdot}g^{-1}$ Burst index =3.75 to 4.85 $kPa{\cdot}m^2{\cdot}g^{-1}$ Scott bond = 976.8 $J{\cdot}m^{-2}$	(González et al., 2013)
Bleached softwood sulphite pulp	Mechanical beating Enzymatic treatment Homogenisation	Bleached softwood pulp	Xyloglucan	10	Tensile Index = 84.2 $N{\cdot}m{\cdot}g^{-1}$ TEA =123 $J{\cdot}m^{-3}$ Wet tensile index = 0.75 $N{\cdot}m{\cdot}g^{-1}$	(Sehaqui et al., 2013)
Pure cellulose fibres	High pressure homogenisation	Bleached eucalyptus kraft pulp	PAE	75	Tensile index increase = 602 $N{\cdot}m{\cdot}g^{-1}$	(Su et al., 2014)
	High pressure homogenisation	Unbeaten bleached hardwood kraft	PAE	10	Tensile strength = 228 $N{\cdot}m{\cdot}g^{-1}$	

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Table 1 A Review of studies published on the impact of CNF on paper properties (continued)

CNFs Source	CNFs production method	Type of pulp for papermaking	Additive or retention aid	CNFs (wt%)	Mechanical properties of sheets	Reference
Bleached softwood sulphite pulp	Enzymic pre-treatment PFI beater High pressure homogenisation	Beaten bleached hardwood and softwood kraft mixture	Calcium carbonate C-PAM Colloidal silica	5	Tensile strength = 24 $kN{\cdot}m{\cdot}kg^{-1}$ Tensile stiffness index = 3.8 $mN{\cdot}m{\cdot}kg^{-1}$ Tear index =5.3 $mN{\cdot}m^2{\cdot}g^{-1}$ Fracture toughness = 4.5 $J{\cdot}m{\cdot}kg^{-1}$ Z-strength = 490 kPa Bending resistance = 60 mN	(Ankerfors et al., 2014)
Bleached soda bagasse pulp	Enzymic pre-treatment Refining Homogenisation	Bleached soda bagasse pulp	C-PAM	5	Tensile index = 60 $N{\cdot}m{\cdot}g^{-1}$	(Petroudy et al., 2014)
Bleached kraft pulp (BKP)	Mechanical	Unbeaten Chemo thermomechanical pulp (CTMP) and bleached softwood kraft pulp	-	15	Tensile index = 31 $kN{\cdot}m{\cdot}kg^{-1}$ Tensile energy absorption = 910 $J{\cdot}kg^{-1}$ Z-strength = 694 ± 2.1 $kN{\cdot}m^{-2}$ Tear index = 18.16 $N{\cdot}m^2{\cdot}kg^{-1}$ Burst index = 2.18 $kPa{\cdot}m^2{\cdot}g^{-1}$ E-modulus = 2.42 $GN{\cdot}m^{-2}$ Strain at break = 3.67%	(Osong et al., 2014)

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Table 1 A Review of studies published on the impact of CNF on paper properties (continued)

CNFs Source	CNFs production method	Type of pulp for papermaking	Additive or retention aid	CNFs (wt%)	Mechanical properties of sheets	Reference
Commercial bleached eucalyptus pulp	TEMPO-mediated oxidation High-pressure homogenisation.	Deinked recycled pulp suspension and old newspapers and old magazines	Cationic starch	4.5	Tensile index increase = 82% Breaking length = 6054 m Tensile Index= 59.36 $N{\cdot}m{\cdot}g^{-1}$ Tensile Strength= 43.13 $J{\cdot}m^{-2}$	(Delgado-Aguilar et al., 2015)
Bleached kraft hardwood pulp	PFI beating Enzyme hydrolysis Homogenisation	Kraft hardwood pulp	Cationic starch and silica colloidal	3	Breaking length = 3891 ± 126 m Tensile index = 37.96 ± 1.23 $N{\cdot}m{\cdot}g^{-1}$	(Delgado Aguilar et al., 2015)
	PFI beating Homogenisation	Kraft hardwood pulp	Cationic starch and silica colloidal		Breaking length = 3512 ± 118 m Tensile index = 34.26 ± 1.15 $N{\cdot}m{\cdot}g^{-1}$	
	TEMPO-oxidation pH = 10 Homogenisation	Bleached kraft hardwood pulp	Cationic starch and silica colloidal	-	Breaking length = 4128 ± 112 m Tensile index = 40.30 ± 1.09 $N{\cdot}m{\cdot}g^{-1}$	
	Acid treatment Homogenisation	Bleached kraft hardwood pulp	Cationic starch and silica colloidal	-	Breaking length = 3595 ± 105 m Tensile index = 35.27 ± 1.02 $N{\cdot}m{\cdot}g^{-1}$	
	TEMPO-oxidation pH = 7 Homogenisation	Bleached kraft hardwood pulp	Cationic starch and silica colloidal	-	Breaking length = 3874 ± 120 m Tensile index = 37.79 ± 1.17 $N{\cdot}m{\cdot}g^{-1}$	

