

Mechanical Properties of Eco-friendly Polymer Nanocomposites

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Abstract Biopolymers are an alternative to petroleum-based synthetic polymers that are renewable, do not contribute to environmental pollution, and are biodegradable. However, some of their properties like tensile strength, impact strength, thermal stability, and permeability are not of sufficiently high standard and must be improved. One way to improve the properties of biopolymers and thus enhance their commercial potential is to incorporate nano-sized bio-based reinforcements in the polymers. The composites thus formed are called eco-friendly polymer nanocomposites. The research in these composites has increased substantially in the last few years with a corresponding increase in research papers. These composites are finding applications in various fields like medicine, packaging, electronics, the automotive sector, and the construction industry. Polysaccharide polymers that are abundant in nature are increasingly being used for this purpose. The biopolymers most commonly used in these composites are thermoplastic starch (TPS), polylactic acid (PLA), cellulose acetate, chitosan, polyvinyl alcohol (PVA), and epoxidized plant oils. Some examples of the bio-based reinforcements used in these composites are cellulose nanowhiskers, chitin whiskers, and starch nanoparticles (SNP). Extrusion and injection molding are the most widely used methods for manufacturing of these composites. Results show that incorporation of bio-based nanoreinforcements in biopolymers results in improvement in mechanical properties of these composites. These include tensile, flexural, and impact properties. Poor dispersion and agglomeration of nanoreinforcements in biopolymers and their poor interfacial bonding are issues which impose a limit on these composites' mechanical performance. Various physical and chemical methods for surface treatments of nanoreinforcements are used. These methods have been shown to result in improvements of mechanical properties of these composites. There are a number of other issues like sensitivity to moisture and temperature, expensive recycling processes, high variability in properties, nonlinear mechanical behavior, poor long-term performance, and low impact strength, which are hindering the

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development of these materials. However, as the investment and research in these materials increase, they are expected to replace many conventional materials in optical, biological, and engineering applications.

Keywords Biopolymers · Nanocomposites · Cellulose · Chitosan · Starch · Mechanical properties

1 Introduction

This chapter aims to present an overview of the mechanical properties of eco-friendly polymer nanocomposites. The main constituents of these composites and their properties are discussed first, which is followed by a discussion of the mechanical properties of these composites.

1.1 Polymer Nanocomposites

Polymer nanocomposites are now a well-established class of materials which exhibit superior mechanical, thermal, and barrier properties at low reinforcement levels (typically 5 wt%), as well as better recyclability, transparency and low weight, compared with conventional polymer composites (Lin et al. 2011a, b, c; Thakur et al. 2012a). These nanocomposites are based on conventional thermoset and thermoplastic polymer matrices, most of which are not biodegradable (Thakur et al. 2014a, b, c, d, e, f). Biopolymers are a relatively new class of polymers which are biodegradable, environment friendly, and renewable (Singha and Thakur 2009a, b, c, d). Biopolymers, as stand-alone materials, exhibit poor mechanical properties, low thermal stability, and poor barrier properties (Thakur et al. 2012b, c, d, e). When such polymers are reinforced with natural fibers, their properties are considerably improved with simultaneous improvement in biodegradability. Reinforcement with nanoparticles and nanofibers, derived from naturally occurring polymers, results in further improvement in their properties. Such improvements include, but are not limited to, higher modulus and strength, decrease in gas permeability, increase in heat distortion temperature as well as improvement in the biodegradability of biopolymers.

The most widely used reinforcements in nanocomposites are carbon nanotubes, layered clay, and nanoparticles. The most widely used polymer matrices are polyamides, nonpolar polymers, polyesters, epoxies, and polyurethane. However, this chapter will focus on nanocomposites which are made from both biodegradable fiber/fillers and biodegradable matrices, since only these composites truly justify the definition of eco-friendly and green nanocomposites.

Natural polysaccharides, such as starch derived from corn, wheat, rice or potato, and cellulose and its derivatives, are the main biopolymers employed in the development of green nanocomposites. The biodegradable thermoplastic polyester PLA, starch, and epoxidized vegetable oils are other examples of polymers widely used in the development of reinforced biopolymers.

Cellulose nanofibers are as strong as steel and can be used as an alternative to glass fibers. With just 5–10 % of nanofiber loading, the tensile strength of the nanocomposites can increase by two to three times (Oksman et al. 2009). The composites thus formed are (theoretically at least) completely biodegradable, environment friendly, and renewable; hence they are called eco-friendly polymer nanocomposites. As these nanocomposites continue to find applications in various fields, the research in these composites has increased exponentially in the last decade or so. These applications include medicine, packaging, electronics, the automotive sector, construction, and other areas. Medical applications include artificial implants, wound dressing products, drug delivery, and medical devices. Automotive applications include car panels, door modules, and various load bearing parts (Oksman et al. 2009). A typical example of the research being conducted on these composites is the NanoCelluComp project, which is a consortium consisting of 11 partners from five European countries. This project aims to develop a novel process technology that utilizes the high mechanical performance of cellulose nanofibers combined with biopolymers for the manufacture of 100 % bio-derived high-performance composite materials (JEC Composites 2014). This process technology will be compatible with existing composite manufacturing processes to facilitate industry uptake. Simultaneously, the project is assessing the sustainability of the process and materials in terms of life cycle analysis (including environmental impacts) and costs compared to existing materials.

1.2 Fillers and Matrices

Fillers used as nanoreinforcement are, generally, of three types: isodimensional particles, elongated particles and layered particles, as shown in Fig. 1.

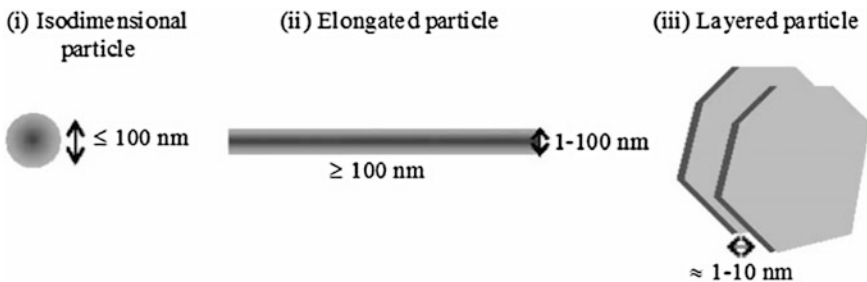


Fig. 1 Three types of fillers used as nanoreinforcement (Angellier and Dufresne 2013)

Table 1 Comparison between cellulose nanocrystals (CNC) and microfibrillated cellulose (MFC)

Cellulose nanocrystals	Microfibrillated cellulose
Consist of crystallites	Consist of crystalline and amorphous regions
Rod-like nanoparticles	Long and flexible nanoparticles
Diameter \sim 5–10 nm; length \sim 100–500 nm	Diameter \sim 10–100 nm; length \sim several microns
Young's modulus \sim 130–250 GPa	Young's modulus \sim 150 GPa

Isodimensional particles have the same size in all directions and their aspect ratio is usually close to one. Some examples of these particles are spherical silica, carbon black, and fullerenes. Elongated particles consist of fibrils with diameters ranging between 1 and 100 nm and lengths of several hundred of nanometers. Some examples of these particles are cellulose and chitin nanofibers and carbon nanotubes. Because of their higher aspect ratio, nanocomposites based on these fillers offer superior mechanical properties compared to other fillers. Layered particles have one dimension, often the thickness, ranging from several angstroms to several nanometers. Their examples are layered silicates and starch nanocrystals (SNs).

Cellulose fibers consist of smaller and stronger long and thin filaments called microfibrils. Nanoscale particles can be derived from microfibrils which are of two types: nanowhiskers, also called cellulose nanocrystals (CNC) and microfibrillated cellulose (MFC). Mechanical shearing actions separate these fibrils into MFC, whereas longitudinal cutting of microfibrils through strong acid hydrolysis treatments results in nanowhiskers. Table 1 summarizes the differences between the two.

In order to produce composites with superior mechanical properties, the reinforcements used in them should have high strength and stiffness, preferably at low density. Nanoscale cellulose fibers and particles satisfy these requirements, with the added benefit of being biodegradable and abundantly available. With a Young's modulus of about 150 GPa (much greater than glass fibers and at par with Kevlar fibers) and a surface area of several hundred m^2/g (Kalia et al. 2011), nanofibers have the potential to significantly reinforce polymers at low filler loadings. For these reasons, Moon et al. (2011) consider them to be ideal materials on which to base a new biopolymer composites industry.

CNC is derived as nanowhiskers for use as reinforcement in biopolymers such as starch, PLA, and PHB. Apart from being biodegradable, these nanowhiskers have high specific strength and stiffness. Similarly, chitin nanowhiskers are synthesized from chitin, the second most abundant biopolymer after cellulose. These nanowhiskers have many desirable properties for use as reinforcements, like low density, nontoxicity, biodegradability, biocompatibility, easy surface modification, and functionalization. Starch nanoparticles (SNP) are synthesized from starch granules for use as reinforcement.

