

Nanotechnology and its applications in lignocellulosic composites, a mini review

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Abstract. Nanotechnology has applications across most economic sectors and allows the development of new enabling science. The ability to see materials down to nanoscale dimensions and to control how materials are constructed at the nanoscale is providing the opportunity to develop new materials and products in previously unimagined ways.

This review covers the academic and industrial aspects of the preparation, characterization, material properties, crystallization behavior; melt rheology, and processing of polymer/cellulose or cellulose/cellulose nanocomposites. Cellulosic materials have a great potential as nanomaterials because they are abundant, renewable, have a nanofibrillar structure, can be made multifunctional, and self-assemble into well-defined architectures. The fibrillation of pulp fiber to obtain nano-order-unit web-like network structure, called microfibrillated cellulose, is obtained through a mechanical treatment of pulp fibers, consisting of refining and high pressure homogenizing processes. Also, nano-whisker can be used as novel reinforcement in nanocomposites; it can be obtained by acid hydrolysis from various sources such as wood, tunicin, ramie, cotton, wheat straw, bacterial cellulose, and sugar beet. The properties of nanocomposite materials depend not only on the properties of their individual parents, but also on their morphology and interfacial characteristics. Compared with plant cellulose, bacterial cellulose has found many applications in the biomedical field as tissue engineering materials due to their good biocompatibility, mechanical properties similar to those of hard and soft tissue and easy fabrication into a variety of shapes with adjustable interconnected porosity. One of the drawbacks of cellulose whiskers with polar surfaces is poor dispersibility/compatibility with nonpolar solvents or resins. Thus, their incorporation as reinforcing materials for nanocomposites has so far been largely limited to aqueous or polar systems. To overcome this problem and broaden the type of possible polymer matrices, efforts of surface modification have been made. These attempts include surfactant coating or graft copolymerization.

Keywords: *nanomaterials, nanocomposites, reinforcements, rheology and mechanical properties*

1. Introduction

1.1. Nanotechnology

Technology is the major driving factor for growth at every level of an economy. At the 1 nanometer (nm) scales and below, quantum mechanics rules, and at dimension above 100 nm classical quantum mechanics, physics, and chemistry dictate properties of matter. Between 1 and 100 nm, a hybrid exists, and interesting things can happen such as

mechanical, optical, electrical, magnetic, and a variety of other properties can behave quite differently [1]. A nanometer is a billionth of a meter, or 80 000 times thinner than human hair. So, nanometer domain covers sizes bigger than several atoms but smaller than the wavelength of visible light. Nanotechnology (based on the Greek word for dwarf) is defined as the manipulation of materials measuring 100 nm or less in at least one dimension.

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Where the physical, chemical, or biological properties are fundamentally different from those of the bulk material. By expanding our understanding and control of matter at such levels, new avenues in product development can be opened [2].

Nanotechnology can be defined as the science and engineering involved in the design, synthesis, characterization, and application of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale or one billionth of a meter [3]. Classified by nanofiller dimensionality, there are a number of types of nanocomposites. Zero-dimensional (nanoparticle), one-dimensional (nanofiber), two-dimensional (nanolayer), and three-dimensional (interpenetrating network) systems can all be imagined [4]. Also, lamellar nanocomposites can be divided into two distinct classes, intercalated and exfoliated. In intercalated nanocomposites, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have defined number(s) of polymer layers in the intralamellar space. In exfoliated nanocomposites, the number of polymer chains between the layers is almost continuously variable and the layers stand $>100 \text{ \AA}$ apart. Determining and altering how materials and their interfaces are constructed at nano- and atomic scales will provide the opportunity to develop new materials and products. Because of this ability, nanotechnology represents a major opportunity for wood and wood-based materials to improve their performance and functionality develop new generations of products, and open new market segments in the coming decades [5]. Now it is possible to ask, why nanotechnology is important.

The answer is [6]:

- a) Less space, faster, less material, and less energy.
- b) Novel properties and phenomena.
- c) Most efficient length scale for manufacturing.
- d) Intersection of living/non-living.

