Research Article

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Cellulose Nanocrystals: Production, Functionalization and Advanced Applications

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Abstract: Cellulose nanocrystals (CNC) are a class of nanoscale biopolymers produced from cellulose sources. CNC materials have gained growing interests which can be attributed to their excellent properties such as excellent biocompatibility, good mechanical properties and high aspect ratio whilst also being an inexpensive material that can be produced from green and renewable sources. Due to the abundant hydroxyl functional groups, the surface of CNC materials are ready to be tuned and functionalized via chemical reactions allowing for many different applications, such as being a reinforcing agent to be incorporated into a hydrophobic polymer matrix. In this review paper, we firstly introduce the general methods for producing CNC from different sources. Different strategies used for surface modification of CNC are then discussed. Finally, the recent progress on the applications of CNC and CNC composite materials are described in detail.

1 Introduction

The use of green and renewable materials has become increasingly important for the sustainable environment of the planet. This focus on environmentally friendly methods has led to a renewed and strengthened interest in the use of natural materials such as cellulose [1] and lignin [2] from plant materials, as well as chitin produced from various sources [3].

Cellulose is the most readily available biopolymer in the world with many different source materials being readily available. Cellulose is primarily found in plants (shown

in Figure 1), as an integral part of the cell walls that help provide strength in the plants structure. Cellulose sources include wood pulps [2, 4–8], algae [8], cotton [8–13], agricultural wastes [14–18] and bacteria [19]. Cellulose has been used for centuries for many purposes including paper, food, pharmaceuticals, and other biomaterials [1, 20–22].

Figure 1: Structure of wood biomass and cellulose characteristics. Reproduced from [119] with permission of the Royal Society of Chemistry.

Cellulose is an organic polysaccharide compound consisting of a linear chain of several hundred to many thousands of $\beta(1\rightarrow4)$ linked D-glucose units [23]. Recently, the production and use of cellulose based nanomaterials has gained a high interest due to useful properties found within them such as high aspect ratio, good mechanical properties, excellent biocompatibility and easily modified surface. Nanocellulose from plants can be broken down into two primary areas, nanofibres and nanocrystals. Nanofibril cellulose (NFC) is the individual fibres of cellulose which have been separated from each other via fibrillation [24]. Cellulose nanocrystals (CNC, also referred to as nanocrystalline cellulose and cellulose nanowhiskers) is the crystalline regions within these individual nanofibres that have been extracted. Despite both being made from cellulose, the two materials are significantly different in structure, size, strength, and composi-

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Figure 2: TEM images of (a): CNC and (b): NFC. Image reproduced from [32]. Copyright 2013 American Chemical Society.

tion. The production of nanofibrils is commonly performed using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) oxidation along with the mechanical treatment such as pressure homogenization or by direct mechanical fibrillation to properly separate the fibres from each other [22, 25–31]. Xu measured the size difference between CNC and NFC using TEM (Figure 2). It was shown that the NFC had an average length of about 1,030 nm which is significantly longer than that of CNC (about 151 nm) [32].

Due to their specific strength, modulus and aspect ratio [15], CNC is desirable for many applications. An area of interest in recent years has been the application of CNC as a filler content or a reinforcing agent within polymer networks [33, 34]. This improvement allows for the creation of cheaper, lighter and stronger materials for industrial applications with the added benefit of using greener sources.

Another advantage of CNC is its surface is easily modified thanks to the presence of hydroxyl groups throughout the polymer chain which give sites for selective modification [35]. These properties combined with its low cost, green and abundant sources allows for a highly desirable nanomaterial for many different applications.

2 Production of Cellulose Nanocrystals

As cellulose is primarily found in plants, it allows for a large opportunity for source materials. Wood is a common industrial material, and there is an abundance of waste materials created during the wood processing such as saw dust or wood pulp. Wood pulp is commonly used to produce CNC as it has already been partly processed removing noncellulose content.

Previous work has also explored the use of wastepaper [36, 37] for the production of CNC due to limitations for recycling paper materials back into paper, thus creating a large amount of waste paper materials that can be exploited for the production of CNC.

Waste cotton cloth is another example of repurposed waste materials for the creation of CNC. Wang *et al.* [38] recently explored the use of bed sheets to produce CNC, the sheets were successfully refined into cellulose based nanomaterials, with the produced CNC varying in size between about 28 to 470 nm in length.

The agricultural industry is an opportunity for the production of CNC [39]. Examples of these materials include rice husk [40], grains [41] and garlic straw [42]. As all three materials are commonly produced on a significant scale globally (particularly rice and grain), the waste materials from these areas alone are an exploitable cheap source of cellulose.

Several methods have been developed for extracting CNC from cellulose. The primary method is via a hydrolysis process which involves the breakdown of amorphous regions of cellulose fibres. There are multiple hydrolysis methods with acid hydrolysis being the most commonly performed due to its short reaction time. Enzymatic hydrolysis has the benefit of not requiring harsh conditions such as highly concentrated acids. However, enzymatic hydrolysis is often not desirable due to the extended time that is required for the process to properly occur. In addition, the use of mechanical energy (such as pressurised homogenisation) is often applied during or after the hydrolysis to help further break down the extracted crystalline regions into the individual whiskers [43].