Owing to its unique properties, such as high mechanical strength, high crystallinity (above 60 %), and a highly pure nanofibrillar network structure, bacterial cellulose (BC), produced by *Acetobacter xylinum*, is becoming a popular biopolymer for use in nanocomposites. BC is available as a tridimensional network of

Table 2 Comparison of properties of cellulose nanocrystals (CNC) with conventional reinforcements (Moon et al. 2011)

Material	Density (g/cm ³)	Tensile strength (GPa)	Elastic modulus (axial) (GPa)	Elastic modulus (transverse) (GPa)
Glass	2.5	3.4–4.3	72–87	–
Carbon	1.8	1.5–5.7	150–500	–
Kevlar-49	1.4	3.5	124–130	2.5
Steel wire	7.8	4.1	210	–
Clay nanoplatelets	–	–	170	–
Carbon nanotubes	–	11–63	270–950	0.8–30
Boron nanowhiskers	–	2–8	250–360	–
CNC	1.6	7.5–7.7	110–220	10–50

nano- and microfibrils with 10–100 nm width for use as reinforcement. Their structure is quite different from plant cellulose with high purity and high degree of polymerization. Their high degree of crystallinity imparts to them a tensile modulus of 114 GPa which is higher than that of synthetic glass (Lee et al. 2009). Their main disadvantage is their high hydrophilicity.

Table 2 compares the properties of CNC with various conventional reinforcements used in composites. It is readily apparent that their properties are comparable to, or even better than, other reinforcements. These superior properties will inevitably result in composites with superior properties.

Depending on their origins, biopolymers used as matrices in composite materials are divided into three main classes: agropolymer based (renewable sources), microbially derived, and chemically synthesized. Some authors also mention a fourth class, which consists of blends of the aforementioned three classes.

Agropolymer-based biopolymers are obtained from biomass by fractionation. They are further divided into two categories: polysaccharides, and proteins and lipids. Polysaccharides are derived from starches (wheat, potato, maize), lignocellulosic products (cellulose), pectins, chitosans, and gums (Thakur and Thakur 2014a, b, c). Proteins and lipids can be either animal derived (casein, whey, gelatin, collagen), or plant derived (soya, gluten) (Thakur and Kessler 2014a, b). These materials and their derivatives offer a wide range of properties and applications.

Microbially-derived biodegradable polyesters are obtained by microbial fermentation from genetically modified plants. For this reason, they are also referred to as bacterial biopolymers. Their best example is polyhydroxyalkanoate (PHA). PHAs occur naturally in a variety of organisms, but microorganisms can be employed to tailor their production in cells. PHAs can be produced by varieties of bacteria using several renewable waste feedstocks. The feedstocks include cellulose, vegetable oils, organic waste, municipal solid waste, and fatty acids depending

on the specific PHA required. Poly(3-hydroxybutyrate) (PHB) is the main representative of PHAs and was, in fact, the first PHA discovered. PHB is similar in its material properties to thermoplastics, with a good resistance to moisture.

Chemically synthesized biodegradable polyesters are obtained by synthesis from monomers obtained from biomass. Their best example is polylactic acid (PLA) derived from corn. PLA shares some similarities with commodity polymers such as polyethylene terephthalate (PET). It has many good characteristics like good transparency, glossy appearance, high rigidity, and ability to tolerate various types of processing conditions.

2 Tensile Properties

Tensile properties are, by far, the most widely studied mechanical properties of eco-friendly polymer nanocomposites. Overall, the mechanical performance of CNC-reinforced composites depends on the aspect ratio, crystallinity, processing method, and CNC/matrix interfacial interaction. The mechanical properties are proportional to aspect ratio and crystallinity of nanoreinforcement and it has been shown that increase in aspect ratio and crystallinity results in increase in mechanical properties. Slow processing methods which encourage water evaporation result in composites with improved properties. This is because nanoparticles have sufficient time to interact and connect to form a continuous network, which is the basis of their reinforcing effect. Nanoreinforcement which is compatible with the biopolymer matrix also exhibits improved mechanical properties of the nanocomposites.

The mechanical properties of CNC nanocomposites have also been found to exceed the predicted values gained from classical models based on filler reinforced nanocomposites. This phenomenon, also called percolation effect, has been explained by the formation of a rigid network of whiskers which is responsible for the unusual reinforcing effect observed (Samir et al. 2005). Above the percolation threshold the cellulosic nanoparticles can connect and form a 3D continuous pathway through the nanocomposite film, cemented by hydrogen bonds. For example, for rod-like particles such as tunicin whiskers with an aspect ratio of 67, the percolation threshold is close to 1 vol%. The percolation approach has been found to fit satisfactorily the experimental data, especially at high filler loading. The similarity between predicted and experimental data demonstrates the major role of filler/filler interaction in the final mechanical behavior of the cellulose-based nanocomposites. Moreover, the percolation approach also accounts for the excellent thermal stabilization of nanocomposites' modulus at high temperatures. Thus the mechanical properties of CNC nanocomposites are mainly affected by factors that ensure or interfere with the formation of the percolated network such the aspect ratio of CNCs and their interfacial interactions (between them or with the host matrix).

There are two main issues with the use of cellulose nanoreinforcement in biopolymer matrices which ultimately affect the mechanical properties of the

composites made from them. The first one is the noncompatibility of the polar fiber and the nonpolar matrix. This results in poor fiber/matrix interfacial adhesion which adversely affects the mechanical properties of composites. The second one is the poor dispersion of fibers in the matrices. The agglomeration of cellulose nanofibers is particularly an issue when used with thermoplastic matrix. Cellulose fibrils have high density of hydroxyl groups on the surface which try to bond with adjacent hydroxyl groups by weak hydrogen bonding. This results in agglomeration of nanofibers. This again results in poor mechanical properties of composites because the reinforcing effect of fibers is greatly diminished. Various surface treatments are used to overcome this issue. These include both physical treatments and chemical treatments. Physical treatments include surface fibrillation, electric discharge (corona and cold) plasma, irradiation, and electric currents. Chemical treatments include the use of silane coupling agents, maleated polypropylene/maleic anhydride grafted polypropylene (MAPP), adhesives, and surfactants/surface active agents. An example of good dispersion of nanocrystalline cellulose in thermoplastic starch (TPS) matrix is shown in Fig. 2. Cellulose crystals appear like uniformly dispersed white dots as shown in figure (b), their concentration being function of the cellulose

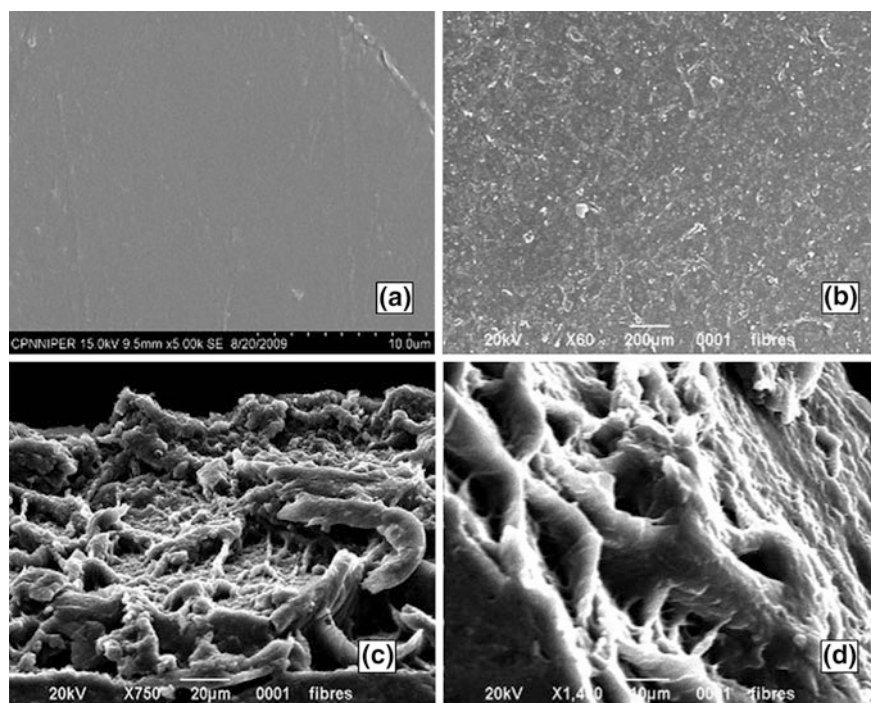


Fig. 2 SEM micrographs of **a** unreinforced TPS film, **b** nanocrystalline cellulose/TPS nanocomposites containing 8 % cellulose, and **c, d** fractured surface of nanocrystalline cellulose/TPS nanocomposites (Kaushik and Kumra 2014)

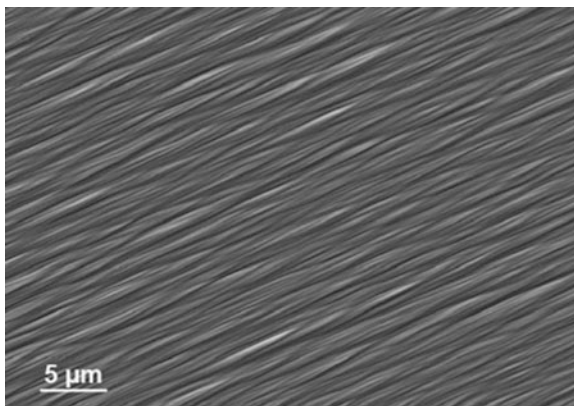
percentage. The figure shows a relatively uniform dispersion of nanocrystals in TPS and no aggregates on the fracture surfaces of the nanocomposites.

