

# Bionanocomposites: State of the Art, Challenges, and Opportunities

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## 1.1 INTRODUCTION

Researchers are currently developing and modifying biobased materials that have various applications in different fields. Ecological concerns are the main reasons behind this renewed interest in natural and compostable materials. Tailoring new products with the perspective of sustainable development is a philosophy that is applied to more and more materials now. The importance gained by natural polymers recently should be viewed from this perspective. Compared with their synthetic counterparts, natural polymers are renewable, biocompatible, and biodegradable. Production of nanocomposites from natural polymers, such as starch, chitin, and cellulose, and specific research in this field aimed at increasing the properties of the products and developing newer techniques are the order of the day. Polysaccharide polymers that are abundant in nature are increasingly being used for the preparation of nanocomposites.

Biopolymers are polymers that are biodegradable. They are designed to degrade through the action of living organisms. They are the best alternatives to traditional nonbiodegradable polymers whose recycling is unpractical or not economical. The input materials for the production of such biodegradable polymers may be either renewable (based on agricultural plant or animal products) or synthetic. Biopolymers from renewable resources are more important than others for obvious reasons [1]. Biopolymers are said to be from renewable sources because they are made from materials that can be grown each year, indefinitely. Plant-based biopolymers usually come from agricultural nonfood crops. Therefore, the use of biopolymers would create a

sustainable industry. In contrast, the feedstock of synthetic polymers derived from petrochemicals will eventually run out. Biopolymers have also been reported to be close to carbon-neutral. When a biodegradable material (neat polymer, blended product, or composite) is obtained completely from renewable resources, we may call it a green polymeric material.

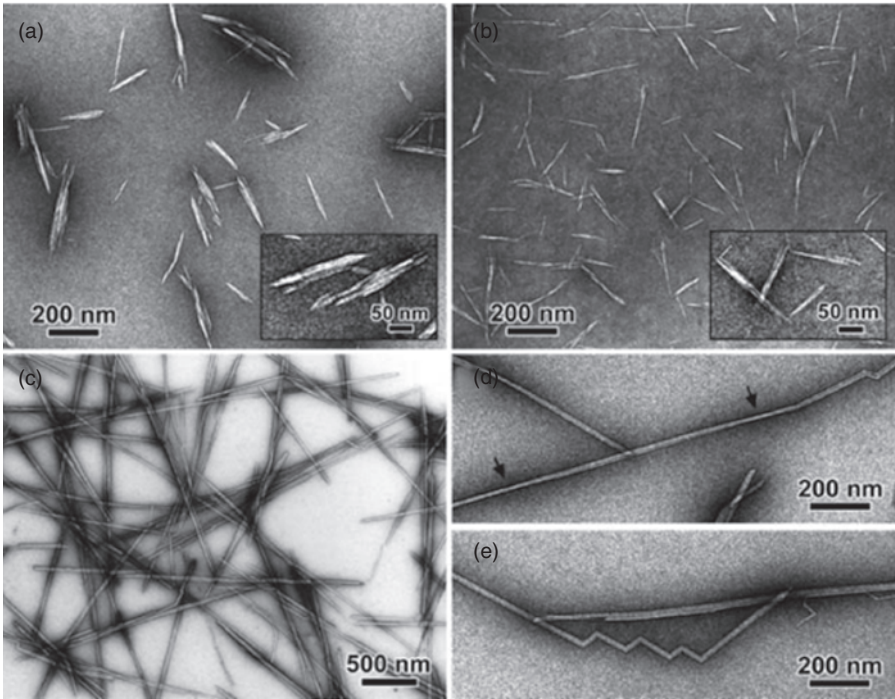
Nature provides an impressive array of polymers that are generally biodegradable and that have the potential to replace many current polymers, as biodegradation is part of the natural biogeochemical cycle. Natural polymers, such as proteins, starch, and cellulose, are examples of such polymers. Polymer nanocomposites represent a new alternative to conventional polymers. Polymer nanocomposites are materials in which nanoscopic inorganic or organic particles, typically 10–1000 Å in at least one dimension, are dispersed in an organic polymer matrix in order to improve the properties of the polymer dramatically. Owing to the nanometer length scale, which minimizes scattering of light, nanocomposites are usually transparent and exhibit properties that are markedly improved over those of pure polymers or their traditional composites. They have increased modulus and strength, outstanding barrier properties, improved solvency, heat resistance, and generally lower flammability, and they do not have detrimental effects on ductility.