Table 1 A Review of studies published on the impact of CNF on paper properties (continued)

CNFs Source	**CNFs production method**	**Type of pulp for papermaking**	**Additive or retention aid**	**CNFs (wt%)**	**Mechanical properties of sheets**	**Reference**
Bleached kraft bagasse pulp	Grinding	Beaten softwood and bagasse pulps	Ground calcium carbonate With bentonite (GCC-B)	0.1	Tensile energy index = 1.27 ± 0.13 g^{-1} Burst = 5.02 ± 0.44 $kPa\cdot m^2\cdot g^{-1}$ Tear = 13 ± 0.7 $mN\cdot m^2\cdot g^{-1}$ Breaking length = 5.44 ± 0.11 km Elongation = 3.54 ± 0.35 mm Young modulus =3.54 ± 0.16 GPa	(Diab et al., 2015)
Softwood fibres	Grinding Acetylation of CNF	Unbeaten softwood acetylated pulp	C-PAM	10	Tensile index = 75 $N\cdot m\cdot g^{-1}$ Burst index = 6 $kpa\cdot m^2\cdot g^{-1}$	(Mashkour et al., 2015)
Rice straw	Grinding	Beaten bleached rice straw and bagasse pulp	None	30	Breaking length = 8.97 km Burst factor = 4.87 Tear factor = 2.12	(Adel et al., (2016))
Cornstalk	Grinding	Beaten bleached rice straw and bagasse pulp		30	Breaking length = 8.78 km Burst factor = 4.74	

					Tear factor = 2.61	
Bagasse	Grinding	Beaten bleached rice straw and bagasse pulp	None	30	Breaking length = 8.40 km Burst factor = 4.20 Tear factor = 2.50	
Cornstalk pulp and rape stalk pulp	PFI mill TEMPO mediated oxidation Homogenization	Old-newspaper and old magazines	Chitosan	0.5	Tensile index =52 $N{\cdot}m{\cdot}g^{-1}$	(Balea et al., 2017)

Table 1 A review of Studies published on the impact of CNF on paper properties (continued)

CNFs Source	**CNFs production method**	**Type of pulp for papermaking**	**Additive or retention aid**	**CNFs (wt%)**	**Mechanical properties of sheets**	**Reference**
Eucalyptus globulus bleac hed kraft pulp	TEMPO-mediated oxidation, NaClO, NaBr. Homogenization	-	Precipitated calcium carbonate (PCC)	3	Tensile index = 23.6 ± 0.1 N·m·g^{-1} Tensile index w/o PCC = 54.9 ± 2.8 N·m·g^{-1}	(Lourenço et al., 2017)
softwood kraft pulp	Grinding Refining	cotton lint	-	10	Tensile index ~ 35 N·m·g^{-1} Folding endurance ~1500	(Park et al., 2018)
bleached hardwood kraft pulp	Grinding Refining	cotton lint	-	10	Tensile index ~ 28 N·m·g^{-1} Folding endurance ~1000	
Recycled old newsprint	TEMPO -mediated oxidation Homogenization	Recycled old newsprint	Cationic polyacrylamide Hydrated bentonite clay (C-PAM-B)	3	Tensile index increase = 35%	(Balea et al., 2019)
Old corrugated containers	TEMPO -mediated oxidation Homogenization	Old corrugated containers pulp	C-PAM-B	3	Tensile index increase ~ 70% Burst index increase ~ 20%	(Balea et al., 2019)
Recycled bleached de-inked pulp	PFI-mill refining Homogenisation	*Eucalyptus* pulp	-	20	Tensile index = 55 N·m·g^{-1}	(Ang et al., 2020)

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1.1 THE ROLE PLAYED BY CNFs IN PAPER

The unique dimensions and characteristics of CNF that play a role in improving the strength properties of papers are described in the following sections.

