

Nanocellulose and nanoclay as reinforcement materials in polymer composites: A review

Fathin Najihah Nor Mohd Hussin ^{a, b}, Roswanira Abdul Wahab ^{a, b}, Nursyafreena Attan ^{a, b, *}

^a Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia.

^b Enzyme Technology and Green Synthesis Group, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia.

*Corresponding author: nursyafreena@utm.my

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Abstract

The advancement of nanotechnology has opened a new opportunity to develop nanocomposites using nanocellulose (NC) and nanoclay (NCI). Researchers have regarded these nanocomposites as promising substitutes for conventional polymers because of their characteristic and useful features, which include exceptional strength and stiffness, low weight, and low environmental impact. These features of NC and NCI explain their multifarious applications across many sectors. Here we review NC and NCI as well as various reinforced polymer composites that are made up of either of the two nanomaterials. The structural and physicochemical properties of NC and NCI are highlighted, along with the mechanical behavior and thermal properties of NC. Current nanomaterial hybrid biopolymers for the production of novel high-performance polymer nanocomposites are also discussed with respect to their mechanical properties.

Keywords: nanocellulose, nanoclay, polymer-matrix composites (PMCs), mechanical properties, thermal properties

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INTRODUCTION

Research into the development of sustainable or renewable polymeric materials has increased, particularly with respect to the development of specific features, such as enhanced mechanical properties and thermal stability. The use of organic and inorganic nanomaterials in the preparation of nanocomposites has been thought to be advantageous, as these materials support the concept of ecological safety and could contribute to a future greener environment. In fact, when any given product is under development, sustainability and the creation of environmentally friendly products from renewable and biodegradable sources are more preferable than the alternatives and should be key considerations [1].

Much effort has been dedicated to research focusing on harnessing and developing “green” composites, i.e., using natural fibers as substitutes for conventional inorganic fillers (e.g., glass or carbon fibers). Natural fibers have inherent properties that surpass traditional reinforcing materials. For instance, they are a renewable and low-cost resource; have a low density, which results in reduced tool wear; have acceptable specific strength properties and good thermal properties; result in reduced dermal and respiratory irritation; have improved energy recovery and carbon dioxide sequestration; provide an ease of separation and, most importantly, are biodegradable [2]. Nonetheless, progress in terms of the use of biodegradable polymers has been slow, largely because of issues related to their performance, namely, heat distortion at relatively low temperatures, brittleness, low gas barrier properties, and higher costs when compared with other common polymers or plastics such as polyethylene terephthalate and polyolefins [3].

To overcome inherent physical inadequacies of biopolymers, the integration of nano-reinforcement materials has been recognized as among the several effective avenues to improve their properties [2, 4]. Cellulose and layered silicate clay are among the most abundant polymers and minerals in nature, respectively, both of which show good compatibility with the surface chemistry of the polymer composite. In the case of cellulose, its nano-scale form, i.e., nanocellulose (NC), is a promising candidate for the production of polymer nanocomposites. Aside from its cost-effectiveness of production, NC has interesting properties such as a low density, high strength, high degree of stiffness, and remarkable mechanical properties. NC has been demonstrated to be a possible renewable reinforcement material or nano-filler in polymer composites, resulting in hybrid composites that display better overall properties as compared with a micro- or macro-cellulose composite. The design flexibility of NC-polymer composites and the ability to tailor and process these composites explain their extensive utilization in the automotive, electronics, packaging and biotechnology industries, among others. Notably, the discovery of NC has spurred the rapid adoption of natural cellulose polymers in various fields related to nanocomposite and sustainable materials. The high surface area of NC permits powerful interactions with surrounding species, such as water, organic and polymeric compounds, nanoparticles and living cells [2].

Nanoclay (NCI) is a natural mineral widely used as a nano-reinforcement material in various composites. Characteristic properties inherent to NCI include flame retardancy and mechanical and barrier properties, which account for its widespread use in multiple industries, e.g., in coatings, inks, and pharmaceuticals, as well as in automotive applications [5]. Generally, these materials are on the order of 1 nm in thickness with a high aspect ratio that lies between 10:1 and 1000:1.

With such high aspect ratios, these nanometer-scaled silicates tend to produce good reinforcement. Although NCl is not renewable, this nanomaterial has properties that are appropriate for the reinforcement of other polymeric materials, including its ability to boost the mechanical properties of the polymer while ensuring that the end-product is biodegradable [6]. NCl is a naturally occurring material, unlike NC, which must undergo chemical treatment.

This review offers a concise insight into the use of organic and inorganic nanomaterials, i.e., NC and NCl, respectively, as reinforcing agents for polymer nanocomposites. This review article is divided into three sections: the first section highlights the type, properties and ability of NC to reinforce polymer composites. The second section reviews the different types and abilities of NCl as a reinforcing agent in polymer nanocomposites. Future avenues of research related to these nanomaterials and their applications are covered in the final section.

NANOCELLULOSE

Cellulose is the most abundant and widely distributed natural polymer, recognized as a crucial source of renewable material mainly in the form of plant fiber. According to Onoja et al. [1], biomass from oil palm—such as oil palm frond (OPF), oil palm trunk (OPT) and empty fruit bunch (EFB)—contains relatively high amounts of cellulose. This cheap and biodegradable polymer is tough, fibrous, and water insoluble with an impressive annual total production of 10^{11} – 10^{12} tons [7]. Because cellulose is non-toxic, non-polluting, biocompatible, easily modified, and consistent across sources, it has been used extensively in various applications. Cellulose consists of D-glucopyranose repeating units connected by β -1,4 glycosidic linkages with a degree of polymerization as high as 10,000 to 15,000, particularly in wood cellulose, and even higher in native plant fibers. Cellulose also exists in the cell walls of plants and of sea creatures such as algae and tunicates and bacteria such as *Acetobacter xylinum* [8], the cell walls of which are constructed from proteins and carbohydrates. As it is a major component of plant cell walls, cellulose makes up over 50% of the carbon content in the botanic field. Cell walls of plants are constructed from three organic compounds: cellulose, hemicellulose and lignin, which occur in a 4:3:3. However this ratio vary from sources such as hardwood, softwood, and herbs. Hemicellulose and lignin constitute ~40–50% of plant wood, whereas cotton may contain >90% cellulose [9].