Polymer nanocomposites are produced by incorporating materials that have one or more dimensions on the nanometer scale ($<100 \text{ nm}$) into a polymer matrix. These nanomaterials are in the literature referred to as for example nanofillers, nanoparticles, nanoscale building blocks or nanoreinforcements. Nanocomposites have improved stiffness, strength, toughness, thermal stability, barrier properties and flame retardancy compared to the pure

polymer matrix. Nanoreinforcements are also unique in that they will not affect the clarity of the polymer matrix. Only a few percentages of these nanomaterials are normally incorporated (1–5%) into the polymer and the improvement is vast due to their large degree of surface area [7]. Because of the nanometric size effect, these composites have some unique outstanding properties with respect to their conventional microcomposite counterparts. Since the pioneering work by the Toyota group [8–10] polymer nanocomposites have attracted an increasing amount of attention.

The properties of nanocomposite materials depend not only on the properties of their individual parents, but also on their morphology and interfacial characteristics. In the particular case of polymer reinforced with rigid nanofillers, various parameters seem to be of importance in characterizing the fillers: geometrical factors such as the shape, the size, and the aspect ratio; intrinsic mechanical characteristics such as the modulus or the flexibility; surface properties such as specific surface area and surface treatment [11]. The type of polymer matrix used and the possible effects of nanofillers on its microstructure and its intrinsic properties are also essential parameters determining the composite properties. In addition, the processing conditions can affect on composite properties. To study this factor high aspect ratio nanofibers/poly (styrene co-butyl acrylate) composites were prepared with two different processing conditions. It was found that, in case of evaporated cellulose filled composites; the highest mechanical reinforcement (with a mechanical percolation phenomenon) coupled to an increase in composites thermo-mechanical stability. While in case of freeze-dried cellulose filled composites; the freeze-drying process prevents the creation of strong contacts between nanofibrils, a lower mechanical reinforcement is measured [12]. Whereas the general class of inorganic nanocomposites has enjoyed much discussion and is still a fast-growing area of research, exciting new research on bio-based nanocomposites have a greater potential because the bio-resource can be both sustainable and genetically manipulated. Wood cellulose nanofibrils have about 25% of the strength of carbon nanotubes, which are expected to be the strongest fibers that can be produced. Their potential cost, however, might be 10 to 100 times less, giving cellulose nanofibrils a unique economic advantage [5].

1.2. Nanocomposite materials

The definition of nanocomposite materials has significantly broadened in the last few years. This term now encompasses a large variety of systems combining one-, two-, and three dimensional materials with amorphous materials mixed at the nanometer scale. Natural fibers are pervasive throughout the world in plants such as grasses, reeds, stalks, and woody vegetation. They are also referred to as cellulosic fibers, related to the main chemical component cellulose, or as lignocellulosic fibers, since the fibers usually often contain a natural polyphenolic polymer, lignin, in their structure.

The use of lignocellulosic fibers derived from annually renewable resources as a reinforcing phase in polymeric matrix composites provides positive environmental benefits with respect to ultimate disposability and raw material use [13]. By comparing with inorganic fillers, the main advantages of lignocellulosics are;

- Renewable nature
- Wide variety of fillers available throughout the world
- Nonfood agricultural based economy
- Low energy consumption
- Low cost
- Low density
- High specific strength and modulus
- High sound attenuation of lignocellulosic based composites
- Relatively reactive surface, which can be used for grafting specific groups.

- The recycling by combustion of lignocellulosic filled composites is easier in comparison with inorganic fillers systems.

Therefore, the possibility of using lignocellulosic fibers as a reinforcing phase has received considerable interest. In addition, it is necessary to discuss the intrinsic nanoscale properties of wood and similar lignocellulosic materials for developing advanced nanomaterials and use nanoprocesses to modify lignocellulosic materials.

1.2.1. Structure of wood fiber

The structure of wood spans many length scales: meters for describing the whole tree, centimeters for describing structures within the tree cross section (pith, heartwood, sapwood, and bark), millimeters for describing growth rings (early wood, latewood), tens of micrometers for describing the cellular anatomy, micrometers for describing the layer structure within cell walls, tens of nanometers for describing the configuration of cellulose fibrils in a matrix of hemicellulose and lignin, and nanometers for describing the molecular structures of cellulose, hemicellulose, and lignin and their chemical interactions.