The problem of noncompatibility is not generally encountered with biopolymer matrices. However, even in these matrices, the strong interfibrillar hydrogen bonding still impedes proper dispersion of cellulose nanofibers.

The use of a particular manufacturing method of nanocomposites can also affect their mechanical properties. The most commonly used manufacturing methods for cellulose nanocomposites are solvent casting, impregnation of a fiber network or nanopaper with a polymer and melt compounding (Oksman et al. 2009). The solvent casting of nanocomposites entails dissolution of the polymer matrix and proper dispersion of nanocellulose in the same solvent. The impregnation of nanofiber paper/network of films requires the polymer matrix to be in the dissolved stage or have a low viscosity. In this method the final product shape is limited to films or flat products. Melt compounding needs to be done using a specific extruder where the nanocelluloses are mixed with a polymer melt. This is the most widely used method because of the possibility of scaling up the process, and because of the choice of injection molding or compression molding the products.

In one landmark study on the effects of manufacturing processes on mechanical properties of nanocomposites, Oksman et al. (2009) used solvent casting process to make aligned CNC/poly(vinyl alcohol) (PVA) nanocomposites. CNCs were aligned by using a strong magnetic field. The SEM analysis of the nanocomposites showed cellulose nanowhiskers aligned in the direction perpendicular to the magnetic field (Fig. 3). The dynamic mechanical properties of the nanocomposites were studied in the parallel and transverse direction. The results showed that the storage modulus below the T_g (at 25 °C) was remarkably higher (2 GPa) in the transverse direction (whiskers in parallel direction) than the parallel direction of the magnetic field (whiskers in perpendicular direction). This improvement is significant and can be considered as a direct impact of orientation of nanowhiskers in the PVA matrix. These results showed that aligned CNCs can have a similar reinforcing effect on the matrix as the synthetic fibers.

Fig. 3 SEM micrograph of CNC/PVA nanocomposite showing highly oriented structure (Oksman et al. 2009)



They also used modified impregnation method to make cellulose/cellulose nanocomposites. These nanocomposites also showed improved tensile and creep properties over neat CNCs. They then used melt compounding technique to manufacture CNC/poly(lactic acid) nanocomposites, where polyethylene glycol (PEG) was used as plasticizer and maleic anhydride (MA) was used as a coupling agent. Composites made with and without plasticizer both showed increase in tensile properties. However, the maximum improvement in tensile properties was observed for composites made without plasticizer. The tensile modulus of these composites for 5 wt% CNCs improved by about 35 %, the tensile strength by about 90 %, and elongation to break by about 35 %.

2.1 Chitosan

Chitin is a semicrystalline biopolymer which forms microfibrillar arrangement in living organisms like shrimp, crab, tortoise and insects, with diameters ranging from 2.5 to 25 nm. These fibrils can be separated as nanofibers and nanoparticles, also called chitosan, and used as reinforcements in nanocomposites. They have similar structure as nanocrystalline cellulose. Chitosan possesses many properties like biocompatibility, biodegradability, and nontoxicity which encourage their use as reinforcements and matrices in eco-friendly composites. They have been widely studied in inorganic fillers like hydroxyapatite, clay, carbon nanotubes, and grapheme oxide. However, their mechanical properties have been found to be short of expectations. Their use with organic fillers has been less extensively studied.

2.1.1 Chitosan as Filler

The studies have shown increase in tensile properties of nanocomposites for α -chitin whisker (ChW)/PVA (Junkasem et al. 2006; Uddin et al. 2012), α -ChW/chitosan films (Sriupayo et al. 2005), and α -ChW/soy protein isolate films (Lu et al. 2004). In these studies an optimum ChW loading was reported, above which there was negligible improvement in these properties. These values were 5.1 % for α -ChW/PVA, 2.96 % for α -ChW/chitosan films, and 20 % for α -ChW/soy protein isolate films.

Junkasem et al. (2006) reported that the tensile strength of ChW/PVA nanocomposites increased with initial addition of the chitin whiskers to reach a maximum value (5.7 ± 0.6 MPa) at the chitin whisker to PVA ratio of about 5.1 % and decreased with further increasing the whisker content. The presence of ChWs within the nanocomposites increased Young's modulus by about 4–8 times over that of the neat matrix.

Uddin et al. (2012) also reported an optimum loading of ChW in PVA matrix. At 5 wt% ChW loading, the optimum values of tensile strength (1880 MPa) and

toughness (68 J/g) were obtained. However, tensile modulus continued to increase with increase in ChW loading, attaining a peak value of 50 GPa at 30 wt% loading.

In an interesting study, all chitosan nanocomposites were made of ChW reinforced chitosan films by Sriupayo et al. (2005). The tensile strength increased with initial increase in the whisker content to reach a maximum value at the whisker content of 2.96 wt% and decreased gradually with further increase in the whisker content, while the percentage of elongation at break decreased with initial increase in the whisker content, and leveled off when the whisker content was greater than or equal to 2.96 wt%.

Chang et al. (2010) studied the mechanical properties of chitosan nanoparticle CNP/TPS nanocomposites. When the CNP content increased from 0 to 6 wt%, the tensile strength increased from 2.8 to 10.8 MPa, while the elongation at break decreased from 59 to 23 %. This was attributed to the interfacial interaction between chitosan nanoparticles and the glycerol plasticized starch matrix because of the similar polysaccharide structures of CNP and starch. At CNP concentration of 8 wt%, the tensile strength showed deterioration, possibly due to the agglomeration of CNP. Thus CNP nanoparticles were also shown to have an optimum concentration in TPS, above which their mechanical properties decreased.

2.1.2 Chitosan as Matrix

Li et al. (2009) prepared bio-based nanocomposite films using cellulose whiskers as the reinforcing phase and chitosan as the matrix. The results showed that the whisker content had a profound effect on the mechanical properties of the composites as shown in Fig. 4. The tensile strength of the composite films in the dry state increased from 85 to 120 MPa with increasing filler content from 0 to 20 wt%, whereas the elongation at break decreased from 20 to 6 %. This indicated that the incorporation of cellulose whiskers into the chitosan matrix resulted in strong interactions between filler and matrix, which restricted the motion of the matrix. In the wet state, the tensile strength of the composite films increased from 9.9 to 17.3 MPa with an increase of whisker content from 0 to 15 wt%, and then decreased with further increasing filler content. The composites containing more than 20 wt% cellulose whiskers exhibited a decrease in both the tensile strength and elongation at break in both dry and wet state due to the microphase separation and the stiffness of cellulose whiskers. Thus optimum filler content was found to exist for cellulose whiskers in chitosan matrix.

Similar increases in mechanical properties have been reported for cellulose nanofiber reinforced chitosan films by Gallstedt and Hedenqvist (2006) and Nordqvist et al. (2007).

Khan et al. (2012) reported an optimum content of 5 wt% of CNC in chitosan matrix. The nanocomposites showed a 25 % increase in tensile strength and an 87 % increase in tensile modulus at this CNC content.

Fernandes et al. (2009) prepared nanocomposite films based on different chitosan matrices (two chitosans with different DPs and one water-soluble

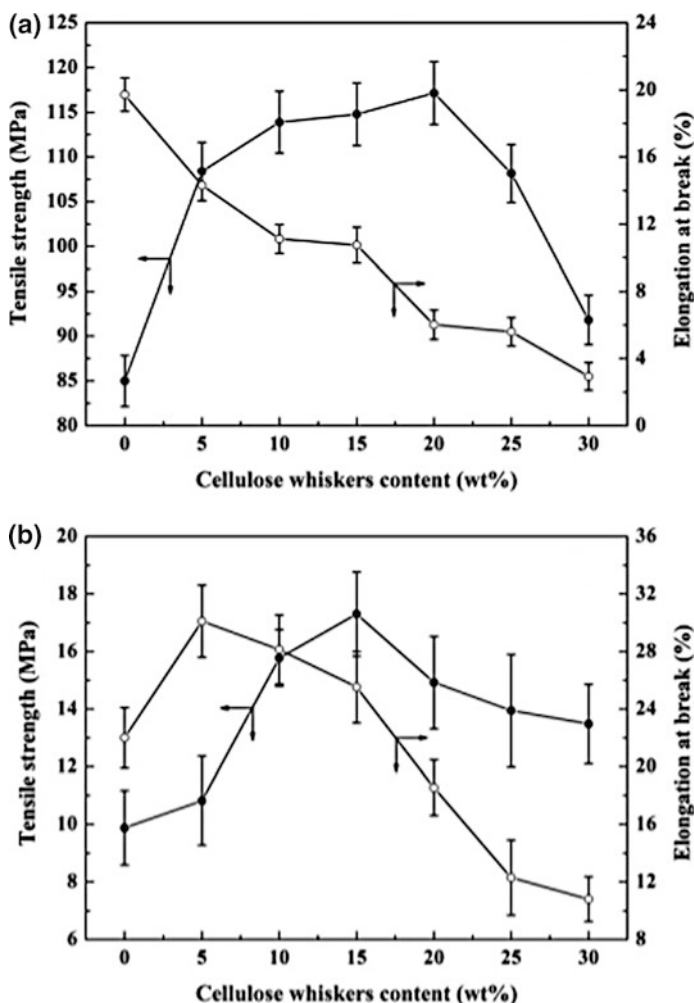


Fig. 4 Dependence of the cellulose whisker content on the tensile strength (●) and elongation at break (○) of the chitosan films in dry (a) and wet (b) states (Lee et al. 2009)

derivative) and BC nanofibrils. The incorporation of nanofibrils resulted in considerable increase in the strength and modulus of the nanocomposite films. Additionally, the presence of nanofibrils caused a significant decrease in the elongation at break which was more pronounced for higher cellulose contents. The superior mechanical properties of the films compared with those of the neat matrix confirmed the good interfacial adhesion and the strong interactions between the two components. These results were explained by the inherent morphology of BC with its nanofibrillar network and the similar structures of the two polysaccharides.