2.1 Acid hydrolysis

Sulphuric acid is the preferred acid for the acid hydrolysis process as it requires relatively mild conditions in comparison to other alternative acids. Nevertheless, it is not the only acid being used, other acids such as formic acid [29] and hydrochloric acid [44] have also been used for the successful breakdown of the cellulose into nanocrystals.

The general consensus for the hydrolysis method involves a relatively high acid concentration (between 50 and 70 wt%), a temperature approximately around 40–50°C and a hydrolysis time between 30 and 90 minutes [45]. A summary of a typical production method is shown in Figure 3. The alteration of these parameters has been shown to impact the quality of the produced CNC including the length of the crystals and the efficiency of removing the amorphous regions of the base cellulose.

Figure 3: Typical procedure for producing CNC materials.

This has led to research on the optimal conditions for CNC production especially, when it comes to the acid concentration. Researchers have investigated how the acid concentration affected the yield and characteristics of the produced CNC. For example, Chen and his colleagues explored how three potential variables (concentration, time and temperature) impacted the yield of CNC produced from a bleached eucalyptus kraft pulp [5]. From this work, it was found that the yield was improved with increasing acid concentration up to about 62 wt%, after which there was a drop. However, the length of produced crystals decreased with increasing acid concentration due to further depolymerisation of the cellulose chains. A comparatively rapid hydrolysis time of less than half an hour was sufficient if a temperature of above 50°C was used for the hydrolysis. From the work it was concluded that the key parameter for hydrolysis process was in fact the concentration of the acid. Even rather minor changes in concentration led to significant changes in the outcome. The valid acid concentration was between 56 and 58 wt%, in which below 56% was not adequate to properly depolymerize CNC while above 62% also hindered the production of CNC. High acid concentration would significantly in-

crease the cellulose hydrolyzation process to produce glucose rather than CNC. It has been found that keeping the same conditions but extending the hydrolysis time would lead to a degradation in the crystallinity for the same reasons.

Whilst the hydrolysis process itself is very rapid, the post treatments of the produced CNC including neutralising excess acid and drying extend the total production time to being closer to two weeks.

An alternative procedure for acid hydrolysis has been explored involving the use of acid vapour instead of a solution [46]. In this method, a desiccator had a 35% HCl solution poured into the bottom and allowed to sit for at least 5 days with the valve open to create a HCl environment. Then, a filter paper (from cotton linters) was placed inside the desiccator and the hydrolysis was allowed to proceed for 12 hours. This method has the advantage of significantly reduce the post treatment after dialysis

Whilst the conditions of the hydrolysis process such as the acid concentration, temperature, and time can affect the properties of the produced crystalline regions due to degradation from over exposure to acidic conditions, the properties of the produced CNC are also affected somewhat by the type of acid used as the acid residue would adsorb on the surface of the nanocrystals. In addition, the CNC material source also have a significant impact on the sizes of CNC produced due to different cellulose contents and growing environment.

2.2 Enzymatic hydrolysis

Enzyme hydrolysis is an alternative method that involves the use of enzymes to breakdown the cellulose [47]. These enzymes are commonly found in fungi and bacteria which are used to breakdown cellulose into sugars as a food source. The amorphous regions of cellulose are normally broken down earlier than the crystalline regions due to weaker chemical bonds.

Cui *et al.* investigated the production of CNC from a wheat straw using cellulase with the aid of ultrasonication treatment [48]. From their work it was reported that the process required a significant amount of time (120 hours) for the highest CNC yield to be produced from the source cellulose. Sonication could facilitate the enzymatic hydrolysis process. Extended sonication time (one hour in every 12 hours) led to the highest yield of about 22.6%. This obtained yield is rather similar to yield from acid hydrolysis but still has the disadvantage of requiring such a significant time investment.

2.3 Subcritical water hydrolysis

An alternate method for hydrolysis has been explored using subcritical water [49, 50]. Subcritical hydrolysis has the advantage of not requiring harsh conditions as found in acid hydrolysis whilst also being a relatively quick process unlike enzymatic hydrolysis. The method to produce CNC via subcritical water hydrolysis is represented in Figure 4, where cellulose materials were added to a reactor filled with water and heated to the desired temperature of either 120 or 200°C for 60 minutes with the pressure being maintained. The produced CNC material was then separated from the solution via filtration and was then dialysed for 5 days to remove any soluble sugars that formed during the process. Finally, the suspension was sonicated and filtered again to remove unhydrolyzed cellulose leaving only the CNC suspension.

Figure 4: Schematic showing methodology for subcritical water hydrolysis. Reproduced from [50] Copyright 2015 American Chemical Society.

2.4 Mechanical processing

The use of mechanical energy has also been explored to facilitate the production of nanocellulose. The breakdown of microcrystalline into nanocrystalline via mechanical processing involves the shearing of the fibres across a plane. This process is repeated multiple times to separate and reduce the overall size of the fibres. Typically, the methodology used involved the application of pressure homogenization or ultrasonication [51].

The application of sonication post hydrolysis has been explored [43, 52] and was found to be helpful to further refine the produced CNC by breaking down the large crystalline regions into individual nanowhiskers and creating smaller crystals with improved aspect ratios. This additional sonication was done at relatively low frequencies of about 20 kHz with the longest application being 10 minutes [43].