Wood fibers, the most abundant biomass resource on earth, are hollow tubes made up of cellulose embedded in a matrix of hemicellulose and lignin. Most of the cell-wall materials are located in the second layer, which consists of a helically wound framework of microfibrils (Figure 1) [14]. The most important attribute of wood is its mechanical properties, in particular its unusual ability to provide high mechanical strength and high strength-to-

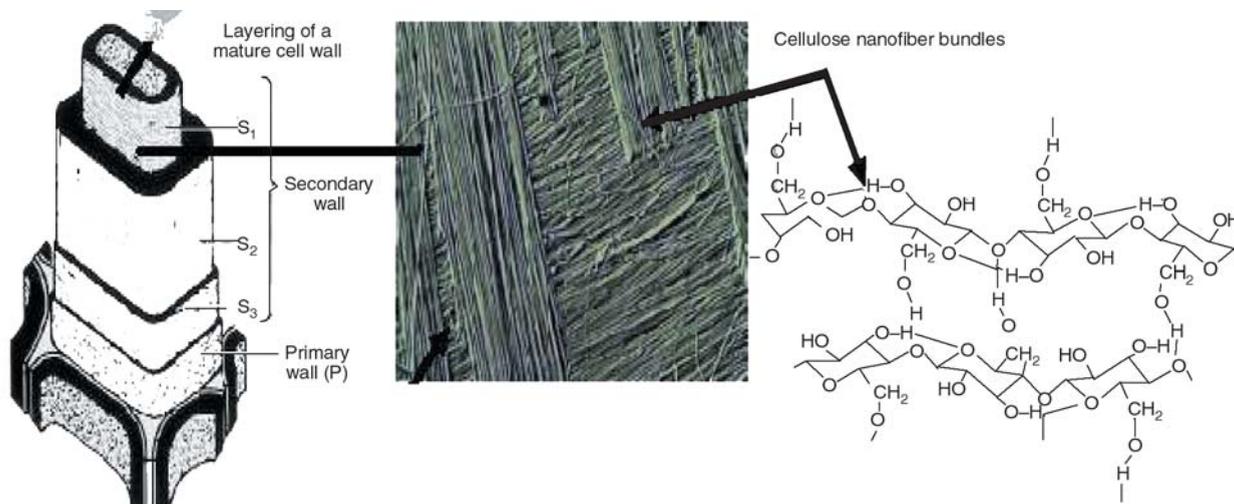


Figure 1. Microstructure of wood fiber cell wall: S_1 , S_2 , and S_3 are the inner, middle and outer layers of the secondary wall, respectively. Reproduced from; Jupiter.phys.ttu.edu/corner/1999/dec99.pdf

weight ratio while allowing for flexibility to counter large dimensional changes due to swelling and shrinking. These unique properties of wood are a direct result of its hierarchical internal structure. Microfibrils, nano-order-unit (10 nm×3.5 nm) [15] fibers that compose most fiber cell walls, consist of monocrystalline cellulose domains with cellulose chains parallel to the microfibril axis. As they are devoid of chain foldings and contain only a small number of defects, each microfibril can be considered a string of polymer whiskers having a modulus close to that of the perfect crystal of native cellulose, which is estimated to be 150 GPa, and possessing a strength of about 10 GPa [16]. Cellulose is a polydisperse linear polymer of poly- β (1,4)-D-glucose. The monomers are linked together by condensation such that glycosidic oxygen bridges join the sugar rings. In nature, cellulose chains have a degree of polymerization of approximately 10 000 glucopyranose units in wood cellulose and about 15 000 in native cellulose cotton. These cellulose chains are biosynthesized by enzymes, deposited in a continuous fashion and aggregate to form microfibrils, long threadlike bundles of molecules stabilized laterally by hydrogen bonds between hydroxyl groups and oxygen of adjacent molecules. Depending on their origin, the microfibril diameters range from about 2 to 20 nm for lengths that can reach several tens of microns. These microfibrils highly ordered (crystalline) regions alternate with less ordered (amorphous) regions [17]. Properties of cellulose crystallites from different earlier reports are concluded and shown in Table 1 [13, 17–22].