The use of BC nanofibers reinforced chitosan has also been explored for use in medical applications. Ciechanska (2004) reported improved mechanical properties and moisture holding capacity of these nanocomposites.

2.2 Starch

After cellulose, starch is the second most abundant biomass material. It is found in many plants' roots, stalks, crop seeds, and staple crops such as rice, corn, wheat, tapioca, and potato. It is a semicrystalline biopolymer. Because of its versatile properties and high availability at low price, it has great potential to be used in bionanocomposites. It can be used either as SNP or starch nanocrystals (SNC) or as a matrix. The main issue is the immiscibility of starch with polymer matrices which results in processing issues and poor mechanical properties. This issue can be overcome by mixing with water or nonaqueous plasticizer (generally polyols, such as glycerol). The resulting material is called TPS and is more suitable for thermoplastic processing. However, TPS shows some drawbacks such as a strong hydrophilic character, lower T_g and melting point, poor mechanical properties (high strain to failure and low tensile strength) compared to conventional polymers and post-processing variation of the properties which reach equilibrium only after several weeks. To improve these material weaknesses, TPS is usually blended with other polymers like aliphatic polyesters. For a plasticizer content of up to 12 %, mechanical properties of TPS are similar to the anti-plasticization effect generally observed in synthetic polymers; that is, both the stress and strain at break decrease. For higher amounts of plasticizer, mechanical properties are controlled by the glass transition, which involves the molecular motions. This results in an increase in the strain at break and a decrease in both the strength and Young's modulus.

Nanocrystals extracted from starch are also used as fillers in polymer matrices. These nanoparticles not only increase the mechanical properties but also the physical properties such as permeability and fire retardancy of these composites. Unlike cellulose or chitin which exhibit needle-like nanocrystals, SNs occur as platelet-like nanoparticles. Thus starch has the versatility of being used both as a matrix and a filler.

2.2.1 Starch as Matrix

The use of CNC/MFC as filler in starch matrix has been shown to result in improvement in mechanical properties of the composites as shown in Table 3. This has been attributed to strong interfacial interactions between the cellulose crystallite surface and the starch matrix, and also to the formation of a rigid network of nanofibers connected by hydrogen bonds.

Cao et al. (2008a, b) studied the properties of plasticized starch-based nanocomposites reinforced with flax CNCs. The CNC content had a profound effect on

Table 3 Tensile properties of (untreated) cellulose CNC/MCF reinforced biopolymer composites

Matrix/fiber content (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Strain (%)	References
TPS/15	6.8 (yield)	220	–	Kaushik et al. (2010)
TPS/40	6.9	480	13.6	Lu et al. (2006)
TPS/10	–	271	–	Alemdar and Sain (2008)
TPS/30	11.9	498	7.2	Cao et al. (2008a, b)
TPS/39	–	6000	–	Dufresne et al. (2000)
TPS/25	12	6000	1	Anglès and Dufresne (2001)
TPS/25	10.3	7200	1	Mathew et al. (2008)
TPS/30	3.1	10,000	0.45	Lu et al. (2005)
TPS/10.3	–	9000	3.3	Orts et al. (2005)
TPS/10	1.75	2450	–	Alemdar and Sain (2008)
TPS/30	2.95	2580	0.1	Cao et al. (2008a, b)
TPS/10	1.95	–	2.1	Chen et al. (2009)
TPS/20	1.4	1600	1.8	Teixeira et al. (2009)
PLA/?	30	–	2.5	Qu et al. (2010)
PLA/5	58	2600	2.8	Mathew et al. (2006)
PLA/5	71.1	2900	–	Wang and Sain (2007)
PLA/3–20	55–75	4700	1.6–3	Iwatake et al. (2008)
PLA/3–20	61–71	3800–5700	1.7–2.7	Suryanegara et al. (2009)
PLA/0–90	35–180	5000–13,000	1–3.3	Nakagaito et al. (2009)
PLA/5	71	3600	2.7	Jonoobi et al. (2010)
PCL/0–12	18–25	400–600	–	Siqueira et al. (2009)
Chitosan/20	120	–	6	Li et al. (2009)
PVA/5	82	400	–	Cho and Park (2011)
PVA/90	84	7.7	2	Leitner et al. (2007)
PVA/10	178	1010	–	Bhatnagar and Sain (2005)
PVA/10	108	6600	2.1	Wang and Sain (2007)
PVA/50	145.1	8490	–	Bruce et al. (2005)
PVA/15	62	5200	–	Lu et al. (2008)
PVA/10	160	8000	4.1	Kakroodi et al. (2014)
NR/10	4	17	–	Bras et al. (2010)

the mechanical properties. The tensile strength increased from 3.9 to 11.9 MPa with increasing filler content from 0 to 30 wt%, Young's modulus increased significantly from 31.9 to 498.2 MPa, and the elongation at break decreased from 68.2 to 7.2 %. This was attributed to the reinforcement effect of the homogeneously dispersed high-performance nanocrystals in the TPS matrix and the strong hydrogen bonding interaction between nanocrystals and TPS molecules.

Orts et al. (2005) studied the properties of cellulose microfibrils obtained from different sources of cellulose fibers added at low concentrations (2–10 % w/w) to starch gels and films as reinforcing agents. Significant changes in mechanical

properties, especially maximum load and tensile strength, were observed for fibrils derived from cotton, softwood, and BC. For extruded starch plastics, the addition of cotton-derived microfibrils at 10.3 wt% increased Young's modulus by fivefold relative to a control sample with no cellulose reinforcement. Addition of microfibrils did not always change mechanical properties in a predictable direction. Whereas tensile strength and modulus were shown to increase following the addition of microfibrils to starch thermoplastic and a cast latex film, these parameters decreased when microfibrils were added to a starch-pectin blend, implying that complex interactions are involved in the application of these reinforcing agents.

Kaushik et al. (2010) showed that a 15 % cellulose nanofibers content in TPS matrix resulted in a considerable increase in properties over neat TPS. Yield strength increased from 4.7 to 6.8 MPa, whereas tensile modulus registered an increase from 78 to 220 MPa. This increase was again attributed to the formation of a rigid network of nanofibers connected by hydrogen bonds and also by mutual entanglements.

Mathew et al. (2008) studied properties of tunicin whiskers reinforced TPS nanocomposites at different relative humidity (RH) levels. The nanocomposites exhibited good mechanical strength due to the strong interaction between tunicin whiskers, TPS matrix, plasticizer (sorbitol) and water, and due to the ability of the cellulose filler to form a rigid three-dimensional network. An even distribution of whiskers (as determined by SEM) and plasticizer in the matrix contributed to the mechanical performance. For all RH levels, the modulus increased gradually with filler load, and above 5 % whiskers, a significant improvement was observed. The tensile strength and Young's modulus were high at lower RH levels, and elongation at break remained constant, irrespective of RH and filler content.

Dufresne et al. (2000) reported a 350 % increase in tensile modulus of MFC/starch nanocomposites at 50 wt% cellulose content compared to neat starch. However, at high humidity levels (75 % RH), the reinforcing effect was clearly diminished. This was attributed to the hydrophilic nature of both the starch and the cellulose, which resulted in the plasticization of starch and weakening of cellulose/starch interfacial adhesion. On the other hand, the addition of cellulose to starch resulted in a decrease of both water uptake at equilibrium and the water diffusion coefficient.

Alemdar and Sain (2008) investigated the properties of wheat straw nanofiber/TPS composites. At 10 % nanofiber loading, the tensile modulus increased from 111 to 277 MPa.