1.1.1 Nanometre lateral dimension

In general, CNFs have a large surface to volume ratio and specific surface area (SSA) because of their nanosized lateral dimension (Ottesen, 2018). When CNFs are combined with microfibres present in pulp suspensions, the SSA of the fibrous network increases, resulting in an increased available surface for bonding (Adel et al., (2016)). In this situation, two phases are formed, namely the microscale and the nanoscale. Spence et al. (2010) reported that the SSA of unbleached softwood pulp fibres (UBSWP) was in the range of 3 ± 2 $m^2 \cdot g^{-1}$ whereas CNFs obtained from bleached hardwood pulp ranged from 30 $m^2 \cdot g^{-1}$ to 70 $m^2 \cdot g^{-1}$. As an example, the addition of 6 wt% of CNFs with a SSA of 55 $m^2 \cdot g^{-1}$ to 100 g of UBSWP fibres with SSA of 1 $m^2 \cdot g^{-1}$ will subsequently result in the microscale phase generated having a SSA of 100 m^2 per 100 g of pulp and a nanoscale phase of 330 m^2 (Spence et al., 2010, Alcalá et al., 2013). As a consequence of the large SSA, dispersed CNFs enhance bonding between pulp fibres and evenly distribute stress in the paper under loading. Colloidal interaction and mechanical interlocking are also promoted by the large surface area of CNFs (Taipale et al., 2010). An increase in surface area results in an increase of available hydroxyl groups for interaction, thus promoting the formation of fibre to fibre contact and bonding, which in turn solidifies the structure of the paper. The strength of paper increases with an increase in the number of fibre bonds. Therefore the presence of CNFs naturally improves the overall tensile strength of paper by increasing the fraction of fibres that are bonded relative to the total area available for bonding (*viz.*, relative bonded area) (Mörseburg and Chinga-Carrasco, 2009).

Furthermore, the nanosized dimension is also advantageous in reducing the porosity of paper from microsize to nanosize (Mörseburg and Chinga-Carrasco, 2009, Mashkour et al., 2015). It was reported that CNFs offers better packing in the network of pulp fibres and fillers, thus reducing porosity (Mashkour et al., 2015). CNFs fill microvoids and pores around fibre joints extending the contact domain and improving contact between fibres at the molecular level during paper drying (Afra et al., 2013, González et al., 2013). Syverud et al. (2009) reported an increase in air resistance from 41 s per 100 ml to approximately 200 s per 100 ml for paper treated with CNFs, indicating that pores between fibres were closed or reduced in size by the addition of CNFs. The decrease in air permeability was also justified by the densification of CNF reinforced paper, which reflected a high number of fibre to fibre interaction influenced by the presence of CNFs (Taipale et al., 2010, Charani et al., 2013). Su et al. (2014) examined the microscopic structure of hardwood pulp and hardwood pulp reinforced with CNFs. The latter showed a smoother and compact surface. The former sample had a more porous and rougher surface. Alcalá et al. (2013) confirmed that fibres reinforced with CNFs showed a more compact fibre network resulting in a more solid structure. Even though the nanosized lateral dimensions are highly beneficial in enhancing the mechanical strength properties of paper, the drainage rates are always negatively affected (Mashkour et al., 2015).

1.1.2 Micrometre length

Fibre length is one of the significant factors which influences the fracture toughness and tear index quality of paper (Subramanian et al., 2011). The length of the fibres enables a continuous network to be formed even at low concentrations of fibres (Karlsson, 2007). The length of CNFs contributes to the formation of fibres joints, thus creating stronger networks (Johansson, 2011). The length of CNFs differ depending on the production pre-treatment, mechanical treatment and characterisation technique employed. Ishii et al. (2011) reported an average length of 2.2 μm by use of both Transmission Electron Microscopy (TEM) and dynamic viscoelasticity measurements for CNFs produced by TEMPO-mediated oxidation and mechanical disintegration (Ishii et al., 2011). Su et al. (2014) suggested two roles played by the length of CNFs, illustrated in Figure 3. Firstly, CNFs act as a bridge between fibres, which increases connectivity, adhesion and the bonded area. Secondly, shorter CNFs bond together, thus improving the strength of the paper. Fibre to fibre bonds are mostly hydrogen bonds. Hydrogen bonding is only possible for fibres in close proximity (less 0.35 nm apart). By bridging adjacent fibres, CNFs increase the chances of bonding and contribute more hydroxyl groups, thus forming an entangled network of CNFs. Furthermore, CNFs can act as a binder to strengthen fibre-filler interactions by bridging the void created by fillers (Hii et al., 2012, Ämmälä et al., 2013). Phipps et al. (2017) reported that CNFs produced by co-grinding with a calcium carbonate filler acts to fill in the voids created between filler and pulp fibres in paper by wrapping around filler particles promoting bonding by bridging. The presence of CNF curbs the disruption of the bonded area caused by the filler (Phipps et al., 2017). The length of CNFs allows for its entanglement around fibres, consequently filling empty spaces in the paper (Adel et al., (2016)). However, the length of the CNFs is too short to affect tear strength positively. Tear strength is positively affected by bonding points and area in the fibres network (Afra et al., 2013). The decrease in tearing resistance is due to the shortening of fibres and the increase in the number of bonds, causing fibres to break instead of being pulled out of the fibre network (Karlsson, 2007, Afra et al., 2013). The Z-strength of paper is mainly affected by the fibre to fibre bond strength, while the tensile strength correlates with fibre length (Ankerfors et al., 2014). Fractionating CNFs according to length and only using the fraction with longer fibres has been reported to increase the tensile strength by an additional 10% at the same optimal dosage of 10 wt% obtained for none fractioned fibres (Manninen et al., 2011). The dependence of tensile strength on fibre length is represented by Eq.1 below:

$$\frac{1}{T} = \frac{9}{8Z} + \frac{3w_f}{\tau_f\, l_f\, RBA} \tag{1}$$

Where τ_f is tensile strength, Z is the zero-span tensile strength of paper, and w_f is fibre width, τ_f is the breaking stress of bonds, l_f is fibre length, and RBA is the relative bonded area (Page, 1969, Karlsson, 2007).