Cellulose can exist in two forms, crystalline and amorphous. In the crystalline form, the cellulose chains are arranged in a highly ordered manner to generate a cellular hierarchical biocomposite, whereas in the amorphous form, the cellulose chains (which are made up of hemicellulose, lignin, waxes, extractive, and trace elements) are arranged in a much disordered manner [9]. One of the main features of cellulose is the three hydroxyl groups (at positions 2, 3, and 6) present in every glucose unit (Fig. 1a). The hydroxyl (-OH) of the secondary alcohol is sited at the 6th position and is ten times more reactive than those found at the 2nd and 3rd positions. In addition, the -OH group at the 2nd position is two-fold more reactive than the -OH group located at the 3rd position [10]. The hierarchical structure and stiffness of the cellulose chain are stabilized with the help of intermolecular and intramolecular hydrogen bonds. The intermolecular hydrogen bond links the -OH of the C₃ carbon and the ring oxygen of the neighboring glucose unit (O₅). The hydrogen of the OH-6 primary hydroxyl and oxygen at position O₃ in the ring of an adjacent unit, together with hydrogen of OH-2 and oxygen at position O₆, form an intramolecular hydrogen bond [10].

The advent of nanotechnology has resulted in the formation of NC, which has received a considerable amount of attention for applications in advanced materials. NC obtained from cellulose has revolutionized bio-based materials for an assortment of applications. The nano-scale dimension, with its unique optical properties, stiffness, high surface area and high degree of crystallinity, together with the biodegradability and renewability of cellulose, have contributed to its many interesting applications [11].

Types of NC

NC has been referred to as a “pseudo-plastic” material that possesses certain kinds of fluid-to-gel-like properties, although it is

generally more gel-like under typical conditions. In general, NC is classified into cellulose nanocrystals and cellulose nanofibers, both of which are isolated from plant fiber, whereas microbial cellulose comes from bacteria. The following sub-sections further discuss the three types of NC.

Cellulose nanocrystals (CNCs)

This naturally derived bulk cellulose contains both crystalline and amorphous regions, and the ratio of crystalline to amorphous regions may differ according to the source of the cellulose [12]. The crystalline form of the microfibrils can be extracted using combinations of chemical and mechanical treatments [13] to produce stiff rods or similar particles composed of cellulose chain fragments organized in a nearly perfect crystalline structure. CNC is being developed as a potential nanocomposite reinforcement agent and has been extensively researched for the past two decades because of its relatively low density (1.6g/mL), high modulus (143 GPa), and high strength [14]. CNCs may vary in size, from 4 to 7 nm in width and from 100 nm to a few micrometers in length [15], and have multiple names such as whiskers, microcrystallites, nanofibers, and nanoparticles. Plant cell walls, cotton, algae, animals, and bacteria are examples of renewable sources of CNC. Generally, lignocellulosic natural fibers can be loosely divided into five parts: (1) leaf, (2) grass, (3) bast or stem, (4) seed or fruit, and (5) straw fibers [16]. Among these sources of lignocellulosic fibers, woody and non-woody plant are regarded as outstanding raw materials for manufacturing CNCs. The number of CNC-related patents and peer-reviewed articles as well as the large number of marketed products attest to the versatility of CNCs [15].

Currently, CNCs can be manufactured from lignocellulosic sources via top-down technologies in which wood is used as the main source of cellulosic fiber. However, fierce competition between many manufacturing sectors, e.g., pulp and paper industries, building and furniture producers, make it increasingly challenging to offer all sectors reasonably priced wood in high quantities. The most recent alternative to the above predicament is the utilization of non-woody plants. Some of the recently explored sources for CNC production are summarized in Table 1. Non-woody plants comprise cellulosic microfibrils that are less tightly wound in the primary cell wall than in the secondary wall. This feature essentially facilitates the process of preparing CNCs [15]. Additionally, CNCs can be isolated using controlled preferential acid hydrolysis of the disordered regions. The process produces low-molecular-weight carbohydrates (mostly glucose) and releases the crystalline domains.

Table 1 Various sources of CNCs and CNFs.

Sources	Types	Ref.
Woody plants	Softwood pulp	[17]
	Hardwood pulp	[18]
Non-woody plant and agricultural waste	Bamboo pulp	[19]
	Potato peel waste	[20]
	Rice husk	[21]
	Oil palm	[2]
	Sugarcane bagasse	[22]
	Pineapple leaf	[23]
Algae	Green algae (<i>Cladophora rupestris</i>)	[24]
	Red algae (<i>Gelidiella aceroso</i>)	[25]
	Red algae (<i>Gelidium elegans</i>)	[26]
Animals	Tunicates	[27]

Cellulose nanofibers (CNFs)