In a study on BC/TPS composites, Martins et al. (2009) exhibited superior mechanical properties of BC fillers compared to vegetable cellulose fillers. The Young modulus increased by 30 and 17 fold (with 5 % fibers), while the elongation at break was reduced from 144 % to 24 % and 48 % with increasing fiber content, respectively, for composites with bacterial and vegetable cellulose. SEM micrographs of fractured samples also corroborated these findings as shown in Fig. 5, which provided evidence of the strong interfacial adhesion between the cellulose fibers and the TPS matrix, as shown by their good dispersion within the matrix, without noticeable aggregates. It was observed that the characteristic nano- and

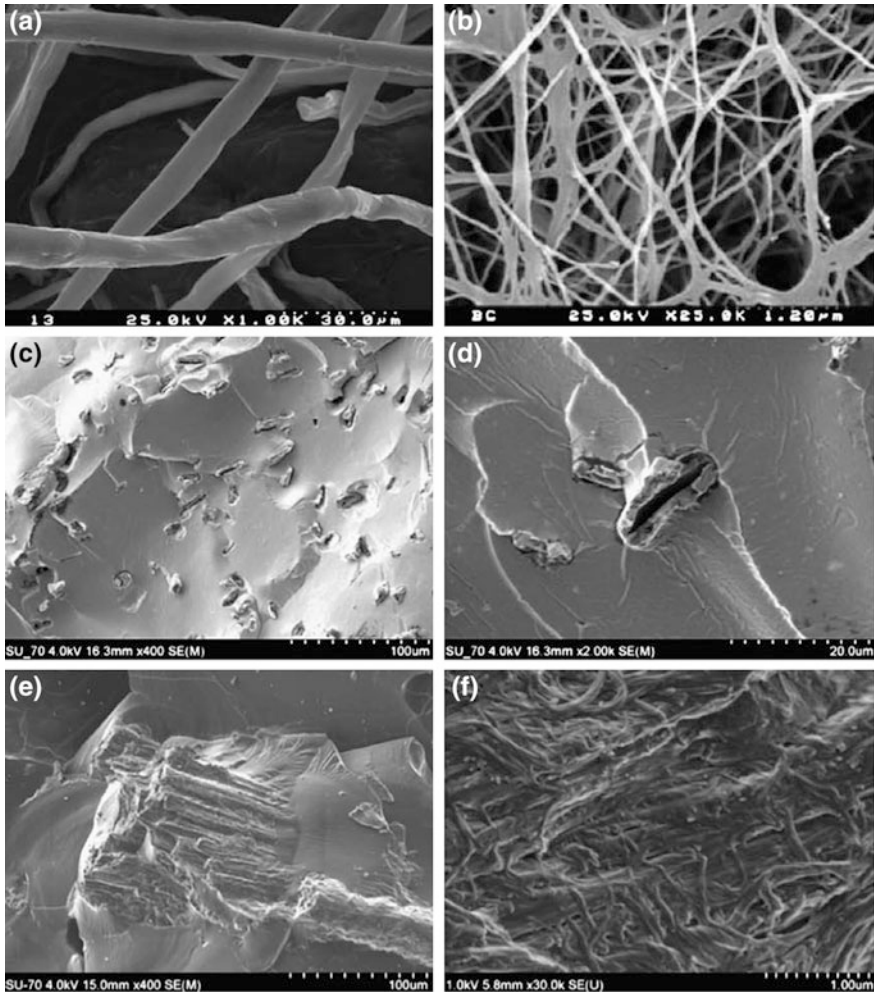


Fig. 5 SEM micrograph of vegetable cellulose (VC) and bacterial cellulose (BC), and the fractured surface of TPS filled with VC and BC: **a** neat VC, **b** neat BC, **c** and **d** TPS/VC composites (5 wt%); **e** and **f** TPS/BC composites (5 wt%) (Martins et al. 2009)

microfibril network of BC was maintained and totally impregnated with TPS. These results corroborated the superior mechanical properties of the BC-based composites compared to their vegetable cellulose counterparts.

Wan et al. (2009) studied BC reinforced TPS composites. At 22 wt% filler loading, the nanocomposites showed 137 % increase in tensile strength and 132 % increase in tensile modulus compared to neat BC. Thus BC was shown to be a good filler in TPS.

In a novel application of BC, Grande et al. (2009) added starch to the culture medium of cellulose-producing bacteria in order to introduce the granules into the forming network of cellulose which allowed the preservation of the natural ordered structure of cellulose nanofibers. Microscopic analysis revealed that starch acted as a matrix which filled the voids in the BC network. Using MCF as reinforcement, the nanocomposites showed considerable improvement in mechanical properties.

Lu et al. (2006) studied ramie CNC reinforced TPS composites. The results indicated that the synergistic interactions between fillers and between filler and TPS matrix play a key role in reinforcing the composites. The nanocomposites, conditioned at 50 % RH, showed increases in both tensile strength and Young's modulus from 2.8 MPa for TPS film to 6.9 MPa and from 56 MPa for TPS film to 480 MPa, respectively, with increasing nanocrystal content from 0 to 40 wt%.

The effects of various surfactants on the properties of starch-based nanocomposites have also been studied and most of the studies point to their positive effects on mechanical properties of nanocomposites. For example, glyceryl monostearate (GMS) was used by Mondragon et al. (2008) in MFC/TPS, which resulted in improvement in mechanical properties. Similar improvements in properties were reported by Takagi and Asano (2008a, b) for CNC/esterified starch nanocomposites.

2.2.2 Starch as Filler

SNs have been successfully used as filler in biopolymer matrices such as waterborne polyurethane (Chang et al. 2009; Chen et al. 2008a, b), starch (Angellier et al. 2006a, b; Vigié et al. 2007; Garci et al. 2009, 2011), pullulan (Kristo and Biliaderis 2007), PLA (Yu et al. 2008), PVA (Chen et al. 2008a, b), PCL (Habibi and Dufesne 2008), poly(butylene succinate) (PBS) (Lin et al. 2011a, b), and soy protein isolate (SPI) (Zheng et al. 2009), and the results have been very encouraging. Another advantage of using SNs is that they possess a highly reactive surface covered with hydroxyl groups, which provides the possibility of modification via chemical reaction. As discussed earlier, these treatments can be used to improve the properties of these composites.

Lin et al. (2011) compared the mechanical properties of PBS nanocomposites reinforced by CNCs and SNs. The results are shown in Fig. 6. With the addition of just 2 wt% CNC, the tensile strength of the nanocomposites improved from 26.2 MPa for the neat PBS sheet to 29.0 MPa, with a simultaneous increase in elongation to break from 6.33 to 7.43 %. When the CNC loading level exceeded 2 wt%, the tensile strength and elongation to break gradually decreased, whereas the Young's modulus of the nanocomposites sharply increased. In the case of PBS/SN nanocomposites, the addition of 5 wt% SN resulted in simultaneous increase in the strength, toughness, and rigidity of the nanocomposites. For SN content of greater than 5 wt%, the Young's modulus of these nanocomposites gradually increased at the expense of tensile strength and elongation to break, similar to the PBS/CNC nanocomposites. The greater improvements in PBS/SN composites compared to

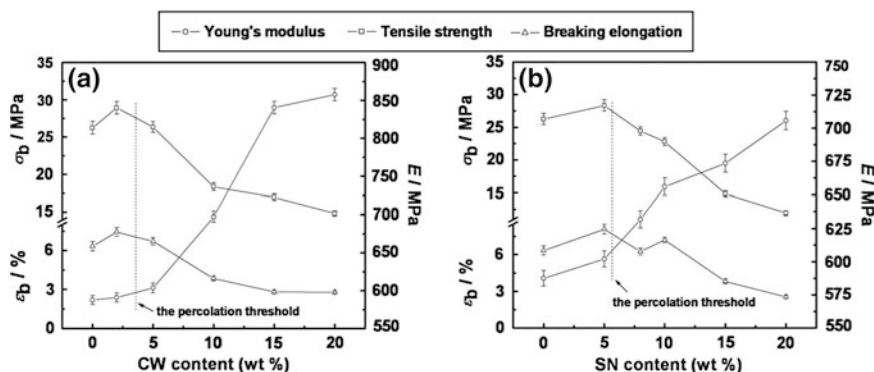


Fig. 6 Effects of CW and SN content on tensile strength, elongation at break and Young's modulus for the PBS/CW (a) and PBS/SN (b) nanocomposites (Lin et al. 2011)

PBS/CNC composites were ascribed to the percolation phenomenon as discussed earlier. Since the percolation threshold is inversely proportional to the aspect ratio of the nanofillers, it was calculated to be 3.6 wt% for rod-like CNC and 5.5 % for platelet-like SN, as shown in Fig. 6.

Habibi and Dufresne (2008) also compared the mechanical properties of CNC and SN reinforced nanocomposites. However, the matrix they used was PCL and both nanocrystals were grafted with PCL to improve compatibility with the matrix. The addition of unmodified CNC or SN in PCL resulted in improvement in their tensile modulus but, at the same time, reduced drastically all the other mechanical properties, especially the elongation at break. The elongation at break decreased from 637 % down to 8.0 % and 2.3 % at 20 wt% of cellulose and SNs, respectively. The addition of PCL-grafted CNC and SN nanocrystals resulted in continuous increase in the tensile modulus of composites, whereas the decrease in both the strength and the elongation at break was much more gradual. The elongation at break decreased from 637 % down to 420 % and 83 % at 20 wt% of PCL-grafted cellulose and SNs, respectively. This behavior was ascribed to the better dispersion of the fillers within the polymeric matrix, induced by the grafting of PCL chains on the surface of the nanoparticles. The possibility of chain entanglements between the grafted chains and the PCL chains from the matrix could also play an important role in this phenomenon.