Hierarchical structures in the form of different lateral and length scales of fibres are formed in CNFs and pulp mixtures (Sehaqui et al., 2011). The presence of two length scales (micro and nano) has been reported to be the reason for the increased strength of paper bio-composites. The nanoscale network of fibres transfers the load between wood fibres, thus delaying the material's damage and failure when exposed to stress and strain (Sehaqui et al., 2011). This mechanism is believed to take place at fibre to fibre joints in the paper (Sehaqui et al., 2011).

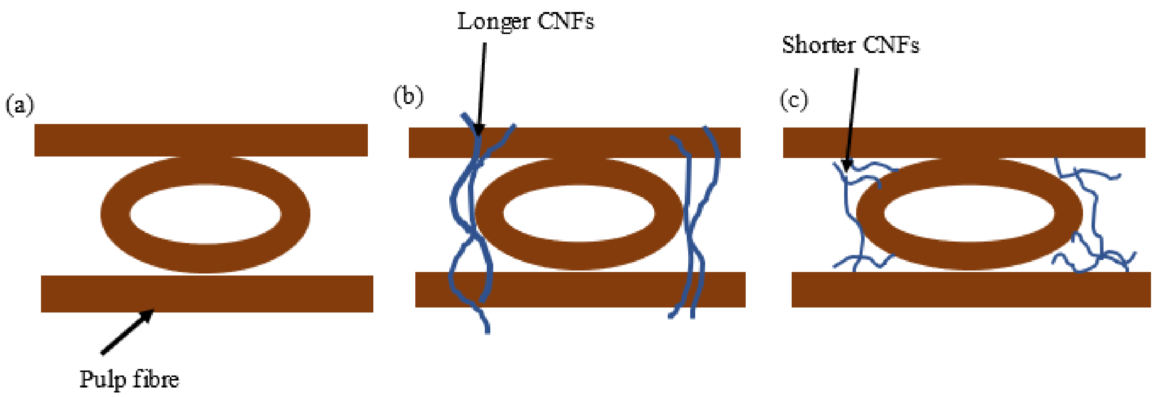

Fig.3 Role played by longer CNFs vs shorter CNFs in pulp fibre matrix redrawn from (Su et al., 2014).

1.1.3 Semi-crystalline structure

The crystalline structure is responsible for rigidity, the resistance of flow and the strength of CNFs (Hubbe, 2014). The strength of CNFs contributes to the overall strength of paper and increases its load-bearing capacity. On the other hand, the amorphous region contributes to the flexibility of CNFs. High fibre flexibility increases fibre conformability around each other, affecting the chances of fibre-fibre contacts, the number of bonds, and the bonded area in a paper sheet (Karlsson, 2007). The flexibility of CNFs increases the degree of bonding, hence the increased tensile strength of paper and also decreases its susceptibility to brittle failure (Johansson, 2011, Hubbe, 2014). The flexibility of fibres promote better conformity to the fibre surfaces and, therefore, a larger bonded area (Kajanto and Kosonen, 2012). Due to their slenderness and flexibility, CNFs are prone to entanglement, which is responsible for the increase in the wet strength of paper (de Oliveira et al., 2008, Sehaqui et al., 2013).

Also, an additional nanoscale network is formed due to the web of flexible CNFs. The nanoscale network may also form in between pulp fibres resulting in a non-porous, smooth surface (Petroudy et al., 2014). This web implanted among the pulp fibres contributes to the mechanical properties of paper (Bardet and Bras, 2014). De Oliveira et al. (2008) compared the effect of flexible CNFs and rigid glass fibres. An increase in the solid content of CNFs resulted in entanglement friction between CNFs and pulp fibres. The friction became more pronounced upon drying, thus increasing the cohesion between fibres and the web strength of paper (de Oliveira et al., 2008). In contrast, the rigid glass fibres reduced the wet web strength of paper due to lack of entanglements.

The amorphous region is important because it offers more hydrogen bonding groups (Kajanto and Kosonen, 2012). However, the amorphous region retains a lot of water which negatively impacts the drainage rate of paper (Balea et al., 2020).