2.5 Bacterial cellulose

Bacterial cellulose is another form of nanocellulose. As the name suggests, it is a form of cellulose produced by bacteria as a source of energy. It takes on a gel like form. Laboratory controlled production has been gaining interest for multiple uses especially within the biomedical industry [19]. Due to its high water absorbance and biocompatibility, bacterial cellulose has been used for bandages and wound treatment to help the wound healing process [53]. Bacterial cellulose has also been used in tissue engineering for promoting cell growth [54].

2.6 Yield

As nanocellulose is produced from many different natural sources, there is variation between source materials leading to differences in the yield obtainable. For plant materials, the useable crystalline cellulose content is often only a small percentage of the total composition, with much of the content being composed of lignin and hemicellulose instead.

The most common method for extracting cellulose from the source material, such as wood pulp, involves pulping to breakdown the solid material followed by a bleach and NaOH treatment, which is performed to remove the non-cellulose content [55]. The exact composition varies between individual plants, but it is quite common for a plant to only have about 40% cellulose content total. The potential yield of CNC is then further reduced due to the amorphous regions of cellulose also being part of the product. This then combined with the efficiency of the production process can lead to quite a lot of variation for the potential yield. Typically, an optimal yield of CNC from cellulose could be around the 70-80% range making the total yield from starting source material approximately 20-30% [29].

3 Properties of CNC

3.1 Size and Aspect ratio

The size and aspect ratio of the produced CNC varies depending on the source material as well as the production method used. The size of the nanocrystals is directly related to the size of the crystalline regions of the cellulose fibres but can be reduced because of the degradation caused during the hydrolysis process. The variation in size can be

Table 1: Comparison of the size and yield of CNC extracted from different source materials.

Source Material	length (nm)	Yield %	Technique	Reference
Cotton	270-280	33	Sulphuric acid	[8, 109]
Wood pulp	100-500	20-30	Sulphuric acid	[8, 31]
Cassava Bagasse	1150	30	Sulphuric acid	[84]
Sisal fibres	215	-	Sulphuric Acid	[67]
Kelp	-	9.6	Sulphuric Acid	[110]
Red Algae	432	20.5	Sulphuric acid	[8]
Cattail fibres	249	17	Sulphuric acid	[8]
Waste Cotton	28-470	46.7	Sulphuric acid and hydrochloric acid	[38]
Tunicin	1073	-	Sulphuric acid	[109]
Garlic straw	400-700	19.6	Sulphuric Acid	[41]
Wheat straw	84-306	12.4	Sulphuric acid	[18]

seen in Table 1 which shows CNC produced from different sources.

To measure the size of the cellulose nanocrystals, microscopy techniques such as SEM, TEM or AFM [4] are employed to look at the dimensional properties of individual nanocrystal, with TEM being the most commonly used of the three. Particle sizing techniques such as dynamic light scattering can also provide size information but are not desirable due to the shape of the CNC.

The size of CNC varies quite significantly. The length of CNC are from 100 nm up to the μm range and the width usually is within a range of below 10 nm to about 50 nm. The wide width range of CNC could be potentially caused due to multiple individual fibres not being properly separated during the production. As the produced nanofibres have a small width of a few nanometres and a length of a few hundred micrometers on average, the aspect ratio of CNC is very high. This large aspect ratio allows for the CNC to have a high surface area compared to its volume which helps in a nanocomposite situation as it allows for more interaction between the filler content and the surrounding matrix.

3.2 Mechanical properties

CNC has been proven to have excellent mechanical properties such as a high tensile strength and modulus (tensile strength 1.7 GPa and tensile modulus 100-140 GPa, [56]). Measurement of the modulus can be performed using AFM. However, these results might not truly accurate due to the resistance of the surface used for AFM.

Paper-like films produced using nanocellulose has also been shown to have a very good tensile and mechan-

ical strength compared to paper produced from purely macroscopic materials [39].

3.3 Crystallinity

The crystalline index of CNC is most commonly performed using Segal's method [57] in which the crystallinity is determined from an XRD spectra, using the following equation.

$$I_{Cr} = \left(\frac{I_{002} - I_{am}}{I_{002}} \right) \times 100$$

Where I_{Cr} is the crystallinity index, I_{002} is combination of crystalline and amorphous region taken at the intensity at $2\theta = 22.6^\circ$ and I_{am} represents the amorphous region using the intensity at $2\theta = 18^\circ$.

Segal's method allows for a quick and simple way of determining crystallinity for cellulose and its derivatives. However, as a method in terms of accuracy there are some problems as it is a relative measurement [58].

3.4 Toxicity

Whilst CNC is derived from cellulose which is a commonly consumed material, CNC is a nanomaterial that leads to new potential health hazards. Cytotoxicity of CNC has been tested to ensure that it is safe to consume. According to the test results, there was found to be no significant health risks involved with the consumption, inhalation or general handling [59].

Eco-toxilogical effects of CNC have also been explored to ensure the safety of marine life [60]. From the testing it was found that CNC was of low concern to aquatic life even

at worst case conditions for the testing. The only concern was at a concentration of 29 mg/L at which fish reproduction was hindered. This concentration is significantly high and well above what could be expected to occur in the environment.

Whilst there have been no shown health concerns involving CNC materials, the toxicity of nanocellulose materials could be affected by production methodology and how the surface has been treated (such as the presence of sulphate groups or modifying agents on the surface). This could lead to potential health hazards, suggesting that testing should be performed on a case by case basis.

