Composites Enhanced With Nanocrystalline Cellulose (NCC): A Comparative Study

Sara Al Braiki, Sangarappillai Sivaloganathan,
Department of Mechanical Engineering, United Arab Emirates University,
P.O.Box: 15551, Al-Ain city, UAE.

1 Introduction

Palmero [1] defines Nanotechnology as the creation, processing, characterization and utilization of materials, devices and systems with dimensions of the order of 10 – 100 nm, exhibiting novel and significantly enhanced physical, chemical and biological properties, functions, phenomena and processes, due to their nano-scale size. She further differentiates that a nanomaterial has a typical grain size <100 nm, whereas ultrafine-grained materials are characterized by grain size <500 nm. Composites are materials in which the distinct phases are separated on a scale larger than the atomic, and in which properties such as the elastic modulus are significantly altered in comparison with those of a homogeneous material. In this category a “nanocomposite” comprises multiphase materials, where at least one constituent phase has dimension of less than 100 nm. The most important and largely attained organic entity is that of the cellulose which portrays a distinctive variety of nano-sized and micro-sized structures[2]. The pure Cellulose in a crystalline form, with dimensions of the nano size, is termed as Nanocrystalline Cellulose (NCC) which is derived from over a diverse range of natural sources such as cotton, algae, bacteria and wood. This paper summarizes the advances made in NCC technology in terms of its (a) morphology and dimensions (b) its physical and chemical properties (c) surface functionalizing properties (d) applications and (e) the challenges in the use of NCC.

2 Morphology and Dimensions

The proper geometrical dimensions, consists of the length (L) and width (W) of the NCC, are found to vary widely based on the source for the cellulosic material in addition to the conditions which the hydrolysis is conducted [2].

Table 1 shows the summary of the NCC geometrical characteristics, which are obtained from diversified cellulose sources. The NCC width is approximated to be in the range of several nanometers, whereas the length spans from tens of nanometers to few micrometers [3 – 10].

Table 1: Overview of the dimensions of NCC depending on the source

Source	Length (nm)	Width (nm)	Aspect Ratio (L/W)
Wood	100-300	3-5	20-100
Cotton	100-150	5-10	10-30
Ramie	70-200	5-15	12
Sisal	100-300	3-5	60
Valonia	1000-2000	10-20	50-200
Tunicates	>1000	10-20	100
Bacteria	100-1000	10-50	2-100

It was reported that NCC which is produced from tunicate and bacterial cellulose is normally larger in size comparing with the ones produced from wood and cotton. The reason behind such an occurrence is the fact that tunicate and bacterial cellulose are highly crystalline in nature, therefore the amorphous regions are in lower fractions, that are needed to be cleaved, which produces larger nanocrystals as a result [3].

The ratio of the length to the width (L/W) for the NCC is defined as the aspect ratio. The value of the aspect ratio depends on the source and varies from 1 to 100 in general. NCCs, derived from wood, are varied from 3 to 5 nm in width and approximately from100 to 300 nm is their length, this makes the range of aspect ratio to be varied between 20 to 100 nm [3, 4].

The properties of the final uses of the NCC are influenced by the aspect ratio when used in nanocomposites, such as percolation threshold in addition to the corresponding reinforcing effect [2]. This is referred to the fact that when the NCC interacts physically with the continuous phase, the dispersion degree and the area of interfacial are found to be higher [11].

3 Physical and Chemical Properties

NCC has garnered an extreme attention to the materials community, not only because of their unique physical and chemical properties, but also for their renewability and sustainability features in addition to their extensive availability [2]. Due to the advantages of the NCC such as low cost, light weight, availability, renewability, and nanoscale dimension, the NCC has been a topic of a wide range of researches which are interested in studying the NCC as filler in nanocomposites [12-14].

NCC considers as a low density material which is stronger than steel with an elastic modulus of 145 GPa, and stiffer than aluminum with tensile strength of 7.5 GPa. NCC properties are summarized in Table 2 with common engineering materials [15-22].

Table 2: comparison of material properties of cellulose.

Material	Tensile Strength (GPa)	Young's Modulus (GPa)	Density (g/cm^3)
NCC	7.5	145	1.6
Glass Fiber	4.8	86	2.5
Steel Wire	4.1	207	7.8
Kevlar	3.8	130	1.4
Graphite	21	410	2.2
CNT	11-73	270-970	1.0

The intra and inter molecular hydrogen bonding in the cellulose, which are appeared between the hydroxyl groups of neighboring molecules, considers as the main contributor for the relative stiffness [23, 24].

4 Surface Functionalizing Properties

The NCC is suitable for many types of surface functionalization due to the high surface-to-volume ratio. The existence of hydroxyl groups make the structure more suited in terms of functionalization of the surface [25]. If any chemical functionalization is introduced on the surface, then the type of interactions, which the material displays with its surroundings, can be modified [26].