## 1.2 NANOCRYSTALLINE CELLULOSE

The hierarchical structure and semicrystalline nature of polysaccharides (cellulose, starch, and chitin) allow nanoparticles to be extracted from naturally occurring polymers. Native cellulose and chitin fibers are composed of smaller and mechanically stronger long thin filaments, called microfibrils, consisting of alternating crystalline and noncrystalline domains. Multiple mechanical shearing actions can be used to release these microfibrils individually.

The extraction of crystalline cellulosic regions, in the form of nanowhiskers, can be accomplished by a simple process based on acid hydrolysis. Samir et al. have described cellulose whiskers as nanofibers that have been grown under controlled conditions that lead to the formation of high purity single crystals [2]. Many different terms have been used in the literature to designate these rod-like nanoparticles. They are mainly referred to as whiskers or cellulose nanocrystals. A recent review from Habibi et al. gives a clear overview of such cellulosic nanomaterials [3].

Nanocrystalline cellulose (NCC) derived from acid hydrolysis of native cellulose possesses different morphologies depending on the origin and hydrolysis conditions. NCCs are rigid rod-like crystals with a diameter in the range of 10–20 nm and lengths of a few hundred nanometers (Figure 1.1). Acid treatment (acid hydrolysis) is the main process used to produce NCC, which are smaller building blocks released from the original cellulose fibers. Native cellulose consists of amorphous and crystalline regions. The amorphous regions have lower density than the crystalline regions. Therefore, when cellulose



**Figure 1.1** NCCs are rigid rod-like crystals with diameter in the range of 10–20 nm and lengths of a few hundred nanometers. Reproduced with the permission from Reference [5].

fibers are subjected to harsh acid treatment, the amorphous regions break up, releasing the individual crystallites. The properties of NCC depend on various factors, such as cellulose sources, reaction time and temperature, and types of acid used for hydrolysis.

Polysaccharide nanoparticles are obtained as aqueous suspensions, and most investigations have focused on hydrosoluble (or at least hydrodispersible) or latex-form polymers. However, these nanocrystals can also be dispersed in nonaqueous media using surfactants or chemical grafting. The hydroxyl groups present on the surface of the nanocrystals make extensive chemical modification possible. Even though this improves the adhesion of nanocrystals with nonpolar polymer matrices, it has been reported that this strategy has a negative impact on the mechanical performance of the composites. This unusual behavior is ascribed to the reinforcing phenomenon of polysaccharide nanocrystals resulting from the formation of a percolating network due to hydrogen bonding forces.

As a result of its distinctive properties, NCC has become an important class of renewable nanomaterials, which has many useful applications, the most

important of which is the reinforcement of polymeric matrices in nanocomposite materials. Favier et al. were the first to report the use of NCC as reinforcing fillers in poly(styrene *co*-butyl acrylate) (poly(S-*co*-BuA))-based nanocomposites [4]. Since then, numerous nanocomposite materials have been developed by incorporating NCC into a wide range of polymeric matrices. Owing to their abundance, high strength and stiffness, low weight, and biodegradability, nanoscale polysaccharide materials can be used widely for the preparation of bionanocomposites. In fact, a broad range of applications of these nanoparticles exists. Many studies show its potential, though most focus on their mechanical properties and their liquid crystal self-ordering properties. The homogeneous dispersion of cellulosic nanoparticles in a polymer matrix is challenging. In addition, there are many safety concerns about nanomaterials, as their size allows them to penetrate into cells of humans and to remain in the system. However, finding newer applications for nanocellulose will have a very positive impact on organic waste management. To date, there is no consensus about categorizing nanocellulosic materials as new materials.