CNFs are found in various forms based on the method by which they are produced. The most basic unit of the CNF is the cellulose microfibril, which occurs as a single cellulose nanofiber [28]. CNFs have been extensively studied for their remarkable flexibility, mechanical strength, biodegradability, thermostability, chirality, and

possibility of functionalization and blending, as well as their low thermal expansion [29]. Interestingly, CNFs are extracted from the same sources as CNCs (refer to Table 1). The abundant availability of CNF sources and its superior mechanical properties because of its long, flexible fiber network—which is made up of fibers with a diameter similar to or larger than that of a CNC—have made CNFs a desirable reinforcing material for polymer nanocomposites [30]. The CNF type of nanofibrils has nearly equal amounts of amorphous and crystalline regions, in contrast to CNC, which largely consists of crystalline cellulosic regions [31]. CNF is formed by energy-intensive processes such as mechanical defibrillation involving refining, homogenization and grinding. The energy demand to produce CNF could exceed 30,000 kWh/ton using high-pressure homogenization, as described by Nakagaito and Yano [32]. Thus, several cellulose pretreatments prior to CNF preparation have been extensively investigated to reduce energy consumption, especially for wood cellulose. The pretreatments involve the use of enzymatic hydrolysis based on a monocomponent endoglucanase for defibrillation via specific hydrolysis of the glycosidic bonds along the less-crystalline regions of the cellulose chain [33]. Habibi et al. [34] reported that an acid-hydrolyzed preparation of wood CNC has dimensions of 50–500 nm in length and 3–5 nm in width with a crystallinity index in the range of 54–88%. Conversely, mechanical refining to produce wood CNF results in nanofibers with dimensions in the range of 500–2000 nm in length and 4–20 nm in width that retain both amorphous and crystalline regions with a crystallinity index in the range of 46–65% [35].

Bacterial Cellulose (BC)

Bacterial cellulose (BC), also known as microbial cellulose, is produced extracellularly in cultures of *Glucoacetobacter*, *Agrobacterium*, *Acetobacter*, *Achromobacter*, *Aerobacter*, *Azobacter*, *Alcaligenes* and *Pseudomonas* in the form of a pellicle at the air–liquid interface. Its interphase characteristics make it an alternative to plant-derived cellulose for certain applications in the medical field and in food and other industries [36]. BC microfibrils, which were first described by Muhlethaler in 1994, are 100 times smaller than those of plant cellulose [36]. The resulting material is highly porous and thus can be used to allow the transfer of antibiotics or other medicines into a wound while acting as an efficient physical barrier against any external infection. It is therefore used extensively in wound healing [37].

The basic structure of BC is as a fibril that consists of β -1,4-glucan chains with the molecular formula $(C_6H_{10}O_5)_n$, with each chain being firmly held in place by intermolecular and intramolecular hydrogen bonding (Fig. 1b). The fibrous network of BC is coordinated by well-arranged three-dimensional nanofibers, which form a porous hydrogel sheet and thus generate a large surface area. During the synthesis process, glucose chain protofibrils are liberated through the bacterial cell wall and clustered together into nanofibril cellulose ribbons. The process eventually leads to the formation of a web-like network of highly porous microbial cellulose [38]. The microfibrils from each synthetic site then amass to create a large cellulose ribbon in the growth medium, and the associated cells intertwine into a floating pellicle. The formed biopolymer facilitates the growth of these strictly aerobic bacteria under the higher oxygen pressure at the surface of the growth medium [39].

BC also differs from plant cellulose with respect to its physical and chemical features. BC is of particularly high purity and crystallinity, has a large water-holding ability, is notably biodegradable and has excellent biological affinity [40]. These valuable and distinctive properties stem from the specific ultrastructure of BC, is constructed from a net of ultrafine cellulose ribbons [41]. As an example of its diverse applications, BC produced by *Acetobacter* strains forms a constituent of diet foods and is used to fashion new high-performance materials for makeup pads, speaker diaphragms, paint thickeners, medical pads, and artificial skin [36].

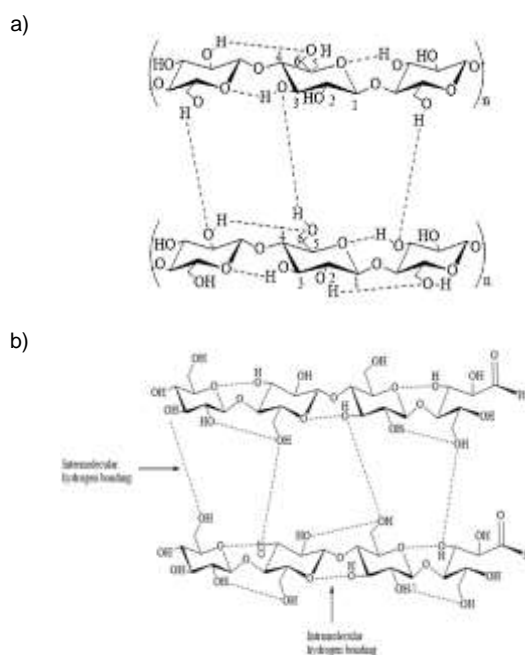


Figure 1 a) Hierarchical structure of cellulose and b) structure of bacterial cellulose. Both intermolecular and intramolecular hydrogen bonds are indicated in the bacterial cellulose.

Characteristic properties of NC

The natural nanoscale of NC contributes to characteristics that are comparable to those of traditional materials (i.e., cellulose). The degree of crystallinity and specific surface area, rheological properties, alignment and orientation and mechanical reinforcement are among its morphological and geometrical dimensions [42]. NC are typically categorized based on their mechanical and thermal aspects, and the following sub-sections discuss the tensile strength, tensile modulus, and thermal stability or thermal degradation of NC.

Mechanical properties

Mechanical properties of NC vary across the crystalline and amorphous regions. Cellulosic chains in disordered (amorphous) regions result in the plasticity and flexibility of the bulk material as compared with the ordered (crystalline) regions. The latter structure specifically imparts elasticity and stiffness of the material. Likewise, different kinds of NC display varying moduli that result from a mixing rule between the moduli of the crystalline and amorphous regions. This explains the higher stiffness and modulus of CNC, as it has a greater quantity of crystalline domains relative to CNF and BC [43].