Beside cellulose I, cellulose II, III and IV are present with the possibility of conversion from one form to another [23]. Regenerated cellulose II is formed whenever the lattice of cellulose I is destroyed for example on swelling with strong alkali or on dissolution of cellulose. Since the strongly hydrogen bonded cellulose II is thermodynamically more stable than cellulose I, so cellulose I can be converted into cellulose II but cellulose II can not be converted into cellulose I [17].

Table 1. Properties of cellulose crystallites

Property	Cellulose crystallites
Length [nm]	300–2000
Diameter [nm]	5–20
Aspect ratio, L/d	20–60
Tensile strength [MPa]	10 000
E -modulus [GPa]	150

1.2.2. Cellulosic whiskers

Native cellulose that reinforces most plant cell walls is a typical example of a material that can be described as whisker-like. Since amorphous regions act as structural defects, it is responsible for the transverse cleavage of the microfibrils into short monocrystals under acid hydrolysis [24, 25]. This procedure can be used to prepare highly crystalline particles called microcrystalline cellulose [26]. Microcrystalline cellulose consists generally of stiff rod-like particles called whiskers. Whiskers are obtained from natural fibers such as wood [27, 28], sisal [29], ramie [30], cotton stalks [31] wheat straw [22], bacterial cellulose [32, 33], sugar beet [34], chitin [35, 36], potato pulp [37, 38] as well as tunicin [39, 40].

The sea animals have a mantle consisting of cellulose microfibrils or tunicin embedded in a protein matrix. After deproteinization and acid hydrolysis, tunicin breaks down in the form of whiskers having several microns in length [41, 42].

Starting from the raw material and after successive chemical processing steps and, ultimately, controlled acid hydrolysis, the cellulose whisker microcrystals are suspended in aqueous media. Geometrical characteristics of cellulose whiskers depend on the origin of cellulose microfibrils, as well as on acid hydrolysis process conditions such as time, temperature, and purity of material. De Souza *et al.* [43] studied two rodlike systems in aqueous suspensions, cotton and tunicate whiskers the average size whisker dimensions are $L = 255$ nm and $d = 15$ nm for the cotton (ratio $L/d = 17$) while $L = 1160$ nm and $d = 6$ nm (ratio $L/d = 72.5$) for the tunicate whiskers. The whiskers are relatively easy to prepare as they are dispersible in water, in a variety of sizes, and can be used in composite liquids.

The main characteristics of the whiskers are their high aspect ratio and their nanoscopic size. For this reason, the interface area offered by the whiskers surface is high. This might lead to the formation of an interphase in which mechanical properties of the matrix are modified like the nanocomposite of plasticized poly (vinyl chloride) matrix reinforced by cellulose whiskers [44]. In addition, Dong *et al.* [45] also studied the effect of preparation conditions (time, temperature, and ultrasound treatment) on the resulting cellulose microcrystals structure from sulfuric acid hydrolysis of cotton fiber. They reported a decrease in microcrystalline cellulose

length and an increase in their surface charge with prolonged hydrolysis time. On the other hand, using of sulfuric acid for cellulose whiskers preparation leads to more stable whiskers aqueous suspension than that prepared using hydrochloric acid [29]. Indeed, the H_2SO_4 -prepared whiskers present a negatively charged surface, whereas the HCl prepared whiskers are not charged. Another way to achieve charged whiskers consists of the oxidation of the whiskers surface [46, 47] or the post-sulfation of HCl-prepared microcrystalline cellulose [48]. So, whiskers can be defined as the fibers that have been grown under controlled conditions that lead to the formation of high-purity single crystals [49–51]. Acid hydrolysis of native cellulose leads to aqueous rod-like suspensions of elongated microcrystals with high aspect ratio. Depending on their origin, their lateral dimensions range from 2 to 50 nm, with length up to several micrometers. When suspended in water, the cellulose whiskers do not flocculate as they are stabilized by electrostatic repulsion arising from ionic species grafted during the acidic treatment.