3.5 Surface chemistry

CNC has been shown to have a negative surface charge which can be seen from zeta potential tests. This is due to the presence of the hydroxyl groups and partially explains the highly hydrophilic properties of it. Part of the hydrophilic property can also be explained by being part of a plant that requires the storage of water to be able to survive.

The hydroxyl groups of CNC can also be a problem as they can create hydrogen bonding between individual fibres. These hydrogen bonds create larger agglomerates of CNC. This agglomeration can be a hindrance when attempting to modify and disperse CNC within a polymer network.

3.6 Piezoelectric properties

Cellulose itself is not conductive or have any inherent electrical properties. Cellulose has been shown to exhibit piezoelectric properties which means that it produces an electrical charge in response to mechanical stress being applied onto it [61].

4 Surface functionalization of CNC

CNC is limited in its use as nanofiller content due to its hydrophilic nature. Surface modification is thus necessary to reduce the hydrophilic property, increasing compatibility with organic networks. This has been explored using various methods such as polymer grafting, functionalization using silane coupling agents, isocyanates and surfactants. This hydrophobic surface modification greatly improves the dispersion of CNC within an organic network. When choosing what material/functional group to modify

on the surface of CNC, some consideration on the type of material that CNC will be interacting with has to be considered. Different modifications may be more successful in different situations. For example, modifying the CNC with an isocyanate helps its dispersion within a polyurethane network [62].

Similar to other nanomaterials, many of the current modification pathways exploit the hydroxyl groups which are on the surface of the cellulose. Such as in the case with silane coupling agents where silanization occurs binding the silica group to the surface of the CNC. The same is also true for isocyanates in which the modification process exploits the hydroxyl group to react with the end of the chain creating a urethane chain on the surface of the CNC.

4.1 TEMPO oxidation

One of the main methods for nanocellulose functionalization that have been explored is the oxidation by TEMPO. TEMPO is a commonly used oxidation agent that turns alcohols into aldehydes, but it can also be used to produce carboxylates and ketones. TEMPO oxidation for cellulose based materials is commonly carried out in the presence of sodium hypochlorite and sodium bromide (as shown in Figure 5).

This process has been shown to selectively oxidise the hydroxyl groups present on the surface of the cellulose fibres to carboxylate groups [30]. From conductometric titrations it was shown that the oxidation of the cellulose increases as the sodium hypochlorite concentration increases. Whilst the oxidation was changed it was not shown to impact the crystallinity of the material.

This process can be performed on the starting cellulose when it is broken down into individual nanofibrils, which allows for a simple one-pot production of modified nanocellulose. TEMPO oxidation is commonly used as a precursor modification before further functionalization is performed such as polymer grafting [63].

4.2 Silane coupling reactions

Silane coupling agents have been relatively unexplored for the modification of CNC. The coupling agents that had been explored involve the reaction of the oxy group to the hydroxyl groups present on the surface of the CNC (represented in Figure 6). This process also creates alcohol as a by-product. Silane coupling agents typically have long chains that is useful in the context of trying to reduce the hydrophilic properties of CNC. Silane coupling agents have

the advantage of allowing for further modification onto the grafted chain depending on the used coupling agent. Different methods and silane agents have been explored for the modification process.

Kargarzadeh *et al.* used *N*-(β -aminoethyl)-aminopropyltri-methoxysilane (APS) to modify the surface of CNC [64]. The method was performed by dispersing CNC in a mixed solution of water and ethanol containing

Figure 5: Oxidation of Cellulose by TEMPO/NaBr/NaClO at pH 10-11. Reproduced from [119] with permission of the Royal Society of Chemistry.

Figure 6: Schematic for silane reacting with hydroxyl surface groups of CNC.

silane agent. After pH adjustment using acetic acid, the solution was sonicated for 3 minutes and then rested for 2 hours. This method has the advantage of being a one-pot reaction which does not require much additional energy outside of sonication to properly disperse the CNC within the ethanol/water solution. The modified CNC was shown by TEM to have an improved dispersion with less agglomeration when mixed into the polymer matrix in comparison to the starting CNC indicating an improved hydrophobic property. The same group used an updated version of the above method which was the same in most ways except adding an extra step of being heated for 3 hours at 60°C to remove any excess silanes that remained [65].

APS is not the only silane coupling agent that has been explored for the surface modification of CNC. De Oliveira Taipina *et al.* looked at using 3-isocyanatepropyltriethoxysilane (IPTS) as a surface modifying agent for CNC. They used a rather simple method for the production in which CNC were dispersed within DMF in an inert nitrogen environment before being reacted with the silane coupling agent for 8 hours, then the catalyst was added and mixed for another 30 minutes [9]. From optical microscopy modified CNC was shown to have an improved dispersion within a non-polar solvent.

Crosslinking between PLA and CNC has been explored using vinyltrimethoxysilane which is a vinyl based silane coupling agent [66]. This modification was first done by melt mixing the silane agent with the PLA creating binding through the vinyl groups with this combined a CNC suspension which was heated to create the silanization allowing it to bind to the PLA.

4.3 Isocyanates

The methodology for isocyanates is somewhat similar to when using a silane coupling agent, in which the hydroxyl group is the point of interaction for the functionalization process reacting with the oxygen at the end of the functional group. This forms a urethane chain grafted onto the surface of the CNC.