In the late 1930s, the elastic modulus of crystalline cellulose was first investigated by both theoretical and experimental analyses such as Raman spectroscopy, wave propagation, X-ray diffraction and atomic force microscopy. However, the accurate determination of the modulus and strength of NC is quite challenging. As far as we know, Young's modulus for crystalline cellulose (which is like CNC) is typically 58–180 GPa [4], comparable to that of Kevlar (60–125 GPa) and potentially sturdier than steel (200–220 GPa) [42]. However, a previous work by Gillis [44] reported that the projected stiffness of cellulose crystals may reach as high as 300 GPa, if the interchain hydrogen bonds and the straightening of the cellulose chains are considered in the calculations. In another study, Dri et al. [45] used tandem quantum mechanics to compute the Young's modulus of crystalline cellulose, which was ~206 GPa.

Conversely, a wide range of the longitudinal modulus for the cellulose microfibrils that make up CNF and BC was reported based on theoretical and experimental bases. According to the literature, the accepted average modulus value of cellulose microfibrils is ~100 GPa [42] based on a three-point bending assay with the cellulose microfibrils using an atomic force microscope. The dimensions of cellulose microfibrils can substantially influence their mechanical properties, and the longitudinal modulus of pulp CNF is estimated to

be 81 ± 12 GPa [42]. Recently, Raman spectroscopic analysis showed the modulus value of BC to be ~ 114 GPa, based on estimates of local molecular deformation of BC via a shift in the central position of the 1095 cm^{-1} Raman band [42]. Hence, the impressive mechanical properties of NC suggest the prospective use of this nanofiller as a load-bearing element in many host materials. The strong interfacial adhesion and homogenous dispersion of NC [46] permit an appropriate stress transfer from the host material (matrix) to the reinforcing phase (NC).

With regards to the tensile strength of cellulose, theoretical predictions estimate that cellulose crystals have a high tensile strength, observed to be 0.3–22 GPa [4]. The strength of cellulose is directly attributed to several factors such as the extended chain confirmation of crystalline cellulose [4], the high density of covalent bonds per cross-sectional area and the existence of a large number of intermolecular and intramolecular hydrogen bond sites. The current limited state of knowledge does not, however, support reliable quantitative predictions of the tensile properties of cellulose.

Thermal properties

Since the 1990s, NC has been investigated as nano-reinforcement material for nanocomposites [8] based on its exceptional properties. Briefly, the thermal properties of NC are gauged base on thermal chemical degradation and thermal expansion coefficient (TEC) using a thermogravimetric analyzer, which measures the reduction in the weight of a sample as a function of temperature for a given heating rate. Thermal chemical degradation of NC is usually observed within the range of 200–300 °C, but factors such as the particle type, heating rate and surface modification may produce variations [47]. Reports consistently show that NC has a low TEC but has high strength and modulus elasticity [48]. The influence of chemical modifications on thermal chemical degradation was demonstrated by Petersson et al. [49]. A series of thermogravimetric analyzer-based estimations on freeze-dried chemically modified CNC suspensions, microcrystalline cellulose (MCC) and CNC (produced via chemical treatment of the same MCC) revealed that 300 °C and 260 °C was the onset temperature for thermal chemical degradation of MCC and CNC, respectively.

Correspondingly, studies by Nishino et al. [50] and Nakagaito et al. [51] estimated that the thermal expansion of crystalline cellulose occurs in the axial direction at $\sim 0.1\text{ ppm K}^{-1}$. The projected value is more than an order of magnitude lower than that of most metals and ceramics but appears to be comparable with other high-modulus anisotropic fibers, e.g., carbon fibers [47]. Another study measured the in-plane TEC of self-organized and shear-oriented CNC films [8], which had an isotropic TEC of $\sim 25\text{ ppm K}^{-1}$ and an anisotropic TEC response, respectively.

TEC is a crucial consideration for various sectors in consideration of the crystalline and macroscopic length scale of materials, as this phenomenon can lead to changes in dimensional shape due to anisotropic TEC and TEC mismatch. In the electronics sector, for example, thermal mismatches can cause important components such as electrodes and composites to stop functioning. Ever since NCs began to be used as substrates in electronics and as nanofillers in composites [52], the accurate determination of the TEC of NC and NC-based polymer matrices and the mechanisms of their thermal expansion has been thought to be quite important. This is especially true when considering the anisotropy and structural organization of the bulk TEC of free-standing films.

NC as a reinforcing agent for polymer nanocomposites

The use of NC as a reinforcing agent in various polymer matrices has gained interest with the development of a new class of cellulose-based building blocks that result from chemically active hydroxyl groups on the surface of cellulose, in addition to its low density and its abundance [53]. Various types of polymers such as polypropylene, polystyrene and polyethylene has been used for NC incorporation. Favier et al. [54] used NC whiskers (6 vol.% loading fractions) from tunicate as a nano-filler to reinforce styrene and butyl acrylate copolymer latex and showed that the nanocomposite has significantly increased in mechanical properties with low NC loading, compared with the neat polymer in its polymeric state. This phenomenon was due

to the percolation of the NC whiskers, which causes the formation of a rigid cellulose whisker network within the nanocomposite. Since then, substantial research efforts have focused on the manufacturing and production of high-performance and/or multifunctional NC-reinforced polymer composites. The following sections will address the use of NC (both CNF and BC) as a nanoreinforcement for polymer composites.

CNF and BC as a potential reinforcement for polymer nanocomposites

The development of bionanocomposites has attracted an enormous amount of interest during the past few years, specifically the use of renewable and biodegradable nano-fillers such as polysaccharide-based nanoparticles to obtain materials with a more environmentally friendly life cycle. The major driver for using NC in structural composites is the potential to exploit the theoretical stiffness and strength of cellulose crystals [55]. Theoretical calculations and numerical simulations estimated the stiffness and strength of cellulose crystals to be as high as 180 GPa and 22 GPa, respectively [56]. Therefore, both CNF and BC could potentially be valuable reinforcing agents because of their low toxicity and density ($\sim 1.5\text{ g cm}^{-3}$) [57]. When comparing CNF to BC, the main difference between them is their purity and crystal structures, even though both have a similar reinforcing ability for polymer composites. Cellulose mainly consists of two coexisting crystal structures in their native state, namely I_α and I_β [58], but the relative amount of cellulose- I_α and cellulose- I_β varies depending on the origin of the cellulose [47]. For example, CNF is I_β rich, whereas BC is I_α rich.