Either negative or positive electrostatic charges can be introduced over the surface of the NCC while using chemical functionalization. This is considered as the main advantage of chemical functionalization because it allows a better dispersion of the polymer or the solvent. In addition to that, it adjusts the surface energy characteristics, which leads to amend, mainly when it is used with nonpolar or hydrophobic polymer matrices [2].

Perhaps, the chemical modification of the NCC is the major utility in the fabrication process of polymers in the nanocomposite materials. Whereas, the main challenge that lies in the procedure is keeping the integrity of the NCC in addition to the original morphology [25].

The chemical modification of the NCC can be implemented at the hydroxyl groups on the crystalline structure based on the desired application [27]. Due to these modifications, some reactions are used such as sulfonation, oxidation [28], cationization [29], grafting [30] and silylation [31], as shown in Figure 1. The grafting can be done via acid chloride [32], acid anhydride [33], or isocyanate [34].

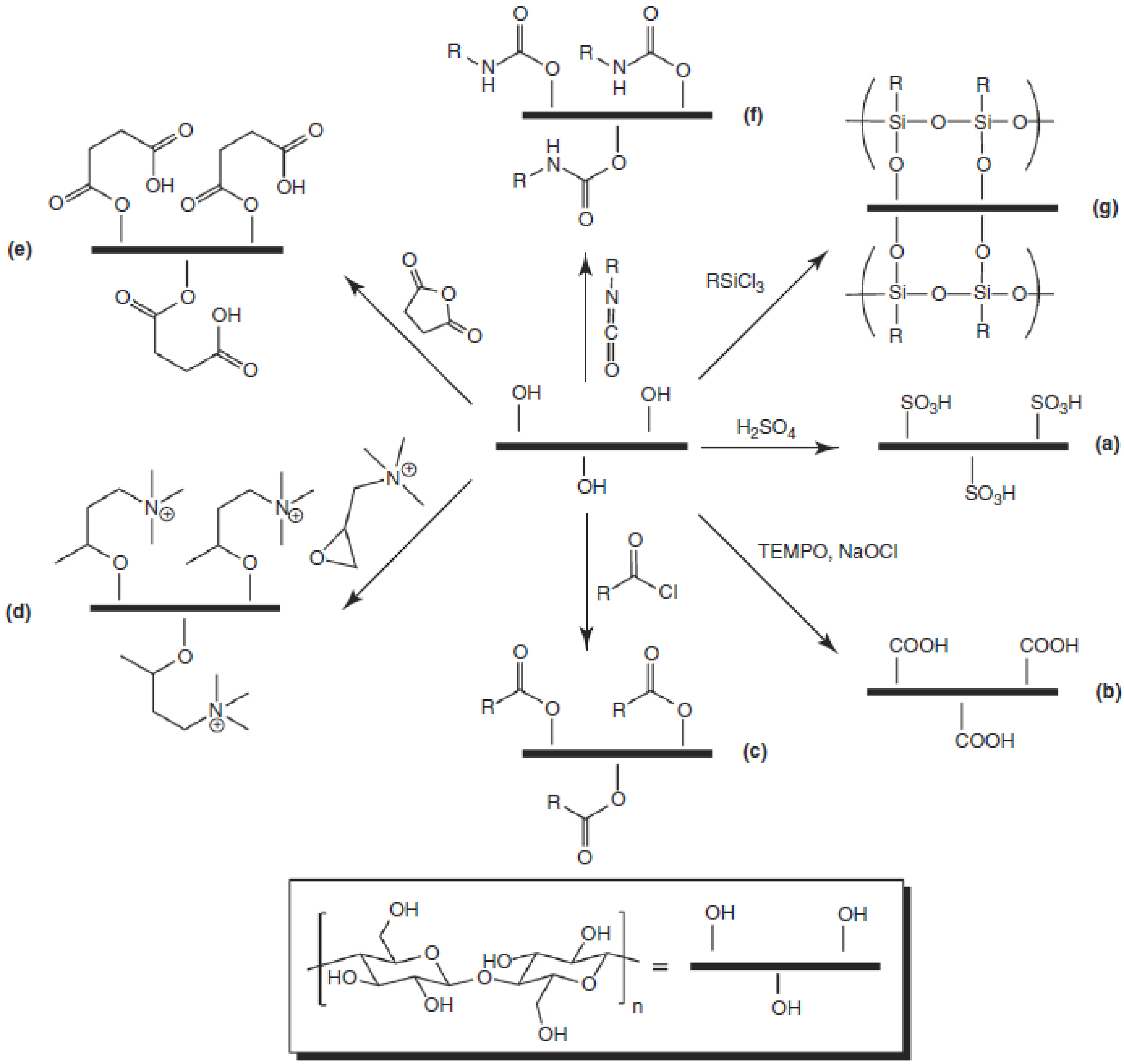

Figure 1: Some possible routes for chemical modification of NCC (clockwise from right): (a) sulfonation; (b) oxidation by TEMPO; (c) ester linkages via acid chlorides; (d) cationization via epoxides; (e) ester linkages via acid anhydrides; (f) urethane linkages via isocyanates; and (g) silylation.