NCC is an environmentally friendly material that could serve as a valuable renewable resource for rejuvenating the beleaguered forest industry. New and emerging industrial extraction processes need to be optimized to achieve more efficient operations, and this will require active research participation from the academic and industrial sectors. The application of nanotechnology in developing NCC from the forest industry to more valuable products is required because the availability of materials based on NCC is still limited. Increasing attention is devoted to producing NCC in larger quantities and to exploring various modification processes that enhance the properties of NCC, making it attractive for use in a wide range of industrial sectors [5]. As the second most abundant biopolymer after cellulose, chitin is mainly synthesized via a biosynthetic process by an enormous number of living organisms such as shrimp, crab, tortoise, and insects and can also be synthesized by a nonbiosynthetic pathway through chitinase-catalyzed polymerization of a chitobiose oxazoline derivative [6, 7].

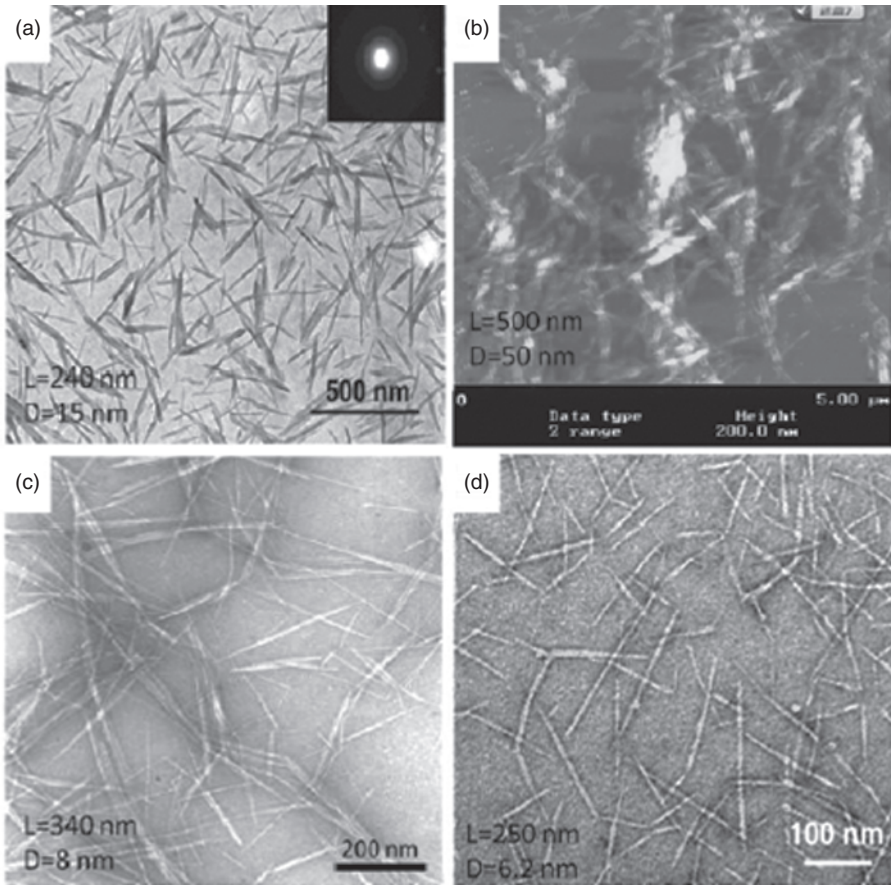
Chitosan, as the most important derivative of chitin, can be prepared by deacetylation of chitin. Chitin and chitosan have many excellent properties including biocompatibility, biodegradability, nontoxicity, and absorption, and thus they can be widely used in a variety of areas such as biomedical applications, agriculture, water treatment, and cosmetics. Chitin has been known to form microfibrillar arrangements in living organisms. These fibrils with diameters from 2.5 to 25 nm, depending on their biological origins, are usually embedded in a protein matrix [8]. Therefore, they intrinsically have the potential to be converted to crystalline nanoparticles and nanofibers and to find application in nanocomposite fields. The structure of chitin is very analogous to cellulose. Chitin and cellulose are both supporting materials for living bodies and are found in living plants or animals with sizes increasing from simple molecules and highly crystalline fibrils on the nanometer level to composites on the micrometer level upward [9]. Therefore, they intrinsically have

the potential to be converted to crystalline nanoparticles and nanofibers and to find application in nanocomposite fields. Chitin has been known to form microfibrillar arrangements in living organisms [10, 11].