Lee and co-workers [59] investigated the reinforcing ability of CNF and BC on epoxy composites, which were manufactured by impregnating NC paper with an epoxy resin using vacuum-assisted resin infusion. As shown in Table 2, when the tensile moduli of epoxy resin reinforced with CNF and BC were normalized from 58 vol.% (CNF-reinforced epoxy) and 49 vol.% (BC-reinforced epoxy) to 60 vol.% NC loading, the stiffness of the nanocomposites was identical. In addition, when the BC-reinforced epoxy nanocomposites had a lower NC loading, the tensile strength of the resulting BC-epoxy nanocomposite was higher as compared with the CNF-epoxy nanocomposite because of the higher critical surface energy of BC ($\sim 57\text{ mN m}^{-1}$) as compared with CNF (42 mN m^{-1}) (2). BC may also have a higher intrinsic strength, as a higher solid surface tension should result in better wetting by the matrix to enhance the adhesion between the BC and epoxy resin [60].

In a pioneering study by Gindl and Keckes [61], the authors used various BC loading fractions to reinforce cellulose acetate butyrate (CAB). The incorporation of 32 vol.% of BC loading into CAB increases the tensile properties of the resulting nanocomposites five-fold compared with neat CAB (Table 2). Similarly, Wan et al. [62] incorporated BC in a starch plasticized with glycerol via a solution impregnation method. The tensile properties and Young's modulus are higher for the nanocomposites compared with the unreinforced starch. Table 2 lists the tensile properties of the pure starch and BC-starch composites with different loading levels of BC. At a BC loading of 7.8, 15.1 and 22.0 wt.%, the tensile strength of the BC-starch composites improved by 2.03-, 2.18- and 2.37-fold over pure starch, respectively. This enhancement indicates the effectiveness of the reinforcement, thus implying that BC can serve as an excellent reinforcing agent for polymer composites.

Numerous methods can be used to produce large quantities of CNF in laboratories compared with the production of BC, which depends on the biosynthesis of cellulose bacteria [4]. Dufresne et al. [63] first studied CNF from potato tuber cells as a reinforcing agent to improve the mechanical performance of polymer (CNF-starch). In contrast, Mathew et al. [64] showed that the addition of CNF, which was derived from high-quality wood pulp by acid hydrolysis, produces a negative effect on tensile strength compared with neat PLA, although the modulus is slightly increased (Table 2) because of the brittleness of the PLA. These authors deduced that the mechanical performance of composites is likely to depend on the following factors: a) adhesion between the PLA matrix and the cellulosic reinforcement and the stress transfer efficiency of the interface, b) volume fraction of the fibers, c) aspect ratio of the reinforcements, d) fiber orientation, and e) the degree of crystallinity of the matrix. Kaushik et al. [65] also reported that the

Table 2 Mechanical and tensile properties of polymer matrices when CNF and BC are used as reinforcing agent.

Types of NC and nanocomposite ^b	Content, <i>vf</i> ^a (vol.%)		Content, <i>wf</i> ^a (wt.%)		<i>E</i>		<i>σ</i>
	BC	CNF	BC	CNF	GPa	MPa	MPa
CNF		58	–	–	7.1 ± 0.1	–	102 ± 1
BC	49	–	–	–	8.5 ± 0.2	–	96 ± 1
Neat CAB	0	–	–	–	1.2	–	25.9
BC–CAB	10	–	–	–	3.2	–	52.6
	32	–	–	–	5.8	–	128.9
Pure starch	–	–	0.0	–	–	15.51 ± 2.2	13.1 ± 0.25
BC–starch	–	–	7.8	–	–	32.83 ± 1.5	26.72 ± 0.68
	–	–	15.1	–	–	33.61 ± 1.8	28.55 ± 1.12
	–	–	22.0	–	–	36.14 ± 1.9	31.06 ± 0.89
	–	–	–	–	–	–	–
Neat PLA	–	–	–	0	3.6 ± 0.2	–	49.6 ± 1
CNF–PLA	–	–	–	10	4.1 ± 0.7	–	38.2 ± 0.5
	–	–	–	15	4.4 ± 0.2	–	37.8 ± 0.8
	–	–	–	20	4.7 ± 0.3	–	38.1 ± 0.7
	–	–	–	25	5.0 ± 0.2	–	36.2 ± 0.9
	–	–	–	–	–	–	–
TPS	–	–	–	0	–	76 ± 4.5	4.8 ± 0.28
CNF–TPS	–	–	–	5	–	107 ± 5.3	5.18 ± 0.41
	–	–	–	10	–	175 ± 8.7	5.67 ± 0.49
	–	–	–	15	–	224 ± 15.4	6.78 ± 0.55
	–	–	–	–	–	–	–

^a *vf* denotes loading fractions in volume; *wf* denotes loading fractions in weight; *E* denotes Young's Modulus in gigapascals and megapascals; *σ* denotes tensile strength in megapascals.

^b CAB: cellulose acetate butyrate [61]; PLA: polylactic acid [64]; TPS: thermoplastic starch [65]

tensile strength and modulus of thermoplastic starch (TPS) nanocomposites increases with CNF content extracted from wheat straw using steam explosion, acidic treatment and high-shear mechanical treatment (Table 2). The nanocomposite with 15% fiber loading showed an improvement of 195% in tensile strength over pure TPS, thus indicating good bonding and efficient stress transfer from matrix to fiber. Whilst both NFC and BC can serve as excellent reinforcing materials for the efficient production of nanocomposites it was observed that BC does outperform CNF as reinforcement.