SNs can be more efficient reinforcing agents than the native starch from which they are extracted. This was demonstrated for native pea starch (NPS)/PVA and pea starch nanocrystals (PSN)/PVA nanocomposites by Chen et al. (2008a, b). The PSN/PVA nanocomposites exhibited smoother fracture surfaces, higher light transmittance, higher tensile strength and elongation at break, and lower moisture uptake than the corresponding NPS/PVA nanocomposites. For example, the values of tensile strength and elongation at break for PSN/PVA composites containing 10 wt% of PSN were 40 MPa and 734 %, while those of the corresponding NPS/PVA composites were 35 MPa and 579 %, respectively. This was attributed to the

smaller size of PSN compared to NPS which dispersed more homogeneously in PVA matrix, resulting in stronger interactions with PVA.

All-starch nanocomposites made of SN in a matrix of waxy maize starch plasticized with sorbitol were studied by Viguie' et al. (2007). Adding SNs resulted in an increase of both the tensile modulus and strength and in a decrease of the strain at break regardless of the plasticizer content. However, highly plasticized films (35 wt% sorbitol) showed a higher relative reinforcing effect. For instance, the Young's modulus and the strength of the composites reinforced with 15 wt% SNs increased by a factor of 7 and 12, respectively, when plasticized with 35 wt% sorbitol, and only by a factor 2.7 and 4.2, respectively, when plasticized with 25 wt% sorbitol.

Similar to their use as a matrix, the reinforcing effect of SNs is generally ascribed to the formation of a hydrogen bonded percolating filler network above a given starch content corresponding to the percolation threshold. This threshold has been reported to be 10 % for natural rubber (NR) matrix (Angellier et al. 2005a). It was shown that with a content of up to 20 wt%, SN presented the advantage of effectively reinforcing the NR without significantly decreasing the elongation at break of the material. For example, the elongation at break decreased slightly from 303 to 277 %, whereas the strength increased sharply from 77.1 to 229.5 MPa at 20 wt% SN filler (Angellier et al. 2005b).

2.3 Cellulose

Cellulose nanofibers and nanoparticles have many characteristics which make them suitable for use as reinforcements in composites. These include high aspect ratio, low density, outstanding mechanical properties, and a reactive surface of hydroxyl side groups that facilitates grafting chemical species to achieve different surface properties (surface functionalization). Fillers with a high aspect ratio give the best reinforcing effect. Favier (1995) showed that tunicin whiskers with aspect ratio of 67 had greater effect on modulus increase than bacterial (aspect ratio 60) and Avidel (aspect ratio 10) whiskers.

Studies done by Kvien and Oksman (2007) and Gindl and Keckes (2007) have shown that CNCs have similar reinforcing effect on polymer matrices as synthetic fibers—they have optimum properties in the direction of alignment.

The mechanical properties of CNC reinforced composites have been shown to be dependent on the following factors (Moon et al. 2011):

- (a) the CNC and matrix material properties,
- (b) the degree of CNC in-plane orientation,
- (c) the density of CNC–CNC contacting points within the CNC network,
- (d) interfacial properties, either CNC–CNC and/or CNC–matrix,
- (e) the CNC volume fraction,
- (f) CNC morphology/size, and
- (g) moisture content.

Factors b, d, and f are so crucial that they have been considered to be the main reason for the considerably lower tensile properties of CNC composites than those theoretically predicted. Because of low density of CNC, the specific strength and specific modulus of CNC-based composites becomes comparable to that of metals, ceramics, and conventional composites. This makes CNC composites a suitable material to be considered for application in automotive and aerospace industry.

However, there are some limitations to the use of nanocellulose as reinforcement in polymer matrices, as pointed out by Lee et al. (2014). They studied data on tensile properties of BC and CNC reinforced polymer nanocomposites reported in literature and compared with the tensile properties of the benchmark matrix PLLA. They found that only 20 % of the nanocomposites reported in literature exceeded the tensile properties of PLLA. Moreover, a nanocellulose loading of greater than 30 vol% is required to produce cellulose reinforced polymer nanocomposites with tensile properties exceeding those of PLLA, indicating that low nanofibre content does not lead to dramatic property improvements in nanocellulose reinforced polymer composites. Whilst both CNC and BC serve as excellent nanoreinforcement for the production of high-performance nanocomposites, it was observed that BC outperforms CNC as reinforcement. Tensile modulus and strength values of 21 GPa and 320 MPa, respectively, were obtained for random-in-the-plane BC reinforced epoxy composites at 60 vol% BC, the highest values reported so far for cellulose reinforced nanocomposites.

All-cellulose nanocomposites (cellulose nanofillers in cellulose matrix) are an emerging and interesting class of nanocomposites. Shakeri et al. (2011) manufactured all-cellulose nanocomposite films consisting of dissolved cellulose reinforced with undissolved cellulose crystallites, using partial dissolution of MFC cellulose in ionic solution and subsequent film casting. The randomly oriented nanocrystallite reinforced films were transparent and of high strength and stiffness with regard to comparable cellulosic materials. This composite exhibited a good interface between the fibers and the surrounding matrix from the selectively dissolved/resolidified MFC-fibril surfaces, which resulted in excellent bonding, good mechanical and thermal performances, and optical transparency.

Surface functionalization of CNCs allows better dispersion in the polymer matrix and improves fiber/matrix interfacial bond strength, overcoming two main issues with the nanoreinforcements. This gives cellulose nanoreinforcements an edge over other nanoreinforcements. It is no wonder, then, that cellulose reinforced nanocomposite find wide range of applications in automotive, construction, packaging, display, water treatment, and medical fields. They are also the most widely studied of all the nanobiocomposites. Table 3 lists the tensile properties of some selected composites. The table is not comprehensive, but is intended to show representative values of cellulose nanocomposites with different biodegradable polymer matrices. Although these values point toward a great potential of these composites, they do not represent a competitive advantage over existing materials such as cellophane (Newman and Staiger 2008).

The various surfactants/treatments use include, but are not limited to, corona or plasma discharge, surface derivatization, graft copolymerization, acetylation,

silylation, coupling agents, and grafting. The details of these treatments can be found elsewhere in this book. We shall concentrate on the applications of these processes and their effects on cellulose-based nanocomposites.

The most commonly used matrices with cellulose nanoreinforcement are PLA, PVA, PCL, and NR. We shall now discuss the mechanical properties of a selection of such composites.

2.3.1 Poly(lactic acid) PLA

Apart from its biodegradability, the most attractive feature of PLA is its similar properties to commodity plastics such as polypropylene. Main disadvantages of PLA are its brittleness, low thermal stability, relatively poor barrier properties, and high price. Blending and copolymerization with other polymer are used to overcome these issues.

Jonoobi et al. (2010) studied mechanical properties of CNF reinforced PLA composites. The tensile strength and modulus were improved with increased nanofiber contents. The modulus of the PLA was increased from 2.9 to 3.6 GPa with the addition of 5 wt% nanofibers, a 24 % increase. Similarly, a 21 % increase in tensile strength was observed for nanocomposites compared to neat PLA. On the other hand, strain to failure of nanocomposites was decreased with increase in nanofiber content. Classical models of Halpin–Tsai and Krenchel were used to compare the predicted theoretical data with the experimental data. It was found that experimental data were nearer the predicted value of Krenchel than Halpin–Tsai, which was a confirmation of the random distribution of nanofibers in the matrix, as hypothesized by Krenchel, rather than aligned in longitudinal direction, as hypothesized by Halpin–Tsai.

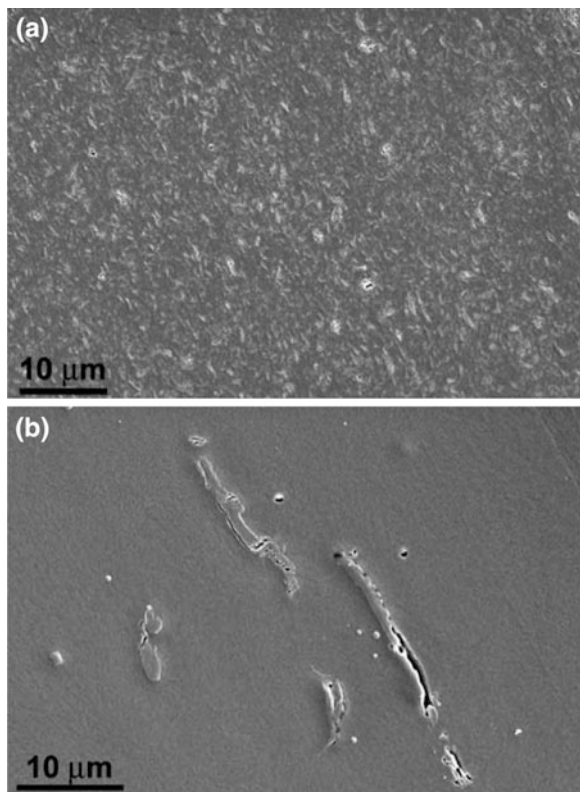
Bondesen and Oksman (2007) studied the feasibility of using PVA as compatibilizer to improve the dispersion of cellulose whiskers in PLA matrix. The hydroxyl groups on partial hydrolyzed PVA are expected to interact with the hydrophilic surfaces of the cellulose and the residual vinyl acetate groups with the hydrophobic PLA. Two feeding methods were used and evaluated: dry mixing with PLA prior to extrusion or pumping as suspension directly into the extruder. Due to immiscibility of the polymers, phase separation occurred with a continuous PLA phase and a discontinuous PVA phase. The whiskers were primarily located in the PVA phase and only a small amount was located in the PLA phase. This inadequate dispersion of whiskers in the PLA phase was probably the reason why no improvements in thermal properties were observed for the nanocomposites. The relatively small improvements in tensile properties of the nanocomposites also indicated that it was principally the PVA phase that was reinforced with whiskers rather than the PLA phase.