1.1.4 High strength and modulus

The strength of paper depends on the strength of fibres and the bonds that connect them (Sehaqui et al., 2013). Mashkour et al. (2015) reported that the strength properties of paper, such as burst strength, were mainly affected by relative bonding area (RBA), bonding strength, and single fibre strength. Individual CNFs fibres have a strength comparable to that of engineering materials. This strength, combined with the inherent tendency of CNFs to form entangled networks, contributes to the overall strength of paper. Different fibres have different shear bond strengths. Reports have shown that the inherent strength of a single CNF were in the range 0.8 to 10 GPa and 30 to 250 GPa for tensile strength and Young Modulus, respectively, depending on the measuring technique, source, production and fabrication method of CNFs (Zimmermann et al., 2004, Alcalá et al., 2013). Saito et al. (2013) reported that CNFs obtained from wood had a tensile strength of 1.6 to 3 GPa by using sonication induced fragmentation for measurement. Given the high values of strength for CNFs, its incorporation in pulp creates a favourable interface for improving the physical and mechanical properties of paper (Alcalá et al., 2013). The dependence of tensile strength on fibre strength is shown in Eq. 2 below:

$$\frac{1}{T} = \frac{1}{F} + \frac{1}{B} \qquad (2)$$

Where T is the tensile strength, F is the fibre strength index, and B is the bonding strength index (Page, 1969).

1.1.5 Aspect ratio

The high length to diameter ratio allows CNFs to be entangled around fibres, thereby filling up empty spaces in a paper (González et al., 2012). Also, the aspect ratio of CNFs is directly proportional to the viscosity of CNF suspensions. High aspect ratio fibres result in high intrinsic viscosity because of the large rotational volume to fibre volume ratio (Jowkarderis and van de Ven, 2014). The high aspect ratio combined with high SSA increases fibre to fibre interactions of CNFs, resulting in gel formation at low concentrations. The viscosity of CNFs is not favourable because of the difficulty to disperse CNFs in the paper furnish (Bajpai, 2016).

1.1.6 Lightweight

In general, CNFs are lightweight due to their nanosized dimensions. However, they increase the density of the paper structure, thus improving the volume fraction load-bearing fibrous material in the paper network (Sehaqui et al., 2013). Sehaqui et al. (2013) demonstrated a direct proportional relationship between the tensile index and paper hand sheets density. Mashkour et al. (2015) reported a 16% and 8% increase in paper density by adding unmodified and acetylated CNF, respectively.

1.1.7 Chemical modification and surface charge

CNFs, just like cellulose, have the potential for chemical modification due to the anionic charges on their surface. However, the anionic charges cause poor retention of CNFs in the paper matrix. The anionic nature of CNFs is advantageous as a retention aid for starch. While pulp fibres can adsorb a maximum of 1 wt% starch, CNFs introduce anionic charges, which result in the formation of complexes with starch, allowing for adsorption of higher dosages of starch and improvement of mechanical properties of paper (Ankerfors et al., 2014).

Chemical pre-treatments such as TEMPO-mediated oxidation, sulphonation, carboxymethylation and quaternisation cause substitution of hydroxyl groups in CNFs with carboxylate (aldehyde), sulphite, carboxymethyl, and carboxyl groups (Lee et al., 2017). Ahola et al. (2008) reported that the carboxyl group content in carboxymethylated CNFs influences adsorption properties and covalent bond formation with PAE, which is a wet strength agent of paper. The addition of PAE mixed with CNFs increased the wet and dry strength of paper.

Acetylated CNFs were used to produce hydrophobic paper (Mashkour et al., 2015). Mashkour et al. (2015) reported a decrease in water absorption of 23.1% for paper reinforced by partially acetylated CNFs. However, acetylation of CNFs decreased the number of hydroxyl groups, negatively affecting the mechanical strength of the paper.

1.2 FACTORS AFFECTING THE IMPROVEMENT IN PAPER QUALITY

The factors affecting quality of CNF reinforced paper is the strategy of CNF addition, CNF grade, CNF dosage, and CNF source, described in the following sections.

1.2.1 Effect of strategy of CNF addition

In general, there are four strategies in which CNFs can be incorporated as an additive in papermaking (Bardet and Bras, 2014, Bajpai, 2016). The first strategy is the direct addition of CNF in the pulp suspension. The second strategy involves pre-mixing CNFs with another furnish component such as filler before addition into pulp. The third strategy involves adding CNFs in layers on pulp (bi-layer system) (Ahola et al., 2008). The fourth strategy is pre-flocculation of CNFs with a retention polymer before adding sheets and adding the retention aid to the fibre furnish before adding CNFs (Bajpai, 2016). In a comparative study, the bi-layer strategy resulted in a better strength-enhancing effect (dry tensile index of 62.5 $N \cdot m \cdot g^{-1}$) than the addition of nano-aggregates of CNFs and PAE to the pulp (dry tensile index of = 62 $N \cdot m \cdot g^{-1}$). This was because the former strategy allowed uniform distribution of substances on the pulp fibre surfaces in the paper matrix. The latter resulted in inhomogeneous distribution on the fibres, and, hence, the strength properties were not improved (Ahola et al., 2008, Brodin et al., 2014). Also, the PAE-CNFs aggregates were very anionic at high CNF dosages resulting in the poor attraction between CNFs and fibres (Ahola et al., 2008). Another approach compared the effect of interchanging layers of clay, CNFs, and fractionated thermomechanical pulp (TMP) in paper sheets. The arrangement that produced the best quality paper was where the top layer comprised clay, followed by the TMP accept fraction of pulp, then CNFs as the next layer, and the bottom layer made up of the TMP reject fraction. This type of arrangement promoted maximum interaction of the hydroxyl groups between CNFs and pulp. It increased the dry tensile index by approximately 5 $N \cdot m \cdot g^{-1}$ greater than when CNFs were either in the bottom or top layers of sheet structure of the paper (Mörseburg and Chinga-Carrasco, 2009).