Girouard *et al.* explored the use of an isocyanate to modify the surface of CNC. In this work, the surface of the CNC was modified using isophorone diisocyanate (IPDI) [62]. CNC was dispersed in DMSO by sonication before being mixed with IPDI and a catalyst and reacted in a nitrogen environment at 60°C overnight. Using polarised light microscopy, the modified CNC materials were shown to have an improved dispersion within a polyurethane matrix when compared to the unmodified CNC.

Figure 7: Protocol for the two surface grafting methods. Adapted from [67] copyright 2010 American Chemical Society.

Siqueira investigated the methods of CNC modification using *n*-octadecyl isocyanate (summarised in Figure 7) [67]. Both methods relied upon a solvent exchange starting with acetone, after which the methods diverged with the first solvent exchanging to dichloromethane and then toluene and the second relying on an in-situ solvent exchange for the acetone to toluene instead. During the solvent exchange to toluene, an excess amount of *n*-octadecyl isocyanate was added drop by drop and then heated to 110°C. From this work, it was found that the first method was a rather poor dispersion compared to the second method which was found to be successfully homogeneous within a polymer film indicating a more successful functionalization.

4.4 Surfactant adsorption

Modification of CNC can be performed by the non-covalent adsorption of materials such as surfactants [68]. The technique was performed by dispersing CNC into the surfactant (such as phosphoric esters) solution and had pH adjusted to be roughly 9. From microscopy images, the modified material was shown to maintain a stable dispersion in a non-polar solvent indicating a successful modification.

As a way of changing the polarity of the CNC to be non-polar, surfactant adsorption has the advantage of being a very simple process which does not require the use of a significant amount of energy for it to be performed.

4.5 Polymer grafting

Grafting polymers onto the surface of the CNC has been explored using different methods. Commonly atom transfer radical polymerization (ATRP) has been used as a method for polymer grafting as it allows for an in-situ polymerization process. Methyl methacrylate and butyl acrylate (BA) are two monomer examples grafted onto CNC [69]. To have the ATRP reaction to occur, CNC first had an initiator bound to its surface in the form of 2-bromoisobutyl bromide. The in-situ polymerization occurs between the bromide groups bound to the surface and the MMA and BA in solution. Deng *et al.* also explored a graft copolymerization procedure using MMA which was performed by dispersing CNC in a solution of ceric ammonium nitrate/nitric acid containing MMA and was allowed to copolymerise for 3 hours at 45°C [70].

Espino-Pérez *et al.* explored the functionalization of polysaccharide nanocrystals via free radical polymerization promoted by ozonolysis [71]. Ozonolysis is the application of ozone to break double bonds in organic chains to create new sites for reactions. After ozonolysis, an additional reagent can be added to allow functionalization to occur. From the work it was reported that the thermal stability of the CNC improved by approximately 100°C post modification. It was also found that the efficiency of the grafting process would further help improve upon the reduction of the hydrophilic properties.

Poly(ethylene oxide) was grafted onto the surface of CNC in an aqueous suspension by Kloser and Gray [72]. The grafting process was performed by the addition of the

(a) Route 1: One-pot, two-step reaction

Figure 8: Summary of methodology used for hydrophobized CNC using a fatty acid. Reproduced from [79] copyright 2016 American Chemical Society.

epoxy terminated PEO into a solution containing sodium hydroxide and the CNC, the solution was heated for an extended period before having dialysis performed to remove any excess material that could remain. After this modification, it was found that CNC remained stably suspended within solution.

4.6 Esterification

Like other techniques, esters can also be produced on the surface of cellulose by reacting the hydroxyl groups of CNC with an alcohol. Alternatively, the cellulose surface can easily be modified using a carboxylic acid via Fischer esterification process. This method has the advantage of allowing for a single step hydrolysis and modification of the cellulose into CNC [73]. Braun and Dorgan explored this process by dispersing the CNC into an acid mixture of hydrochloric acid and an organic acid. After this modification, CNC dispersion in hydrophobic solvents was found to be improved indicating that the hydrophilic properties had been reduced.

CNC has been modified via carboxylation processes using carboxylic acid derivatives such as acid anhydrides. The use of acid anhydrides for the surface modification has been an area of interest [74–77]. The anhydrides react with the hydroxyl groups on the surface of the CNC to create an ester changing the surface properties. Other materials

such as acid chlorides have also been explored as a way to create esters on the surface of the CNC materials [78].

One advantage of esterification is the use of green and safe materials such as fatty acids [79]. The advantage of using these fatty acids in place of more toxic materials, is because it allows for a more industrially viable production due to the reuse of materials in the synthesis process (Figure 8). Two different methods were used for the modification and it was shown that there was a preference between fatty acids and fatty acid esters.

4.7 Degree of Substitution

When nanocellulose reacts with an agent, not all hydroxyl groups react and are modified. This is due to limitations in the available hydroxyl groups for modification. Whilst the anhydrogluco unit (the inner glucose monomers for the polymer chain) contains three hydroxyl groups, not all hydroxyl groups are available for reaction due to the orientation of the fibre. When measuring the total hydroxyl groups being modified, the degree of substitution (Ds) is used [35]. The degree of substitution is measured out of three. For most traditional modification methods, the reported Ds is around 0.5–0.8.

Certain functionalization methodologies that do not entirely rely upon surface reaction can potentially lead to an improved Ds. Methods such as esterification have been

Table 2: List of CNC based composite materials.