Chitin whiskers (CHW) can be prepared from chitins isolated from chitin-containing living organisms by a method similar to the preparation of cellulose whisker through hydrolysis in a strong acid aqueous medium. On the basis of preparation of cellulose crystallite suspension, Marchessault et al. [11] for the first time reported a route for preparing suspension of chitin crystallite particles in 1959. In this method, purified chitin was first treated within 2.5 N hydrochloric acid (HCl) solutions under reflux for 1 hour; the excess acid was decanted; and then distilled water was added to obtain the suspension. Acid-hydrolyzed chitin was found to be spontaneously dispersed into rod-like particles that could be concentrated to a liquid crystalline phase and self-assemble to a cholesteric liquid crystalline phase above a certain concentration [12].

CHWs are attracting attention from both the academic field and industry since it is a renewable and biodegradable nanoparticle. CHWs have numerous advantages over conventional inorganic particles such as low density, nontoxicity, biodegradability, biocompatibility, easy surface modification, and functionalization. Figure 1.2 shows the transmission electron microscopy (TEM) and atomic force microscopy (AFM) images of CHWs obtained by the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) mediated oxidation method. CHWs, with or without modification, are hoped to have extensive application in many areas such as reinforcing nanocomposites, the food and cosmetics industries, drug delivery, and tissue engineering. However, recent studies have focused mainly on the preparation and nanocomposite application of CHWs, and less attention has been paid to other application areas. It is hoped that in the future, more attention will be focused on developing novel applications of CHWs. Even for the CHW-reinforced nanocomposites there will still be much valuable work to be done, for example, developing new simple and effective processing methods so as to commercialize high performance polymer/CHWs composites, producing polymer nanocomposites filled with individual CHWs that would create higher reinforcing efficiency than the conventional CHW due to the high aspect ratio of individual CHWs. Thus, there are abundant opportunities combined with challenges in CHW-related scientific and industrial fields [13].

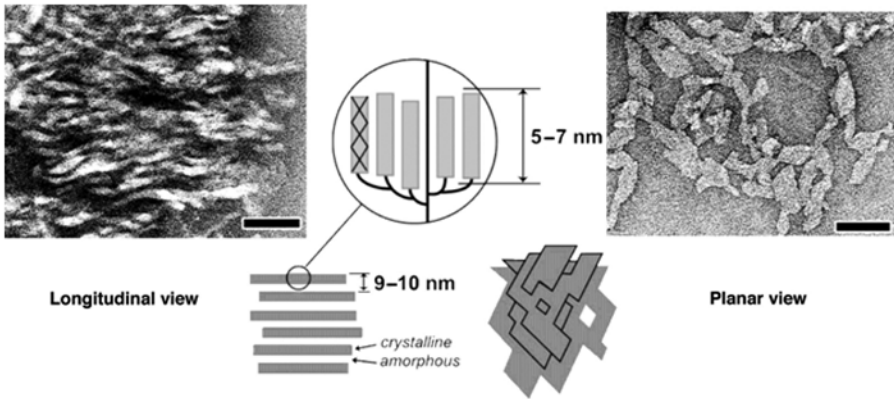
Starch is the second most studied organic material for producing nanocrystals. Starch nanocrystals are the nanoscale biofillers derived from native starch granules and are a suitable candidate for the preparation of semicrystalline polymers for preparing renewable and potentially biodegradable nanoparticles. As a natural biopolymer, starch is abundant, renewable, inexpensive, biodegradable, environmentally friendly, and easy to chemically modify, making it one of the most attractive and promising bioresource materials. Several techniques for preparing starch nanoparticles (SNP) have been developed over the years and render different kinds of SNP, which are described in this book. Acid hydrolysis and precipitation methods are the two main methods employed for the preparation of SNPs. Starch nanocrystals obtained by acid



**Figure 1.2** TEM (a) and AFM (b) images of a dilute suspension of chitin whiskers and TEM images of individual chitin whiskers obtained by the TEMPO method (c) and surface cationization (d). Reproduced with permissions from Reference [9].

hydrolysis of starch have been used as fillers in natural and synthetic polymeric matrices and appear to be an interesting reinforcing agent. Figure 1.3 shows the TEM image of starch nanocrystals [14]. Nanoreinforced starch-based nanocomposites generally exhibit enhanced mechanical and thermal properties when nanofillers are well dispersed, while the nature of the matrix and/or nanofiller contributes to its biological properties.