1.2.2 Effect of CNF grade

Several authors have reported that CNFs produced by different mechanical methods influence the mechanical properties in distinct ways (Eriksen et al., 2008, Syverud et al., 2009). For instance, CNFs produced by homogenisation had a greater effect on the tensile index than CNFs produced by grinding, even though grinding produced on average smaller fibrils than those yielded by homogenisation (Eriksen et al., 2008). The highest tensile strength achieved by adding 4 wt% CNFs obtained by homogenisation was approximately 50 $kN \cdot m \cdot kg^{-1}$. While the addition of 4 wt%, CNFs produced by grinding was approximately 48.5 $kN \cdot m \cdot kg^{-1}$ (Eriksen et al., 2008). It was concluded that these different grades of CNFs have different mechanisms to improve the strength of paper.

Delgado Aguilar et al. (2015) carried out a comparative study between CNFs produced by three different pretreatment methods (chemical (*viz.*, TEMPO mediated oxidation and acid hydrolysis), enzymatic treatment and mechanical beating) before high-pressure homogenisation. The highest index was found in CNFs produced from TEMPO mediated oxidation due to its high fibrillation degree. The acid hydrolysed CNFs also resulted in high tensile index values owing to a high fibrillation degree of 95% facilitated by sulphate ester groups. The lowest tensile index was in CNFs produced by mechanical means because mechanical methods produced non-homogeneous fibres which formed entangled and disordered networks in the paper. However, in order to compensate for low fibrillation, poorly fibrillated CNFs were added in higher dosages to achieve the same effect as that of highly fibrillated CNFs (Delgado Aguilar et al., 2015).

Kim et al. (2019) classified CNFs according to production methods, i.e., refined CNFs (RE-CNFs), enzymatic CNFs (EN-CNFs), and carboxymethylated CNFs (CM-CNFs). The CM-CNFs were more efficient in tensile strength, folding endurance, and sheet density quality improvement than RE-CNFs and EN-CNFs. The EN-CNFs were the least effective compared to RE-CNFs and CM-CNFs. However, in all the cases, the deterioration of the drainage rate as the CNF dosage increased was observed. The CM-CNFs was preferred, where strength improvement was a priority, but drainage could be afforded (Kim et al., 2019).

Su et al. (2014) reported that CNFs produced by homogenisation had better retention in the pulp fibre web due to their inhomogeneous size distribution. On the other hand, CNFs produced by ball milling were poorly retained in pulp fibres due to their small fibre size. However, the small fibres from ball milling produced a more compact and dense paper structure in the presence of a retention aide. Balea et al. (2017) confirmed that the retention system, morphology and composition of CNFs directly impacted the improvement of mechanical properties of paper.

1.2.3 Effect of CNF dosage

González et al. (2012) reported an increase in all tensile properties (tensile index, burst index, Scott bond, and tear index) of paper as the dosage of CNFs increased from 0 to 9 wt%. However, with the progressive addition of CNFs, the drainage rate was severely affected. Syverud et al. (2009) explained that the increase in tensile index with respect to CNF dosage was exponential. The maximum tensile index was achieved at 10% CNFs, however; the most significant change was observed from 5% CNFs. Eriksen et al. (2008) confirmed a similar trend between CNF dosage and increase in tensile strength. After using a dosage range between 0 and 8 wt%, the optimum dosage achieved was at 4 wt% CNFs (Eriksen et al., 2008). In some studies, small dosages of CNFs were enough to produce a significant improvement in mechanical properties. For instance, Adel et al. (2016) reported that 5 wt% of CNFs resulted in a better enhancement in mechanical properties than 20 wt% of softwood applied as a paper additive on rice straw and bagasse pulps. Alcalá et al. (2013) reported a linear increase in tensile strength and Young modulus as the amounts of CNFs added were increased from 3 wt% to 9 wt%. The maximum values for tensile strength and Young modulus were 150 GPa and 60%, respectively, at 9 wt% CNFs dosages. Further increase in dosage to 12 wt% did not yield a significant improvement in mechanical properties due to the decrease in the area available for bondage on the fibre surface as more CNFs were added to the pulp (Alcalá et al., 2013, Jawaid et al., 2017). Taipale et al. (2010) also reported a linear increase of tensile strength with respect to CNF dosage. This confirms that high amounts of CNFs in paper webs create more fibre entanglements and increase inner friction area between fibres, leading to improved wet strength (Su et al., 2013). However, high dosages of CNFs are detrimental to the drainage rates of paper sheets (Ahola et al., 2008, Taipale et al., 2010, Hii et al., 2012). Petroudy et al. (2014) studied the addition of different dosages of CNFs on bagasse pulp in the presence of a retention aid. The conclusion made was that a small dosage of CNFs (e.g., 0.1%) added to pulp required 0.1% of C-PAM (retention aide) to achieve high improvements in the tensile index of approximately 60 $N{\cdot}m{\cdot}g^{-1}$, while maintaining a low drainage rate.