Oksman et al. (2006) studied a new processing technique for manufacturing CNC/PLA nanocomposites. MFC was treated with *N,N*-dimethylacetamide (DMAc) containing lithium chloride (LiCl) in order to swell the CNC and partly separate the cellulose whiskers. It was found that the extrusion process using liquid

feeding of the CNC suspension is a promising way to produce cellulose nanocomposites. However, the mechanical results did not show improvements as expected when compared with pure PLA. A possible explanation given for such behavior was the combination of used additives and the high processing temperature. It was concluded that DMAc/LiCl is not suitable as swelling/separation agent for CNC if high temperature processing is used. Similarly, improvements in mechanical properties have been reported for CNC/PLA nanocomposites by Okobu et al. (2009) and Iwatake et al. (2008). As a result of uniform distribution, the Young's modulus and tensile strength of PLA increased by 40 and 25 %, respectively, without a reduction in yield strain at a fiber content of 10 wt%.

Petersson and Oksman (2006) compared the properties of PLA-based nanocomposites made of CNC and nonbiodegradable layered silicate bentonite. At 5 wt % loading, there was more evidence of agglomeration in CNC/PLA composites than bentonite/PLA composites, as shown in Fig. 7. The PLA/bentonite nanocomposite showed a 53 % increase in tensile modulus and a 47 % increase in the yield strength compared to neat PLA. The PLA/CNC system on the other hand showed no increase in tensile modulus and only a 12 % increase in yield strength compared to neat PLA. These results were lower than expected. Two factors were ascribed for

Fig. 7 SEM of the nanocomposites, **a** bentonite/PLA, **b** CNC/PLA (Petersson and Oksman 2006)



this discrepancy. First, the bentonite added to the PLA/bentonite material had theoretically twice the surface area than CNC. A larger surface area allowed the nanoreinforcement to interact with a larger amount of polymer chains and thereby having a larger effect on the mechanical properties. Secondly, the bentonite clay is organically modified to be compatible with polymers like PLA. Good interaction between bentonite and PLA allowed for good stress transfer to take place in the composite which gave rise to large improvements in the mechanical properties of bentonite/PLA. Authors concluded that better exfoliation of cellulose whiskers within the PLA matrix is expected to result in further improvements in properties of their composites.

The agglomeration of CNC in PLA was also reported by Haafiz et al. (2013). While there was some improvement in tensile modulus of nanocomposites at 5 wt% of CNC loading, both the tensile strength and the strain to failure showed gradual decrease with increase in CNC loading. This was attributed to agglomeration of CNC which resulted in poor interfacial adhesion between the CNC and the matrix. This was also confirmed by the SEM micrographs of the fractured surfaces.

2.3.2 Poly(vinyl alcohol) PVA

PVA is attractive as matrix because it is water soluble, has excellent chemical resistance, and is biocompatible and biodegradable. PVA has been studied in terms of its biomedical applications, like tissue reconstruction and replacement, cell entrapment and drug delivery, soft contact lens materials, and wound covering bandages for burn victims (Siro and Plackett 2010).

Leitner et al. (2007) reported a gradual increase in tensile properties of CNC reinforced PVA composites. At a cellulose content of 50 wt%, the tensile modulus of PVA increased by a factor of 20 and the tensile strength increased by a factor of 3.5. Both properties showed further improvements at cellulose contents of 70 and 90 wt% respectively. Similarly, Bruce et al. (2005) reported approximately five times higher tensile strength for PVA containing 50 wt% MFC when compared to the neat polymer.

In another study Bhatnagar and Sain (2005) made nanocomposites containing 10 % cellulose nanofibers obtained from various sources, such as flax bast fibers, hemp fibers, kraft pulp, and rutabaga. There was noticeable improvement in tensile properties with tensile modulus showing a four to five times improvement over neat PVA. Fortunati et al. (2012) reported that a 5 wt% cellulose content proved ideal to promote a direct mechanical interaction between the PVA and CNC. Zimmerman et al. (2004) reported up to three times higher tensile modulus and up to five times higher tensile strength containing 20 wt% MCF in PVA. Encouraging results have also been reported for BC/PVA nanocomposites for potential applications as medical devices by Wan et al. (2006) and Millon and Wan (2006).

Kakroodi et al. (2014) also reported significant improvements in tensile properties of PVA reinforced with cellulose nanofibers extracted from aloe vera rind. Their results showed that incorporation of even small amounts of nanofibers (as low

as 2 wt%) had significant effects on both the modulus and strength of PVA. Tensile modulus and strength of PVA increased by 32 and 63 %, respectively, after adding 2 wt% of cellulose nanofibers. Samples with higher concentrations of nanofibers also showed improved mechanical properties due to a high level of interfacial adhesion and dispersion of fibers in the PVA matrix. Tensile modulus increased by 68 % at 7 wt% and by 88 % at 10 wt% of nanofibers. Similarly, tensile strength increased by 101 % at 7 wt% and by 125 % at 10 wt% of nanofibers. The most remarkable effect was on elongation at break of the composites, which decreased from 165 % for neat PVA to 4.1 % for composites at 10 wt% of nanofibers.

2.3.3 Poly(caprolactone) PCL

PCL is an oil-derived biodegradable, semicrystalline polymer. Among its good properties for use as matrix are good water resistance, low melting point, low viscosity, good processability, and high strain to failure. Its main disadvantages are low tensile strength and poor dispersion of cellulose nanoreinforcement due to its hydrophobic nature. Various surface treatments have been used to improve fiber/matrix compatibility of which grafting is the most popular method. Lonnberg et al. (2008) grafted MCF and Habibi et al. (2008) grafted CNC with different molecular weights of PCL, whereas Sequiera et al. (2009) grafted nanocellulose with N-octadecyl isocyanate for this purpose. All of these studies reported improvements in fiber/matrix adhesion following the treatments.

2.3.4 Natural Rubber

NR is a biodegradable material which has good mechanical properties and is an ideal matrix material for use in eco-friendly composites (Thakur et al. 2014a). The addition of the filler usually results in the improvement of its stiffness and hardness, and also of the resistance to abrasion, tear, cutting, and rupture. Traditionally, carbon black and silica have been used as the main fillers. However, cellulose nanocrystals have recently been used as filler in NR with encouraging results.

Sareena et al. (2012) used coconut shell powder (CSP) as filler in NR matrix. CSP was also subjected to alkalization treatment to improve particle/matrix adhesion. The optimum tensile strength was found at 10 parts per hundred (phr) of rubber CSP composites which was attributed to smaller particle size and uniform dispersion of filler in NR compounds. At more than 10 phr, the weak interaction and bonding between the filler particles and the NR matrix was responsible for the deterioration of tensile strength. Alkalized CSP composites exhibited improved tensile strength. Young's modulus and hardness of alkalized and non-alkalized CSP composites showed gradual improvement with increase in filler loading which was attributed to the stiffening effect of the filler particles and their proper dispersion in the matrix.

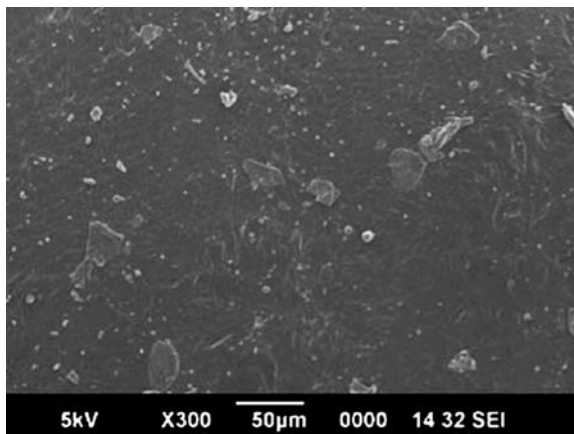
Bras et al. (2010) studied properties of bagasse CNC reinforced NR composites. Both the Young's modulus and the tensile strength significantly increased upon whisker addition to rubber while the strain at break decreased. The maximum increase of strength and modulus was 374 and 530 %, respectively, at 10 wt% of whiskers. This high reinforcing effect was ascribed to the mechanical percolation phenomenon of cellulose whiskers which forms a stiff continuous network of cellulosic nanoparticles linked through hydrogen bonding. As explained earlier, it strongly depends on the aspect ratio of the rod-like reinforcing particles and therefore on the origin of cellulose. Authors also compared the performance of bagasse whiskers as reinforcing agents in NR matrix to other nanoparticles isolated from different sources (starch, date palm tree, and Capim Dourado) reported by other authors. Bagasse nanocrystals had the lowest aspect ratio compared to the other whiskers isolated from the other sources which could be the reason for lower tensile properties of bagasse NR nanocomposites.