NANOCLAY

Clays have been recognized as the most important industrial minerals, and, with advances in nanotechnology, they have been used in multiple applications to improve the quality of the end product, economize on cost and minimize environmental harm [66]. The basic structural unit of clay minerals consists of a silica tetrahedral sheet [SiO₄]⁴⁻ and an alumina octahedral sheet [AlO₃(OH)₃]⁶⁻. In the tetrahedral sheet, the silicon-oxygen tetrahedrons are linked to neighboring tetrahedrons by sharing three corners, whereas the fourth corner of each tetrahedron forms a part of the adjacent octahedral sheet. As for the octahedral sheet, it is comprised of aluminum or magnesium in six-fold coordination with both oxygen from the tetrahedral sheet and the hydroxyl group. The sheets form a layer and several layers may be joined in the form of clay crystallite [66]. Three main forces, Van der Waals forces, hydrogen bonding and electrostatic forces, clutch these layers and form stacks of parallel lamellae, thus creating a gap between the adjacent layers, referred to as an “interlayer” or “gallery”, that can be intercalated by water, organic cations, and polar organic liquids. Thus, the forces between those layers weaken, causing the lattice to expand.

Clays, which are also known as the clay fraction, refer to a class of materials having a particle size of <2 μm with respect to an equivalent spherical diameter and include nanoclays (NCl) of <100 nm in diameter. NCl, which can be described as fine-grained particles in a stacked sheet-like structure, are commonly dominated by phyllosilicates and fine-grained aluminosilicates that form due to the chemical weathering of silicate minerals at the surface of the earth [67]. NCl can be separated from the clay fraction by a combination of various techniques such as energetic stirring followed by centrifugation and freeze drying, ultrasonication and ultracentrifugation, and cross-flow filtration [68].

Table 3 presents the grouping of phyllosilicates (clay minerals) on the basis of their sheet arrangement. In 1:1-type phyllosilicates (e.g., halloysite, nacrite, and lizardite), each layer is made up of one tetrahedral and one octahedral sheet, whereas 2:1-type phyllosilicates (e.g., smectite) consist of an octahedral sheet that merges between two tetrahedral sheets. Smectite is a type of silicate mineral with the general formula (Ca, Na, H)(Al, Mg, Fe, Zn)₂(Si, Al)₄O₁₀(-OH)₂·xH₂O, where x denotes different water level attached to the mineral. Some of the synthetic NCl that belong to the smectite family are montmorillonite, hectorite and laponite. It is worth mentioning that although the sheet arrangements are similar for the member clays of a particular clay group, their lateral dimensions differ. Floody et al. [68] reported that, because of isomorphous substitution, i.e., Al³⁺ for Si⁴⁺ in the tetrahedral sheet and Mg²⁺ for Al³⁺ in the octahedral sheet, many clay minerals such as MMT carry a permanent negative charge that is balanced by exchangeable inorganic cations (Na⁺, Ca²⁺) occupying interlayer sites. The cation exchange capacity of these minerals is therefore independent of the pH of the medium [68, 69].

Types of NCl

Generally, NCl are found worldwide, with large deposits occurring in countries such as Australia, Brazil, Mexico, and Spain. The use of NCl as nano-fillers for support material can provide numerous advantages, including high specific surface area, facile water dispersion/recuperation, high swelling capacity, and high mechanical resistance [70]. The most common NCl used as reinforcing agents called halloysite and montmorillonite is usually known to have a strong impact on properties when incorporated in smaller amounts into polymer matrices. Brief discussions of the NCl halloysite and montmorillonite are provided in the following subsections.

Halloysite

Halloysite was first discovered by Berthier in 1826 as clay minerals of the kaolinite group. However, the name halloysite was adopted later and is based on Omalius d'Halloy, who first investigated the mineral [66]. Halloysite, like other members of the kaolinite group, has a 1:1 sheet arrangement. Its chemical formula is Al₂Si₂O₅(OH)₄, which corresponds to a composition of 20.90% aluminum, 21.76% silicon, and 1.56% hydrogen. Such naturally occurring multiwalled aluminosilicates can be formed by hydrothermal alteration of alumina-

Table 3 Classification of clay minerals [66-68].

Layer type	Sheet arrangement	Group Name	Species/Member minerals	General formula
1:1	Tetrahedral:Octahedral	Kaolinite	Lizardite Nacrite Amesite Halloysite Dickite Nepouite	$Mg_3Si_2O_5(OH)_4$ $Al_2Si_2O_5(OH)_4$ $Mg_2Al_2SiO_5(OH)_4$ $Al_2Si_2O_5(OH)_4$ $Al_2Si_2O_5(OH)_4$ $Ni_3(Si_2O_5)(OH)_4$
2:1	Tetrahedral:Octahedral:Tetrahedral	Smectite	Hectorite Saponite Montmorillonite Laponite Sauconite Volkonskoite	$Na_{0.3}(Mg, Li)_3Si_4O_{10}(OH)_2$ $Ca_{0.25}(Mg, Fe)_3((Si, Al)_4O_{10})(OH)_2 \cdot n(H_2O)$ $(Na, Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ $Na_{0.7}Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4$ $Na_{0.3}Zn_3(SiAl)_4O_{10}(OH)_2 \cdot 4H_2O$ $Ca_{0.3}(Cr^{3+}, Mg, Fe^{3+})_2(Si, Al)_4O_{10}(OH)_2 \cdot 4H_2O$
		Vermiculite	Vermiculite	$(Mg, Fe^{+2}, Fe^{+3})_3[(Al, Si)_4O_{10}(OH)_2] \cdot 4H_2O$
		Brittle mica	Clintonite Anandite Margarite Bityite	$Ca(Mg, Al)_3(Al_3Si)O_{10}(OH)_2$ $(Ba, K)(Fe^{2+}, Mg)_3(Si, Al, Fe)_4O_{10}(S, OH)_2$ $CaAl_2(Al_2Si_2)O_{10}(OH)_2$ $CaLiAl_2(AlBeSi_2)O_{10}(OH)_2$
		Pyrophyllite	Kerolite Pyrophyllite Pimelite Willemseite	$(Mg, Ni)_3Si_4O_{10}(OH)_2 \cdot H_2O$ $Al_2Si_4O_{10}(OH)_2$ $Ni_3Si_4O_{10}(OH)_2 \cdot 4H_2O$ $(Ni, Mg)_3[(OH)_2]Si_4O_{10}$

silicate minerals [71]. The crystalline layers of halloysite are constructed by octahedrally coordinated Al^{3+} and tetrahedrally coordinated Si^{4+} with water molecules between the layers (Figure 2a). The silicate layers have a wall thickness of 10–15 atomic aluminosilicate sheets with an outer diameter and length of 50–60 nm and 0.5–10 μm, respectively, whereas their outer surface is mostly composed of SiO_2 [72].