1.2.4 Effect of the source of CNFs

Balea et al. (2016) compared the effectiveness of cornstalk-CNFs to *Eucalyptus* kraft pulp (EKP) to improve the properties of recycled paper. Only 0.5 wt% cornstalk-CNFs achieved a 20% increase in tensile strength, whereas 1.5 wt% of EKP was needed to achieve the same improvement. The low dose of cornstalk-CNFs required for effective paper improvement compensated for its low production yield (Balea et al., 2016). Hai et al. (2018) conducted a comparative study in which CNFs from various sources (hardwood, softwood, cotton linter and cattail) were used as additives when producing paper from hardwood pulp. The softwood-CNFs, hardwood-CNFs, cattail-CNFs and cotton-CNFs had diameters of 46, 40, 30, and 70 nm, respectively. The highest tensile strength was recorded for paper reinforced with softwood-CNFs (45 $N \cdot m \cdot g^{-1}$) followed by hardwood-CNF (42.5 $N \cdot m \cdot g^{-1}$), cattail-CNFs (40 $N \cdot m \cdot g^{-1}$) and lastly, cotton linter-CNFs (~38 $N \cdot m \cdot g^{-1}$). The non-wood sources showed the lowest tensile strength and bonding properties due to their low hemicellulose content compared to the woody sources (Hai and Seo, 2018, Balea et al., 2016).

Ang et al. (2020) demonstrated that the addition of 20 wt% CNFs produced from recycled de-inked pulp compared with bleached *Eucalyptus* pulp resulted in a 45.6% increase (30 $N \cdot m \cdot g^{-1}$ to 55 $N \cdot m \cdot g^{-1}$) in tensile strength with reference to pure bleached *Eucalyptus* hand sheets without CNFs. Therefore, recycled pulp was proven to be a viable source for CNF production that can be used as a paper additive. González et al. (2013) produced paper with a tensile strength of 60.2 $N \cdot m \cdot g^{-1}$ using bleached *Eucalyptus* pulp-CNFs and bleached *Eucalyptus* pulp. The tensile strength was 68% higher than that of the reference paper made from pure bleached *Eucalyptus* pulp.

Balea et al. (2017) compared the effectiveness of two agricultural residues *viz.*, corn stalk and rape produced by different pre-treatments methods, which were refining, TEMPO mediated oxidation, and bleaching before mechanical treatment to reinforce recycled paper. TEMPO mediated oxidation resulted in the highest yield and quality of CNFs, followed by bleaching and, lastly, refining. The tensile index improvement for the different types of CNFs was approximately 15% when 0.5 wt% CNFs were used to reinforce recycled paper. Therefore it was concluded that a cheaper pre-treatment method such as bleaching could be used to replace the expensive TEMPO mediated oxidation, to obtain a 15% improvement in the tensile index (Balea et al., 2017).

Balea et al. (2019) studied the effectiveness of CNFs produced from recycled fibres in improving the tensile strength of old newspaper prints (ONP) and old corrugated container (OCC) pulps in the presence of a three-component retention system (*viz.*, coagulant, C-PAM, and hydrated bentonite clay). Different amounts of CNFs were added (*viz.*, 1, 2, 3 wt%) when making paper. It was reported that 3 wt% of CNFs improved the tensile index of ONP by 30%. On the other hand, 3 wt% of CNFs improved the tensile index of OCC by 60%. The optimisation of the retention system used counteracted the negative effect on the drainage rate caused by the CNFs.

Park et al. (2018) compared the extent to which CNFs produced from softwood kraft pulp (SBKP) and bleached hardwood kraft pulp (BHKP) improved the mechanical properties of paper made from cotton lint mixed pulp. CNFs produced from SBKP resulted in the greatest improvement in mechanical properties (folding endurance >

1200, tensile index > 30 $N \cdot m \cdot g^{-1}$) of the paper. The CNFs produced from SBKP had high viscosity, lower fibre diameter and higher zeta-potential compared to CNFs produced from BHKP (Park et al., 2018).