Cellulose whiskers have a mechanical strengths equivalent to the binding forces of adjacent atoms leading to highly ordered structure, which produces not only unusually high strength but also significant changes in electrical, optical, magnetic, ferromagnetic, dielectric, conductive, and even superconductive properties. So, it can be used as a reinforcement of polymer matrix [52]. The reinforcing ability of the cellulose whiskers lies in their high surface area and good mechanical properties [53]. However, to obtain a significant increase in material properties the whiskers should be well separated and evenly distributed in the matrix material. One of the drawbacks in using polar surface cellulose whiskers is that they cannot be uniformly dispersed in non-polar media such as organic solvents or monomers. Thus, their incorporation as reinforcement material for nanocomposite processing or their use as complex fluids has so far been mainly limited to aqueous or polar environment. In order to obtain non-flocculated dispersion of cellulose in non-polar solvents such as alkanes, one can envisage two routes, namely (a) coat the surface of the whiskers with surfactants having polar heads and long hydrophobic tails, and (b) graft hydrophobic chains at the surface of the cellulose whiskers. By the first route, Bonini *et al.* [54] dispersed the surfactant coated whisker in toluene by mixing of

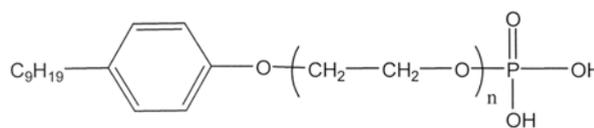


Figure 2. Chemical structure of the surfactant phosphoric ester of poly(ethylene oxide)

surfactants with cellulose whisker in aqueous suspensions. After freeze-drying of these suspensions, the surfactant coated whisker could be dispersed in cyclohexane. By surface acetylation stable suspension of cellulose whiskers with degree of substitutions of 0.75 could be obtained in acetone, but not in solvents of lower polarity [55]. Another recent approach has described suspensions of cellulose whisker in toluene using phosphoric ester of poly(ethylene oxide) as surfactant (Figure 2), these aqueous cellulose whisker suspensions are usually stabilized by steric repulsion between poly(ethylene glycol) chains grafted on the surface.

Using surface silylation of the cellulose whiskers with different silylating agents such as; isopropyl dimethyl chlorosilane, n-butyldimethyl chlorosilane, n-octyldimethyl chlorosilane or n-dodecyldimethyl chlorosilane (Figure 3), the whiskers could be homogeneously dispersed without aggregation in various organic solvents of medium polarity, such as acetone or tetrahydrofuran but not in solvents of very low polarity such as toluene or hexane [56].

As mentioned before, wood cellulose nanofibrils have about 25% of the strength of carbon nanotubes, by comparing the mechanical and electrical behavior of poly(styrene-co-butyl acrylate) nanocomposites [57, 58] reinforced by cellulose nanofibrils (obtained from sugar beet pulp) and multi-walled carbon nanotubes (synthesized from the catalytic decomposition of acetylene at 720°C on supported cobalt/iron catalyst) [59], a high reinforcement effect is achieved for cellulose filled materials, suggesting the presence of a rigid cellulose nanofibril network, linked by strong hydrogen bonds, within the material. With carbon nanotubes as fillers, no strong interactions are possible between multi-walled carbon nanotubes. The soft

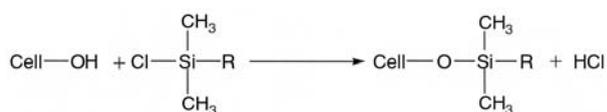


Figure 3. Preparation of silylated cellulose whiskers
R = i-C₃H₇, n-C₄H₉, n-C₈H₁₇, n-C₁₂H₂₅

entangled nanotube network was found to have an influence on the composite tensile behavior only at high temperatures. Such a soft network is efficient for mechanical reinforcement when the polymer matrix is highly viscous. *Opuntia ficus-indica* cladode cells were individualized under alkaline conditions and homogenized under a shear action to produce cellulose microfibril suspensions. Individualized microfibrils consist of flexible and hairy, high aspect ratio fibers almost 5 nm in width. The resulting suspension was used to process nanocomposite materials with a high level of dispersion using latex of poly (styrene-co-butyl acrylate) as a matrix. Cellulose microfibrils bring a great reinforcing effect at high temperature ($T > T_g$ of the matrix) and improve the thermal stability of the composite materials, even at very low filler loading. The swelling behavior of the polymeric matrix was found to strongly decrease even at only 1 wt% of cellulose microfibrils and was almost independent of the filler content [60].