Polymer	Modification of CNC	Processing Method	Reference
PMMA	Polymer grafting	Electrospun	[111]
PMMA	None	Mixing	[112]
Chitosan	None	Mixing	[113]
PVA	None	Mixing	[13]
PVA	Graphene	Mixing	[114]
PVA	None	Electrospun	[115]
PMVEMA:PEG	Crosslinking	Mixing	[116]
Polyethylene	Organic acid chlorides	Mixing	[117]
Polyurethane	Isocyanate	Mixing	[83]
Plasticized Starch	None	Mixing	[85]
Epoxy Resin	Cross linked with polymer	Mixing	[92]
Poly(lactic acid)/Poly(butylene succinate)	Surfactant	Mixing	[87]
PLA	None	Electrospun	[86]
Polystyrene	Polymer grafting	Extrusion	[63]
Unsaturated Polyester Resin	Silane coupling agent	Mixing	[64, 65]
Waterborne epoxy	None	Mixing	[82]
Polypropylene	MAPP	Melt blending	[118]

shown to have a higher D_s indicating that the modification process potentially involved reacting with non-surface hydroxyl groups.

When incorporating CNC into a polymer network, sometimes it is important to take D_s into consideration if the grafted functional groups interact with the polymer network, such as epoxy resin. It is important to recalculate the ratio of the two epoxy components for an optimal reaction.

5 Application of CNC

5.1 Reinforcing Agent

A nanocomposite material is a multi-component material in which at least one component is a nanostructured material which has at least one dimension below 100 nm [80]. Nanocomposites often offer unique properties compared to single materials. The use of reinforcing agents in polymers is a common example. Using the rule of mixture, it is said that when a material with a certain property is added as a dispersed phase it will impart some of that into the continuous phase.

As examples listed in Table 2 show, cellulose nanocrystals have been obtaining interest in being a filler content for use in polymers in recent years [81]. As cellu-

lose's primary role within plants is to add strength and stiffen to cell walls and create stability, it is desirable as a reinforcing agent within a polymer matrix.

CNC has been added into a large variety of different polymer networks to act as a nanofiller content with varying impact on the properties. The addition of unmodified CNC into waterborne epoxies was shown to improve the mechanical properties for polymers, thanks to the high hydrophilicity of CNC leading to a good dispersion within the water based system [82].

One waterborne polymer tested was polyurethane [83]. From their work it was found that it was possible to add up to 30 wt% CNC to the beginning polymer. This is a significant loading in comparison to most work which is usually below 10% loading. The most extreme result was the exponential increase in the tensile modulus for the polyurethane, increasing from 0.5 MPa with the blank sample up to about 344 MPa at 30% loading which is an incredibly significant rise to the tensile modulus. However, the tensile strength did not have a significant improvement in comparison, with only increasing from 4.3 MPa to approximately 14.9 MPa - an improvement of about 246.5%. Whilst the strength and modulus increased, it came at the cost of reducing the elongation breaking point, quite significantly from 1086% the starting length to 186%, reducing greatly the elastic properties of polyurethane. This

result coincided directly with the increase in the tensile modulus.

Unmodified CNC has also been explored for use in natural rubbers [84]. Natural rubbers have the advantage of being commonly obtained from trees which is one of the primary sources of cellulose. This leads to great compatibility between the filler content and the network it is dispersed within. The addition of CNC into a natural rubber system increased the storage modulus which is to be expected when a stiffening agent has been introduced into the network [84].

Plasticized Starch as the name suggests is a thermoplastic produced using starch [85], which is very similar to cellulose in that starch is the same monomer in the polymer chain with the difference being an alpha orientation instead of beta like cellulose. From the work of Cao and their colleagues, it was found that CNC dispersed homogeneously throughout a starch matrix. It was also found that the flexibility of the produced samples was reduced due to the intermolecular interactions between CNC and the starch. This increase in stiffness could be seen from the increase in the tensile modulus which improved from approximately 32 MPa to 823.9 MPa.

Cellulose has been explored in multiple papers for the use as a filler content in poly(lactic acid) (PLA) which is a bioplastic [86–89]. The appeal of this is attempting to improve the produced plastic in a completely environmentally friendly and biodegradable manner. The addition of CNC into PLA was not very successful with poor mechanical properties in comparison to the blank samples [89]. This poor result can be explained by the poor dispersion within the network leading to clusters of the CNC within the PLA creating points of weakness.

As most polymer networks are not water or natural based, instead of using unmodified CNC, modified hydrophobic CNC is used to be properly dispersed, alternatively making CNC part of the network. There are unique types of plastic that have been explored for making nanocellulose composite materials. Primarily most of this work has focussed on thermoplastics [90] with a lower focus on the use of thermoset plastics [91, 92]. As each plastic is comprised of a unique composition and created under different conditions, different modifications or methodologies for dispersion may be required to properly disperse the CNC within the desired network.

The addition of silanized CNC into an unsaturated polyester resin and the improvement to the mechanical properties compared to unmodified CNC was studied [64, 65]. Results showed that the modification of CNC with N-(b-aminoethyl)-aminopropyltrimethoxysilane helped to reduce the hydrophilic properties and in turn improved

the tensile strength and modulus in comparison to the use of unmodified CNC. Part of this improvement can be explained by the addition of amine groups into the network which helped to improve the stiffness of the plastics.