Similar improvements in mechanical properties of nanocellulose/NR and nanolignin/NR composites have been reported by Favier et al. (1995), Hajji et al. (1996), Abraham et al. (2007) and Thakur et al. (2014b). Due to the uniform dispersion of the nanocellulose in rubber latex, the composites showed improved stiffness and strength without any loss of its elastomeric nature, as shown in SEM micrograph of Fig. 8. The research on nanocellulose/NR composites is an emerging field and more work needs to be done in this area.

2.3.5 Epoxidized Vegetable Oils

Epoxidized vegetable oil-based bioresins are another option for making eco-friendly nanocomposites. The three most widely used oils for this purpose are soybean, canola, and linseed oils. However, the fact that these oils are a vital

Fig. 8 SEM micrograph showing good dispersion of nanocellulose whiskers in natural rubber latex (Abraham et al. 2007)



ingredient of food items consumed throughout the world is a major drawback and a strong lobby exists against the use of these oils for nonfood applications.

2.4 The Effects of Surface Treatments/Surfactants/Additives

Fukuzumi et al. (2009) reported the positive effect of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation treatment on softwood and hardwood nanofibrils in PVA matrix. Both the tensile strength and elastic modulus of PVA film were remarkably improved by 20 % nanofibrils addition. Atomic force microscopy confirmed the homogenous dispersion of nanofibrils in the matrix.

Xaio et al. (2012) grafted MFC with L-lactic acid oligomers (g-MC) in PLA matrix. The grafting resulted in improved compatibility between fibers and the matrix, and this was manifested in improved tensile properties of nanocomposites. The tensile strength increased from 30 MPa for non-grafted fibers to 70 MPa for grafted fibers at 30 wt% fiber content. Similarly, strain to failure increased from 0.8 % for non-grafted fibers to 3.2 % for grafted fibers.

The positive effects of grafting CNC with n-octadecyl isocyanate (ICN) on their interaction with PLA matrix were reported by Espino-Pérez et al. (2013). The incorporation of untreated CNC in PLA resulted in decrease in tensile properties. However, the incorporation of CNC-ICN in PLA showed improvements on tensile properties. The best results were achieved at 2.5 wt% CNC-ICN.

Lee et al. (2009) studied the effect of surface functionalization of BC nanofibrils and their use as reinforcement in polylactide (PLLA) matrix. BC was functionalized with various organic acids via an esterification reaction which rendered the otherwise hydrophilic BC hydrophobic and resulted in better compatibility between PLLA and BC. A direct wetting method, allowing the determination of the contact angle of polymer droplets on a single BC nanofiber, was developed to quantify the interfacial adhesion between PLLA and functionalized BC. It was found that the contact angle between PLLA droplets and functionalized BC decreased with increasing chain lengths of the organic acids used to hydrophobise BC. The mechanical properties of the surface functionalized BC reinforced PLLA nanocomposites showed significant improvements compared to neat PLLA and BC reinforced PLLA (tensile modulus by 50 % and tensile strength by 15 %). The thermal degradation and viscoelastic behavior of the nanocomposites were also improved over neat PLLA. Therefore, it was concluded that PLLA nanocomposites with overall improved properties can be fabricated through the surface functionalization of BC.

Similarly Juntaro et al. (2008) studied the effects of acetone-treated sisal fibers attached with BC nanofibrils and incorporated in PLLA matrix. Acetone treatment was used to improve the adhesion of BC/sisal fibers and sisal fiber/PLLA matrix. SEM images showed marked improvement in attachment of BC on sisal fibers following the treatment, as shown in Fig. 9. The interfacial adhesion between the (modified) fibers and the PLLA matrix was quantified using single-fiber pull-out

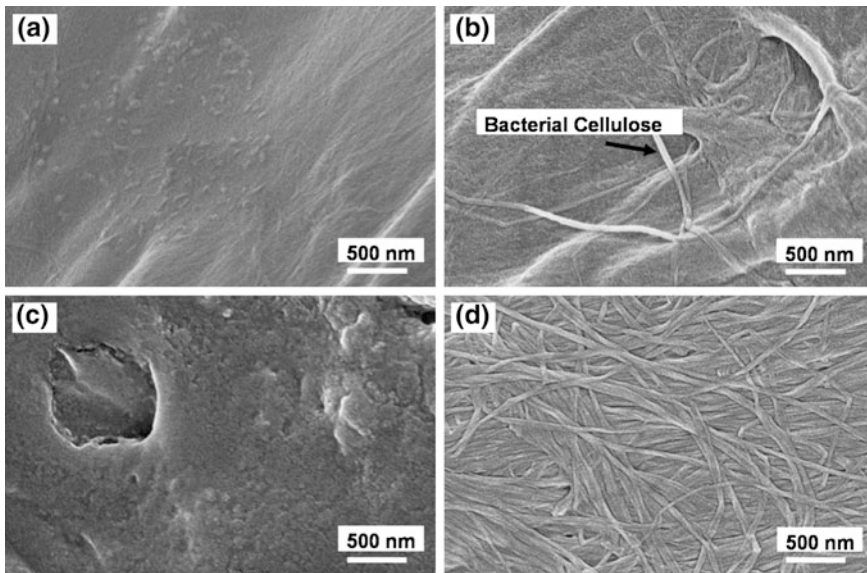


Fig. 9 SEM micrographs of sisal fiber surfaces: **a** natural sisal fiber; **b** sisal fiber after attachment with bacterial cellulose; **c** acetone-treated sisal; **d** acetone-treated sisal fiber after attachment with bacterial cellulose (Juntaro et al. 2008)

tests. The apparent interfacial shear strength of the unmodified sisal fibers was significantly improved from 12.1 to 14.6 MPa after the bacterial cellulose growth. The tensile strength and modulus of the composites also showed improvement of around 40–70 % following the growth of BC. However, the improvement was attributed more to the presence of BC rather than the acetone treatment.

3 Flexural and Impact Properties

The flexural and impact properties of eco-friendly nanocomposites have not been studied to the same extent as their tensile properties. Most of the studies done have been on cellulose nanofibers and nanoparticles-based composites. Takagi and Asano (2008a, b) studied the properties of CNFs in esterified starch at 70 wt% fiber loading. Two different processing conditions were used: vacuum-treated and extra-stirred samples. The latter method showing significantly higher flexural strength of nanocomposites. Nakahara (2008) grafted nanocellulose with either PVA or PLA, followed by dewatering and kneading with PLA. The nanocomposite exhibited high values of flexural modulus of 5.1–5.7 GPa, flexural strength of 100–105 MPa, and an impact strength of 26 J/m. Hashiba (2009) also reported high flexural strength (110 MPa) and modulus (4 GPa) of nanocellulose/PLA nanocomposites.

4 Conclusions

Eco-friendly polymer nanocomposites are exciting new materials which are finding niche in medicine, packaging, electronics, automotive, and construction industry. Their main advantages are biodegradability, renewability, and low carbon footprint. They are based on biopolymer matrices reinforced with nanofibers or nanoparticles, extracted from biopolymers. The exceptionally high tensile properties of biopolymer nanoreinforcement make them an ideal material for use as reinforcements in composites. However, there are some issues which hinder these composites from attaining their optimum properties. The two major issues are poor interfacial adhesion of reinforcements and the matrices because of noncompatibility, and poor dispersion/agglomeration of reinforcements in biopolymer matrices. At the moment a lot of research is going on in various parts of the world on overcoming these issues. Various physical and chemical treatments of reinforcements, compatibilizers, and surfactants have been used for this purpose.

It has been shown that if cellulose nanoreinforcement can be made to align in a biopolymer matrix, they exhibit optimum properties in the direction of alignment, just like in synthetic fiber composites. Chitosan is a semicrystalline biopolymer which is used both as a matrix and as nanoreinforcement in composites. The use of chitosan nanoreinforcements in biopolymer matrices results in improvement in properties of composites. However, an optimum loading limit has been observed, depending on the biopolymer matrix, above which the properties of nanocomposites start to decline. A similar optimum loading limit has been found to exist when CNCs are used as reinforcements in chitosan matrix.

Starch is another semicrystalline biopolymer which can be used both as nanoreinforcement and as a matrix in composites. When used as a matrix, starch is usually blended with plasticizer to improve its processing and mechanical properties. Studies have shown significant improvements in tensile properties of nanocomposites, whether starch is used as a reinforcement or a matrix. BC-based nanocomposites have been shown to exhibit superior properties than vegetable cellulose-based nanocomposites.

Cellulose is the most abundant biomass material and is also the most widely studied in terms of its use in nanocomposites. More importantly, CNCs exhibit optimum properties in the direction of alignment just like synthetic fibers. The most widely used biopolymer matrices with CNCs are PLA, PVA, PCL, and NR. All of these nanocomposites exhibit superior tensile properties. The use of surface treatments and surfactants has also been reported to have positive impact on the mechanical properties of these nanocomposites.

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