Three types of surface characteristics cellulose whiskers were compared; aggregated whiskers without surface modification, aggregated whiskers grafted with maleated polypropylene, and novel surfactant-modified whiskers. The whiskers were incorporated as nanometric fillers in, polypropylene, by solvent casting from toluene followed by film pressing. The crystallization behavior of the films, as evaluated by X-ray diffraction, displayed two crystalline forms (α and β) in the nanocomposites containing aggregated whiskers without surface modification and novel surfactant-modified whiskers, whereas the neat matrix and the material reinforced with aggregated whiskers grafted with maleated polypropylene only crystallized in the α -form. Differential scanning calorimetry experiments also indicated that the aggregated surfactant-modified whiskers acted as nucleating agents for the polypropylene. The α -phase crystallites represent the predominant part of the neat polypropylene, whereas the appearance of the other two phases (β or γ) may eventually be favored by the presence of fillers, under high pressure or by thermal annealing. The mechanical properties of the nanocomposite films were evaluated by dynamic mechanical analysis, and were found to be significantly enhanced by the incorporation of the cellulose whiskers. Particularly, the materials with novel surfactant-modified whiskers and aggregated whiskers without surface modification displayed

increased moduli as compared to the neat matrix and the aggregated whiskers grafted with maleated polypropylene composite. The presence of the β -phase may have an important influence on the mechanical properties of the resulting composites, since its toughness is higher than that of the α -phase [61]. An environmental friendly chemical modification route to confer high hydrophobicity to crystalline cellulose was developed. With low reagent consumption and simple treatment procedures, highly hydrophobic whiskers can be obtained. The acylated whiskers, using *iso*-octadecenyl succinic anhydride and *n*-tetradecenyl succinic anhydride as acylating agent, could disperse in medium- to low-polarity solvents, i. e., dimethyl sulfoxide to 1,4-dioxane. By controlling the heating time, whiskers with different dispersibility could be obtained. Based on its organic-solvent dispersibility, the acylated whiskers are expected to be useful in direct mixing with synthetic resins to form nanocomposites with improved dispersion and adhesion with matrices [55].

1.2.3. Bacterial cellulose

Besides being the cell-wall component of plants, cellulose is also secreted extracellularly as synthesized cellulose fibers by some bacterial species. Bacterial cellulose is produced by *Acetobacter* species cultivated in a culture medium containing carbon and nitrogen sources. It presents unique properties such as high mechanical strength and an extremely fine and pure fiber network structure. This network structure is in the form of a pellicle made up of a random assembly of ribbon shaped fibrils, less than 100 nm wide, which are composed of a bundle of much finer microfibrils, 2 to 4 nm in diameter. Bacterial cellulose microfibrils have a density of 1600 kg/m³ [62–65]. In addition, it has sufficient porosity, 3-dimensional (3-D) network structure, water holding capability, and biocompatibility [66].

Instead of being obtained by fibrillation of fibers, bacterial cellulose is produced by bacteria in a reverse way, synthesizing cellulose and building up bundles of microfibrils. These bundles are somewhat straight, continuous, and dimensionally uniform. In addition, compared with animal-derived polymers, bacterial cellulose is free of any occurrence of cross infection likely associated with collagen. Current applications for bacterial cellulose

include use as a dietary food, as medical pads for skin burns, as reinforcement in high-strength papers, as binding or thickening agents, and as diaphragms of lectroacoustic transducers [67–70]. For the last application, Nakagaito *et al.* [71] reported a markedly high dynamic Young's modulus, close to 30 GPa, for sheets obtained from bacterial cellulose pellicles when adequately processed. Due to this remarkable modulus, bacterial cellulose sheets seemed to be an ideal candidate as raw material to further enhance the Young's modulus of high-strength composite. When bacterial cellulose pellicles compressed into sheets and impregnated with phenolic resin to produce high-strength composites. The Young's modulus of the composites was significantly higher when compared to that of microfibril cellulose-based composites, 28 GPa against 19 GPa, respectively. The higher modulus of bacterial cellulose composites was credited to the extremely fine, pure, and dimensionally uniform ribbon-like cellulose microfibril bundles, arranged in a network of relatively straight and continuous alignment, and also to the planar orienta-

tion of these elements obtained through the compression of the bacterial cellulose pellicles into sheets.