Nanocellulose produced by the bacterium *Gluconacetobacter xylinus* (bacterial cellulose, BC), is an another emerging biomaterial with great potential as a biological implant, wound and burn dressing material, and scaffold for tissue regeneration. This BC is quite different from plant celluloses and is defined by high purity (free of hemicelluloses, lignin, and alien functionalities

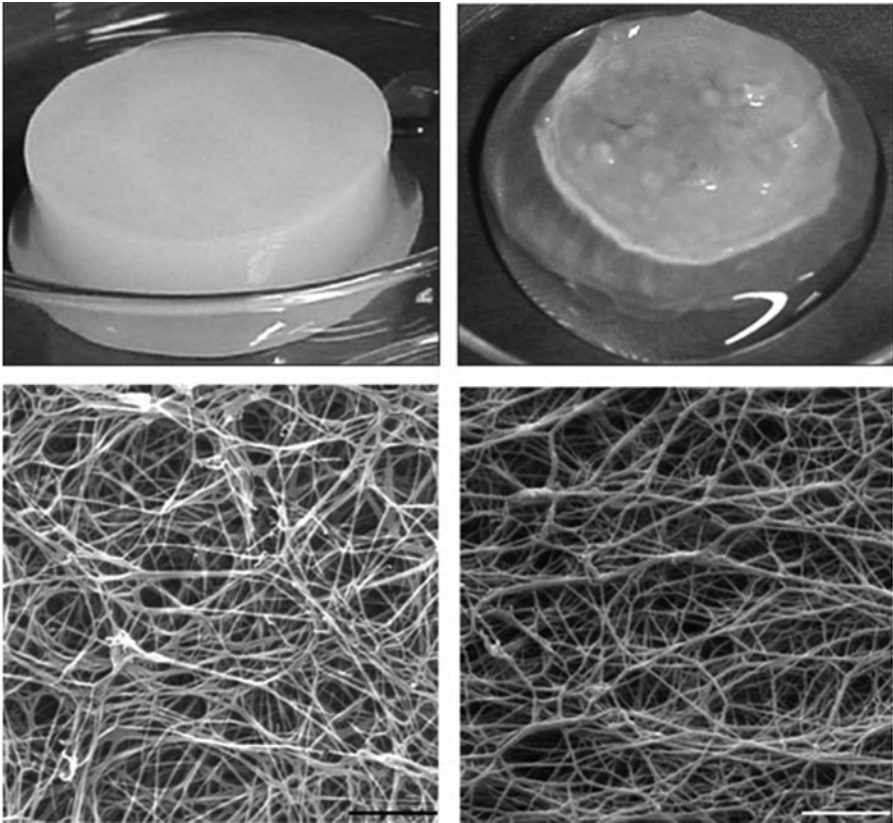


**Figure 1.3** TEM observations of starch nanocrystals: longitudinal view and planar view. Reproduced with permission from Reference [14]. Copyright 2003 American Chemical Society.

such as carbonyl or carboxyl groups) and a high degree of polymerization (up to 8000) [15]. BC has remarkable mechanical properties despite the fact that it contains up to 99% water. The water-holding ability is the most probable reason why BC implants do not elicit any foreign body reaction. Fibrosis, capsule formation, or giant cells were not detected around the implants, and connective tissue was well integrated with the BNC structures. Moreover, the nanostructure and morphological similarities with collagen make BC attractive for cell immobilization, cell migration, and the production of extracellular matrices [16, 17]. Figure 1.4 shows BNC fleeces formed by different *Gluconacetobacter* strains and their network structure.