2.0 TECHNO-ECONOMIC CONSIDERATIONS

The emergence of CNFs can be summed up in stages: basic manufacturing research, proof of concept, production in laboratory, capacity to produce a prototype, capability in production, and demonstration of production rates. Despite the investment gap that has slowed down its commercialisation, the increasing number of CNFs producers at demonstration scale worldwide is evidence of the great efforts in developing a CNF industry. The market of CNFs is growing slowly, with an annual growth rate of 30% due to technical and commercial challenges. In the year 2025, it is anticipated that the market will grow up to 25100 metric tonnes/year (Miller, 2019).

Amongst other consumers of CNFs, the papermaking industry accounts for 36% (Investment and Guide, 2019). The most sustainable way of production and application of CNFs in papermaking is by in situ production. In situ production provides an opportunity for paper producers to expand the range of products and apply expert knowledge in optimisation and development of functional properties for speciality grade papers. The ultimate goal is to replace the existing petroleum-based materials in the papermaking process. This is only achievable if the cost of CNFs is comparable to or lower than traditional additives. Currently, the high production cost of CNFs is attributed to the high energy demands of mechanical treatment and the high cost of chemicals for pre-treatment of CNFs sources. For instance, in situ production of CNF by TEMPO oxidation would increase the cost of paper from 60 to 300 € per tonne of paper (Balea et al., 2020). De Assis et al. (2017) conducted a financial and risk assessment on the minimum product selling price of CNFs. Three scenarios were considered. The first scenario was a stand-alone company that produces CNFs from pulp. The cost of pulp, electricity and depreciation accounted for 60%, 15% and 12 to 14% of the production cost, respectively. The second scenario was the co-production of CNFs in a mill that produces pulp. The minimum product selling price for scenario 2 (USD 2 440/t dry CNFs) was 37% lower than that of scenario 1 (USD1893/t dry CNFs) due to reduced capital investment, labour , pulp, transport, and handling costs. The third scenario was called the on-demand co-location, where the CNFs produced were incorporated in the papermaking process within the same facility. Scenario 3 resulted in additional cost savings on labour. Besides co-location, the cost of CNFs source (pulp) was studied. Choosing a cheaper source of CNFs greatly reduces the minimum selling price of CNFs, which is beneficial in competing with the cost of traditional paper additives (de Assis et al., 2017). Also, if zero cost sources such as agricultural waste and recycled fibres are used, considering that studies have proven that CNFs from waste is as effective as CNFs from bleached pulp, the production process becomes cost-efficient (Balea et al., 2017).

3.0 CONCLUSION

Most of the studies in this review suggest that the main role played by CNFs is that of a binder for fibres in paper. The mechanisms involved in papermaking are influenced by the inherent properties of CNFs, such as the high aspect ratio and the high strength and modulus. The high aspect ratio enables CNFs to entangle around fibres, filling voids and bridging adjacent pulp fibres. The compact and strong network of fibres formed result in improved mechanical properties of paper such as tensile index, burst index, Scott index, breaking length, tear index, Z-strength, E-modulus, strain at break, and tensile stiffness. CNFs provide a sustainable route to papermaking while enhancing the mechanical, functional and barrier properties of paper.

However, the drainage properties are always negatively affected, especially in the pressing and drying sections of the papermaking process. In addition to the properties of CNFs: dosage, the strategy of addition and source of CNFs influence the extent of paper improvement. Despite the wide range of sources of CNFs, high energy requirements are still a major setback in the production of CNFs. However, investigation of the use of CNFs from zero cost agricultural waste and recycled paper pulp as paper additives has been proven to improve paper properties. The negative or zero-cost of the waste compensates for the high production costs of CNFs.

Furthermore, by taking advantage of similar raw materials in papermaking and CNF production, in situ production of CNFs eliminates transport and handling costs and ensures optimisation of the product to meet the required properties for speciality grade paper products. Finally, although CNFs improve mechanical, optical and air barrier properties, the hydrophilicity of paper is increased. This further limits the applications of paper. The main challenges associated with CNFs are poor compatibility with hydrophobic polymers, high polarity (presence of many hydroxyl groups), which cause re-bonding between individual CNFs when dried and when mixed in non-polar solvents or at low pH results in loss of the nanoscale dimension (Jawaid et al., 2017). Therefore, CNFs should be stored as suspensions with low solid content, which is a major limiting factor in large scale applications such as papermaking. Future research should investigate the effect of morphological and biochemical properties of the source of CNFs on its performance as a paper additive. There is limited research on the recyclability of paper reinforced with CNFs.

4.0 Declarations

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Thabisile Brightwell Jele had the idea for the article, Thabisile Brightwell Jele performed the literature search and drafted, Prabashni Lekha and Bruce Sithole critically revised the drafts and approved the review for publication.

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Consent to participate

Not applicable

Consent for publication

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