Nanosized tubular halloysite, which is referred to as halloysite nanotubes (HNTs), is the dominant form of naturally occurring halloysite. The structural formula for HNTs is $Al_2(OH)_4Si_2O_5 \cdot nH_2O$, where n is the number of water molecules. HNTs that contain two molecules of water are called hydrated HNTs or HNTs-10 Å. In contrast, dehydrated HNTs, or HNTs-7 Å, contains no water molecules (i.e., where n = 0). Dehydrated halloysite is created by the loss of interlayer water molecules under mild heating. The resulting nanostructures resemble multiwalled carbon nanotubes with sizes ranging from 0.2 to 2 μm, with an outer width and lumen diameter of 40–100 nm and 10–40 nm, respectively [66]. HNTs have long been used to produce high-quality ceramics such as porcelain and crucibles. The advancement of nanotechnology has resulted in HNTs being studied for new applications such as sorbents for contaminants, drug delivery, catalysts and, of course, as nanofiller for polymer reinforcement [73].

Montmorillonite

Montmorillonite is one of the most familiar smectite NCl (Table 3) and is often used in research because of its well-studied chemistry, in addition to being abundant and environmentally friendly. Montmorillonite, a dioctahedral NCl that is a 2:1 type of phyllosilicate, typically forms microscopic crystals after precipitation from a water solution. When dispersed in polymers, however, montmorillonite assumes a rigid and maze-like structure that lowers its permeation rate [66]. The high aspect ratio and platy morphology of montmorillonite are features that underscore its usefulness as a reinforcement filler [74]. The lateral dimension of an individual montmorillonite layer is 200–600 nm with a thickness of a few nanometers, whereas its crystal lattice consists of layers of 1 nm thick, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets [66]. The sheets are characteristically bound such that the silicon oxide tetrahedron (SiO_4) shares three of its four oxygen atoms with the central octahedral alumina sheets (Figure 2b). During isomorphous substitution within the montmorillonite layers, a negative charge is generated via

cation exchange capacity on each three-sheet layer. For montmorillonite to be miscible with other polymer types, one must exchange the alkali counter ions with cationic-organic surfactants, such as alkylammonium [75]. In their pristine form, different type of metal cations, i.e., Na^+ and Ca^{2+} , present between the montmorillonite layers can accommodate charge imbalances. Montmorillonite eventually becomes hydrated due to the isomorphous substitution, and its structure expands, thus increasing its hydrophilic behavior [66]. Under such conditions, montmorillonite is miscible only with hydrophilic polymers such as poly(vinyl alcohol) and poly(ethylene oxide). In addition to their role as a nanofiller in polymer composites, montmorillonite clays are extensively used in mud drilling by the oil drilling industry. The incorporation of montmorillonite clays increases the viscosity of the mud slurry [76]. Montmorillonite is also the main constituent in a volcanic ash called bentonite. This substance is crucial for keeping the drill head cool during the drilling process as it leads to greater viscosity of the water used to cool the drill head. Montmorillonite that exists in soils and rocks can advantageously reduce the progress of water through these media, a feature beneficial to farmers when crop irrigation becomes a serious issue during extended dry periods [77]. Engineers of earthen dams or levees have used this attribute to prevent leakage of toxic fluids into surface-accessible aquifers used for drinking water [78].

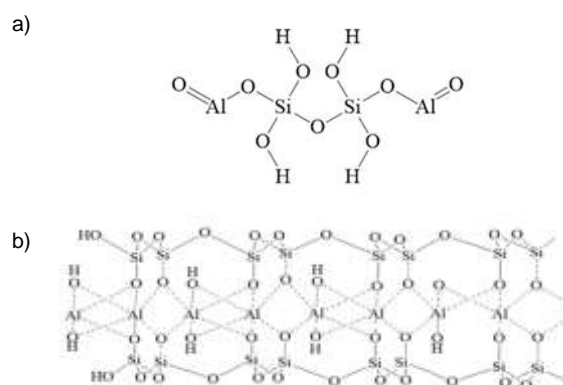


Figure 2 Structure of a) halloysite and b) montmorillonite.

NCl as a reinforcing agent for polymer composites

NClS were introduced into the field of polymeric composites as novel reinforcing agents in the 1980s. NCl consists of layered silicates that can function as rigid fillers to improve the moduli of the matrix material. The nano-sized NCl rigidifies the soft polymeric composites by preventing the free movement of neighboring polymer chains. By reducing internal flexibility of the polymeric composites, their mechanical and diffusional barrier characteristics and fire retardant and ultraviolet light-resistant properties are improved over the micro- or macro- counterparts and pure polymeric resins [66, 79]. NClS have also proven applicable for uses beyond polymer reinforcement in the packaging, automotive aerospace, electronics and medical sectors [80].

that of neat PVA. As the loading level of HNTs increases, the modulus of the nanocomposite also increases. At loading levels of 5 and 10 vol. % HNT, the Young's moduli were 286 and 388 MPa, respectively, and when the HNT loading increased to 20 vol. % the Young's modulus was elevated to 466 MPa, an almost two-fold improvement over the neat PVA. This phenomenon can be directly associated with increased tortuosity of the polymer molecules and the significantly harder nanoparticles, as well as the existence of a greater nanoparticle-polymer interface [87].