The functionalization of CNC using isocyanates resulted in the formation of urethane chains on the surface of the CNC. This modified CNC have been widely explored as a filler for polyurethane materials. Giourard group [62] reported the modification of CNC with isophorone diisocyanate. It was found that this functionalization helped to vastly improve the dispersion of the CNC throughout the polyurethane network. This occurred as the isophorone diisocyanate functionalization created similar chains on the surface of the CNC as found in the polyurethane matrix. The incorporation of CNC was found to greatly improve the tensile strength and fracture toughness. With even a 5 wt% CNC addition, the tensile strength was improved by roughly 226% over the blank tests, and fracture toughness improved by about 257%.

TEMPO oxidised CNC with further modification to form carboxylates on the surface has been used as a nanofiller content for preparing polypyrrole composite to be used as a cheap and green potential supercapacitor. Polypyrrole is a polymer which has gained a lot of interest due to its good conductive properties on its own. It was found that the modified CNC has good dispersion within the polypyrrole network with good interaction between the two components. The addition of CNC was found to improve the conductivity of the polymer network by increasing the surface area of the polymer and forming a porous structure. From the work it was found that the CNC/polypyrrole composite material had a higher specific capacitance compared to many other hybrid structures including polypyrrole hybridized by carbon nanotubes and graphene, obtaining a specific capacitance of 248 F/g [25].

In another work, CNC was modified with PMMA using an ATRP grafting process. The PMMA modified CNC was incorporated into a PMMA plastic network [69]. In this work, it was found that the addition of CNC within PMMA greatly improved the mechanical properties including tensile and elastic properties. Part of this improvement could be potentially explained by the excellent dispersion of CNC within the polymer network. CNC was not simply mixed into the polymer like in most other cases; instead it has become an integral part of the polymer backbone by being directly attached to the monomers.

CNC were thermally cross-linked with an epoxy resin [92]. In this work, instead of modifying CNC to be hydrophobic and then dispersed within the plastic before curing, CNC were incorporated as part of the epoxy resin by binding to the glycidyl group on the end of an epoxy chain

via an etherification reaction. In this work, CNC was dispersed within DMF via solvent transfer before being processed with the co-monomers. The film sample was then cast via an evaporation method and then cured at 150 degrees. The high temperature initiated the cross linking between two monomers to create a thermoset plastic with CNC incorporated into its network. This worked investigated the effect of loading percentage and 75% was found the most efficient loading for the overall crosslinking process. This higher loading was required due to the fact that loadings below 50% were inadequate for cross linking to properly occur. With the addition of the CNC into the epoxy resin, the mechanical properties of the resin were found to be greatly improved, with the modulus being the most significant improvement. This can easily be explained by the CNC addition within the network creating a stiffer plastic compared to the neat one which would be more elastic.

CNC which had surface hydroxyl groups replaced with citrate or formate were used as reinforcing agent in polyester(3-hydroxybutyrate-co-3-hydroxyvalerate) [93]. This reinforcement helped improve the mechanical properties due to the hydrogen bonding occurring between the polymer and the CNC creating a stronger network. This intermolecular bonding also lead to an improvement in the thermal degradation. From the work, the optimal choice was found to be the CNC, which had been modified with citrates due to the additional possibilities.

There are disadvantages for the use of CNC as a filler content in a polymer composite such as the hydrophilic properties limiting the dispersion and mixing capability. Moisture is another disadvantage as moisture can be absorbed by the CNC material causing swelling of the material, altering the dimensions and mechanical properties. Due to CNC burning at low temperatures, it does somewhat limit the application for the material including the polymer matrix used and the processing methodology used.

These disadvantages are outweighed by the overall advantages of using CNC such as renewables source materials, low safety concerns, low weight and adaptability of the material.

5.2 CNC as a barrier material for filters

CNC has been explored for use as a barrier material in different types of filter membranes. The addition of CNC into a film can help reduce water and oxygen permeability [94]. Nanocellulose based aerogels and foams have also been explored for use as air filtration membranes [95–98]. For the production of CNC aerogels, CNC needs to be modified and TEMPO oxidation has been a popular mod-

ification method for this purpose. For example, Nemoto *et al.* reported the use of TEMPO modified cellulose to be dispersed in a water/tert-butyl alcohol mixture [98]. After freeze dry, the CNC formed an aerogel with large specific surface area reaching over 300 m²/g which showed high particle filtration capacity.

5.3 Adsorbents for waste water treatment

Modified CNC has been explored for waste water applications such as the adsorption of heavy metal ions or for the removal of dye from water solutions. For example, CNC modified by succinic anhydride and sodium bicarbonate was used for the removal of Pb²⁺ and Cd²⁺ ions [99]. From the work it was shown that the modification of CNC led to a significant performance improvement compared to the blank CNC, and was also recyclable allowing for the reuse of the modified CNC as an adsorbent.

The use of CNC as an adsorbent for dye removal has been explored for both anionic [100] and cationic [101] dyes. The modification of CNC resulted in improved adsorption of dyes from water showing CNC could be a promising material for waste water treatment.

5.4 Biomedical applications

Thanks to its biocompatibility, CNC has been explored for use in biomedical applications. Toxicity has been tested to ensure that the material is safe for use within a human body showing that there are no significant health hazards associated for neat CNC.