Recently, homogenous NCC has been produced using ammonium persulfate (APS). APS is considered as a strong oxidant material which is used instead of acid hydrolysis [35, 36]. By applying this procedure, a variety of cellulosic biomass can be treated without the need to remove non-cellulosic contents in pretreatments.

5 Applications

There is a great potential that NCC can be an important class of renewable nanomaterials, which could be used in a wide range of applications, because of its distinctive properties. The main application of NCC is to be used as filler in nanocomposite materials.

Various nanocomposite materials were developed by adding NCC into a wide range of polymeric matrices. The main influential factors in the properties of these cellulosic nanocomposites are both the types and characteristics of the NCC and polymeric matrices [37]. On the other hand, potential applications of using NCC could be expanded in various sectors due to the chemical functionalization of the NCC since it improves its dispersibility in organic solvents.

By the gradual developments in the researches, the applications in diverse fields have been suggested ranging from iridescent pigments to biomolecular NMR contrast agents [38]. The solidification of the liquid crystals makes the NCC useful in the application of security paper [39, 40]. The NCC is also under research for the use in lithium battery products [41-44]. However, many industrial applications of NCC have concentrated on nanocomposites field due to the duration of the preparation technique [37].

A polymer nanocomposite is a multiphase material in which the polymer phase is campsite with nanomaterial which is about 100 nm. The properties of these materials overcome some limitations in the mechanical properties such as nanometric size and the variations in the surface area of the material used for reinforcing.

NCC can be used as filler in the nanocomposites which improves the physical, chemical, as well as electronic properties. Reviews regarding this topic have been given in the discussion. [2, 21, 45-54]. Table.3 shows some examples of the polymers.

The various researches regarding the NCC has been able to produce the applications like the making of foam, aerogels [48], building block for permselective membranes [55], improvements in the materials of the adhesives [48] or adhesive by itself [56], uses in the lithium battery has also been introduced to improve the physical properties [41, 43, 44, 57] and also it have been utilized in biomolecular NMR [58]. A broad range of NCC applications exist, even if a high number of unknowns remain to be discovered.

Table 3: list of polymeric matrices used for nanocomposite with NCC as filler

Source	Polymer
synthetic	Poly(ethylene-co-vinyl acetate), EVA Poly-(dimethyldiallylammonium chloride), PDDA Poly-(allylmethylamine hydrochloride), PAH Poly(methylmethacrylate), PMMA Polysulfone Poly(acrylic) acid, PAA Poly(styrene-co-butyl acrylate) Poly(oxyethylene), PEO Polypropylene, PP Polyvinyl chloride, PVC Poly(vinylalcohol), PVOH Polystyrene Polyurethane, PU Polycaprolactone, PCL
Natural	Poly(lactic acid), PLA Regenerated cellulose Cellulose Cellulose acetate butyrate Starch-based polymers Xylan Soy protein Chitosan Poly(hydroxyalkanoate), PHA Poly(hydroxyoctanoate), PHO

6 Challenges in the Use of NCC

The section effectively discusses the challenges paved on the way for the use of NCC nanocomposites. The first limitation is the ability to predict properties. In is difficult to predict the impact of Nano scale filler surface on the morphology and properties of the surrounding polymer [53]. The major drawback of the NCC is that it is very difficult to understand the properties of the macroscopic. The predictions and the control are also not easy to find.

On the contrary the processing techniques create a significant effect on the resultant composite performances. Apart from the costs the main problem is that of dispersing the NCC in a non – polar medium, this is for to use the NCC for composing hydrophobic matrices. There is also distinctive impact on the dispersion of the nano particles within the polymer matrix and the development of decent level of adhesion between the two phases at the same time. To add to this point there is a strong chance for the damaging of the NCC during the composite processing [45, 46, 48, 59, 60].

Based on the stated above challenges and drawbacks, it is strongly need to develop a new application that have an efficient processes and technologies to produce both NCC and nanocomposites.

7 Conclusion

Nanocrystalline cellulose (NCC) is a renewable nanomaterial that can be extracted from wood with an average diameter of 5 nm and length 100 nm. Due to its strength (7 times the steel), low density (1.5 g/cm^3) and environmental friendly nature, the NCC has been considered as an ideal candidate for the processing of reinforced polymer composites.

The advances made in NCC technology in terms of its, morphology and dimensions, its physical and chemical properties, surface functionalizing properties and applications have been summarized in this paper. In addition the challenges in the use of NCC are also numerated.

So far, most of the research has focused on morphology and dimensions, properties and surface modification of NCC. The surface modification of the NCC without affecting on its properties will mainly be the focus of future research. This will make NCC attractive for use in a wide range of industrial applications.

8 References

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