Montmorillonite as a reinforcing agent for polymer matrices as compared with halloysite is also quite well documented in the literature [88]. A single sheet of montmorillonite has a Young's modulus of 178–265 GPa in plane, indicating its greater suitability as a nanofiller

Table 4 Mechanical and tensile properties^a of polymer matrices when halloysite and montmorillonite are used as reinforcing agents.

Types of NCl and nanocomposite ^b	Clay content, <i>v</i> ^a (vol. %)		Clay content, <i>w</i> ^a (wt. %)		<i>E</i>		σ
	HNT	MMT	HNT	MMT	GPa	MPa	MPa
Neat PHBV	–	–	0	0	3.5 ± 0.3	–	37.5 ± 1.0
Modified MMT-PHBV	–	–	–	1	5.1 ± 0.6	–	40.6 ± 0.6
HNT-PHBV	–	–	–	3	4.6 ± 0.3	–	30.7 ± 2.5
	–	–	–	5	7.1 ± 1.9	–	30.4 ± 0.4
	–	–	1	–	4.0 ± 0.2	–	39.3 ± 0.7
	–	–	3	–	3.6 ± 0.1	–	39.4 ± 1.4
Neat PVA	–	0	–	–	245 (20.6) ^c	–	34.3 (13.6)
	5	–	–	–	286 (16.2)	–	29.1 (8.7)
	10	–	–	–	388 (17.0)	–	27.7 (9.8)
	20	–	–	–	466 (11.3)	–	22.0 (10.7)
TPS	–	–	–	0	–	29.8 ± 4.4	3.1 ± 0.4
MMT-TPS	–	–	–	2	–	29.6 ± 12.1	2.7 ± 0.4
	–	–	–	3	–	150.5 ± 25.6	2.4 ± 0.7
	–	–	–	5	–	195.6 ± 38.6	4.1 ± 1.1
	–	–	–	–	–	–	–

^a *v* denotes loading fractions of clay in volume; *w* denotes loading fractions in weight; *E* denotes Young's Modulus in gigapascals and megapascals; σ denotes tensile strength in megapascals.

^b MMT: montmorillonite; PHBV: poly(hydroxybutyrate-co-hydroxyvalerate) [83]; PVA: poly-vinyl alcohol [86]; TPS: Thermoplastic starch [92]

^c Value in the parentheses are % coefficient of variation values.

Halloysite and montmorillonite as a potential reinforcement for polymer composites

Since 1980s, researchers have demonstrated the possibility of functionalizing the surface of layered inorganic silicates into the polymer matrix to increase their affinity. Anjana and George (2012) [81] reported the effect of nano-kaolinite clay on polypropylene/high-density polyethylene blends. The mechanical properties of the blends were elevated without increasing their weight and density. Similarly, Carli and her co-workers [82] investigated the effect of clay types on poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) using HNT and organo-modified montmorillonite. They discovered that the incorporation of clays using a loading fraction of 5 wt. % of halloysite boosts the tensile modulus of the nanocomposite (Table 4), thus highlighting the great potential of halloysite as a reinforcement material as compared with montmorillonite. This might be due to the excellent dispersion of clay mineral particles in the polymeric matrix [83]. The incorporation of organo-modified MMT in the PHBV matrix leads to substantially reduced strength, whereas HNT-PHBV results in improved tensile strength. These results show that HNT nanoparticles are a potentially interesting material for enhancing the biodegradability of the polymer because of their ability to interact with the PHBV matrix [84]. This is because the carbon nanotube-like HNTs are easily dispersed within the polymer matrix by shearing because of their rod-like geometry and limited intertubular contact area [85] thus enhancing the tensile modulus and tensile strength of the polymer.

A study by Qiu and Netravali [86] also showed that HNTs improve the mechanical properties of PVA (Table 4). The authors stated that the modulus value of HNT-PVA nanocomposite was slightly higher than

for reinforcing polymer matrix than that of halloysite, which has a Young's modulus of 130–140 GPa [89]. The nanometer-scale sheets of aluminosilicates, which are 1–5 nm thick and 200–600 nm in diameter, lead to platelets with a high (>50) aspect ratio. Because of these characteristics, montmorillonite, when blended with a polymer, enables stress transfer from the polymer to the mineral, which results in increased mechanical properties of the nanocomposites [90]. More recently, Venkatesan et al. [91] reported that the addition of montmorillonite to high-density polyethylene (HDPE) substantially influences the mechanical properties of the nanocomposite.

To study the effects of these NClS on the properties of starch, Cyrus et al. [92] used montmorillonite to reinforce TPS from potato starch at three different loadings. When MMT at 3 and 5 wt. % was incorporated into the polymer matrix, the modulus of the nanocomposites increased by as much as five-fold over pure TPS (Table 4). For the tensile test, the authors found that amounts below 5 wt. % of clay were beneficial. Beyond this point, the values of Young's modulus did not follow the same trend with the addition of montmorillonite. This behavior might be due to the resistance exerted by the clay itself and to the orientation and aspect ratio of the intercalated silicate layers [92]. Therefore, from these perspectives, it is observed that halloysite does outperformed montmorillonite. Even so, both of these naturally occurring minerals can act as excellent reinforcing materials in polymer nanocomposites [90].

CONCLUSION

It is clear that the application of NC and NCl extends across a myriad of research fields, especially with their use as reinforcement

materials for polymer nanocomposites. Both NC and NCI can significantly improve the physical and mechanical properties of polymer composites. The development of these nano-sized, biodegradable, renewable, and more environmentally friendly polymers is the solution for overcoming the limitations of current biopolymers. Also, more attention could be paid on future studies on NC and NCI, as well as the hybrid composites containing these nanomaterials, using new advance instrumentations the better.

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