Fluorescent CNC have found a promising application within bioimaging and drug delivery systems [102]. The modification of CNC with fluorescent materials was investigated focussing on whether the fluorescent CNC was cytotoxic and potentially damaging cells after cellular intake. From the work it was found that the cellular intake was dependent on the surface charge used, with the positively charged sample showing no damage to the cell membrane or cytotoxicity compared to the negative charged sample causing cells to rupture.

PLA has been widely explored for use in biomedical applications especially in tissue engineering. PLA has the disadvantage of being relatively weak and breaking easily which might lead to potential hazards when looking at application within the body. By incorporation of CNC into PLA followed by cross-linking, the mechanical properties of PLA nanofibers could be greatly improved [66].

Gelatine, which is a derivative based on collagen, is commonly used in drug delivery systems as a form of encapsulation or coating. The addition of CNC is advantageous as both materials are biocompatible and safe for consumption [59]. CNC can be incorporated into the gelatine network by dispersing CNC in solution, adding the gelatine which was then cross-linked to produce hydrogels [40]. Incorporation of CNC helped improve the mechanical properties creating stronger materials which can handle more force. The disadvantage of cross-linking the CNC with the gelatine is that there has been a reduction to the drug loading efficiency with increasing CNC composition.

Wound dressing using CNC over BC has been considered as an alternative method [103], BC has the negative expensive to produce in comparison with CNC due to the long fermentation time and specific conditions required to perform it. The use of cellulose in a wound dressing allows for a moist environment to improve wound healing. This moist condition has the negative impact of also creating an environment that promotes microbial growth potentially leading to infection. Composites with silver nanoparticles were produced to help improve antimicrobial properties of a wound dressing in which the modified CNC would be incorporated.

5.5 Optical applications

CNC has rather interesting optical properties [104] thanks to the liquid crystalline properties creating birefringence [91, 105, 106]. It has been shown that the perceived colour of the produced films changes depending on the angle of incident. This material has been proposed for use in security paper such as that used in identification cards.

Liquid crystalline thermosets (LCT) were produced using lyotropic CNC at high loading contents [91]. With the addition of epoxy monomers, the LCT were produced via an aqueous process in which the CNC was dispersed within the epoxy resin and hardening agent followed by curing. The produced films were formed with high CNC content loading (50-72 wt%). From the work, it was found that the composite films exhibited properties inherited from the addition of CNC such as high elastic modulus and low glass transition. The addition of the liquid CNC was also found to lead to interesting optical properties showing occurrences of birefringence.

CNC have been shown to display iridescent properties [107]. By evaporating droplets containing CNC, an iridescent film was produced. The concentration of CNC had impact on the colour of the region produced (as shown in

Figure 9). This iridescent property can be explained by the orientation of the CNC rods in the network. The addition of glucose into the mixture was shown to lead to a change in the iridescent properties for the overall network.

Figure 9: Digital image of dried CNC film showing iridescent properties. Reproduced from [107] with permission of Springer Nature.

5.6 Piezoelectric Sensors

Thin films which included a layer of cellulose nanofibrils pressed into a paper have been explored for their piezoelectric properties as a sensor [61]. In the experiment, the paper was pressed between two copper electrodes, which were on a PET substrate. These films allow for the measurement of any stress that is imparted onto the films by recording the change in current that occurs. From the work, the composite was found to be somewhat limited in use, which potentially could be explained by the orientation of the fibres reducing the sensitivity of the sensor.

5.7 Paper

Nanocellulose has been used for the production of more refined paper [31, 39, 108]. The production itself is a relatively simple process such as with just the use of a Buchner funnel and a vacuum pump. The advantage of paper produced from nanocellulose over wood pulp has been due to an increase in the tensile strength that could be explained by better interfacial interaction between the CNC in comparison to typical paper. This improved interaction between the crystalline cellulose means the produced pa-

per requires more energy for it to be pulled apart. However, in a day-to-day case there is little value for it because of the added cost and production time in comparison to normally produced paper.

Nanopaper films produced from CNC has been shown to produce a transparent film (Figure 10). This transparency is attributed to the diameter of the individual CNC whiskers within the film. The transmittance of the CNC films for UV light was measured to be above 90% and approximately 98% for visible light. Due to this high transmittance, nanopaper films of CNC have been proposed as a viable replacement for glass or plastics in applications such as solar cells and displays.

Figure 10: Digital Image of CNC nanopaper displaying high transparency. Modified from [31] with permission of Springer Nature.

6 Concluding statement

Cellulose nanocrystals are finding newfound interest in the use as a nanofiller material. The use as a nanofiller tends to increase the tensile modulus of a material. The improvements can also be seen in the thermal stability and tensile strength but not as significantly.

When combined with being green, renewable materials, CNC shows promise for reducing the environmental impact in nanocomposites. From work so far, it has been shown that rather low loadings are adequate to lead to significant improvements in the mechanical properties. At the moment, the usage as a nanofiller is still limited because optimal dispersions have not been properly obtained with agglomeration of material still being a concern.

Thanks to the readily available and renewable source materials, the production of nanocellulose is incredibly cheap especially when compared to other commonly used nanomaterials. Whilst the production is still not to a globally viable point, the foundation has been established as more interest in the production grows.

Their excellent mechanical properties combined with their green potential shows a lot of promise for future development as a nanocomposite material. At current stage however it is not fully viable yet, but as interest grows hopefully the viability will also greatly improve with time.

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