The advanced natural fiber-reinforced polymer composite contributes to enhancing the development of bionanocomposites with regard to performance and sustainability. In the future, these biocomposites will see increased use in optical, biological, and engineering applications. But there are still a number of problems that have to be solved before biocomposites become fully competitive with synthetic fiber composites. These include extreme sensitivity to moisture and temperature, expensive recycling processes, high variability in properties, nonlinear mechanical behavior, poor long-term performance, and low impact strength. As of now, the methods for extracting nanocrystals of these various biomaterials are expensive, and more economical methods will have to be sorted out in future.

The poor interfacial adhesion between natural fibers and polymeric matrix is the key issue that dictates the overall performance of the composites. Interaction of two or more different materials with each other depends on the nature and strengths of the intermolecular forces of the components involved. The mechanical performance of composites is dependent on the degree of



**Figure 1.4** Fleece of bacterial nanocellulose produced by two different *Gluconacetobacter* strains and their network structure. Reproduced with permissions from Reference [17].

dispersion of the fibers in the matrix polymer and the nature and intensity of fiber–polymer adhesion interactions. Therefore, the selection of appropriate matrices and filler with good interfacial interaction is of great importance. The irreversible aggregation of the nanofiller (hornification) in the matrix, which prevents its redispersion in the matrix, is another hurdle to be overcome. This irreversible aggregation results in a material with ivory-like properties that can neither be used in rheological applications nor be dispersed for composite applications. Therefore, it is necessary to continue research in this area to obtain a better understanding of the adhesion interactions including mechanical interlocking, interpenetrating networks, and covalent linkages on a fundamental level to improve interfacial properties with thermoplastics, thermosets, and biopolymers.

This book is an attempt to introduce various biopolymers and bionanocomposites to students of material sciences. Going beyond a mere introduction,



the book delves deep into the characteristics of various biopolymers and bionanocomposites and discusses the nuances of their preparation with a view to helping researchers discover newer and novel applications. Chapter 2, for instance, describes the preparation of chitin nanofibers and their composites and discusses the basics, such as isolation of chitin nanofibers from different sources. Chapter 3 discusses chemical modification of chitosan and its biomedical application. While biometric lessons for processing chitin-based composites are provided in Chapter 4, Chapter 5 deals with morphological and thermal investigations of chitin-based nanocomposites. Mechanical properties of chitin-based nanocomposites are discussed in Chapter 6, and preparation and applications of chitin nanofibers/nanowhiskers is the topic of Chapter 7. Thus, Chapters 2 to 7 are allotted to chitin and related topics.

Various aspects of starch-based composites, such as preparation of SNPs (Chapter 8), chemical modification of SNPs (Chapter 9), processing techniques of starch-based bionanocomposites (Chapter 10), morphological and thermal investigations of starch-based nanocomposites (Chapter 11), mechanical properties of starch-based nanocomposites (Chapter 12), and applications of SNPs and starch-based bionanocomposites (Chapter 13), are the subject matter of Chapters 8 to 13.

Preparation of nanofibrillated cellulose and cellulose whiskers are dealt with in Chapter 14. Chapter 15 is exclusively set apart for BC. It examines the details of production of microorganisms, production of BC, production of BC from food and agro-forestry residues, and the structure of BC. Chemical modification of nanocelluloses is discussed in Chapter 16, and processing techniques of cellulose-based nanocomposites are dealt with in Chapter 17. Chapter 18 is on morphological and thermal investigations of cellulosic bionanocomposites, and Chapter 19 discusses mechanical properties of cellulose-based bionanocomposites. A review of nanocellulosic products and their applications is provided in Chapter 20. In Chapter 21 spectroscopic characterization of renewable nanoparticles and their composites are dealt with. Chapter 22 deals with barrier properties of renewable nanomaterials. Chapter 23 is set apart for biocomposites and nanocomposites containing lignin. While Chapter 24 deals with preparation, processing, and applications of protein nanofibers, Chapter 25 deals with protein-based nanocomposites for food packaging. Thus, this book is a sincere attempt at promoting the use of green materials for sustainable growth of humanity.

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