1.2.4. Starch

There are numerous examples where animals or plants synthesize extracellular high-performance skeletal biocomposites consisting of a matrix reinforced by fibrous biopolymers. Cellulose and chitin are classical examples of these reinforcing elements, which occur as whisker-like microfibrils that are biosynthesized and deposited in a continuous fashion. Starch is another example of natural semi-crystalline polymer that is produced by many plants and occurs as microscopic granules. It acts as a storage polymer in cereals and tubers. These abundant and natural polymers can be used to create high performance nanocomposites presenting outstanding properties. Starch granules become swollen and gelatinized when water is added or when they are heated, and water is often used as a plasticizer to obtain desirable product properties and during

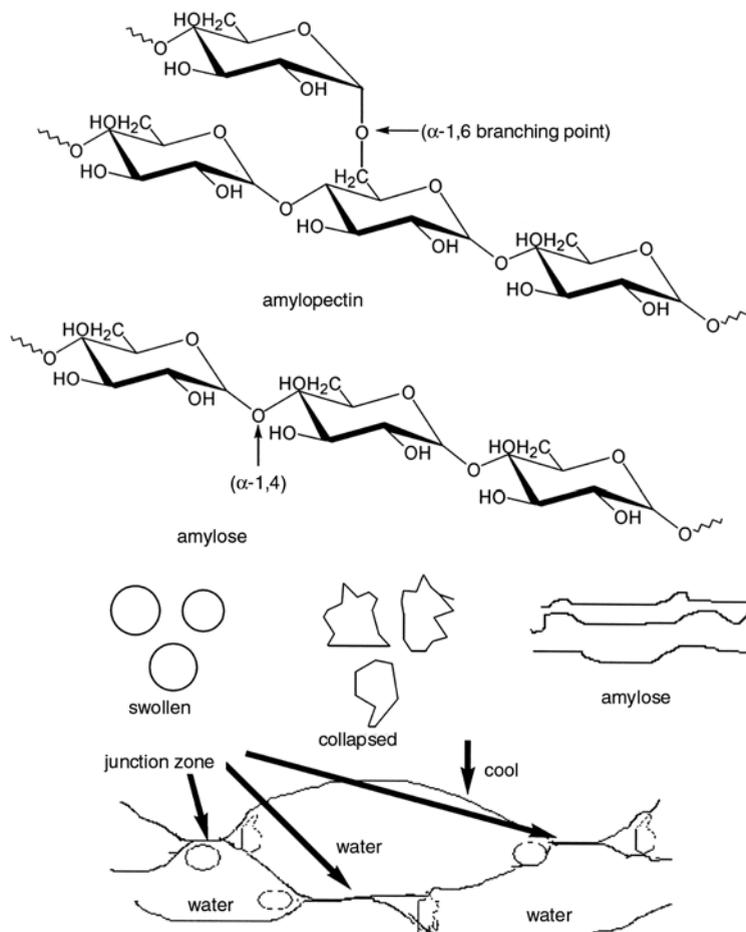


Figure 4. Starch gelation

this swelling amylose leaches out the water but amylopectin forms gel (Figure 4) [72]. Gelatinization of starch was found to lead to the destruction or diminution of hydrogen bonding in granules and a decrease in crystallinity of starch [73].

Aqueous suspensions of crystallites can be prepared by acid hydrolysis of the purified substrates. The object of this treatment is to dissolve away regions of low lateral order so that the water-insoluble, highly crystalline residue may be converted into a stable suspension by subsequent vigorous mechanical shearing action. For cellulose and chitin, these monocrystals appear as rod-like nanoparticles, dimensions of which depend on the biological source of the substrate. In the case of starch they consist of platelet-like nanoparticles. High reinforcing capability was reported resulting from the intrinsic chemical nature of these polymers and from their hierarchical structure [74]. On the other hand, amylose content in starch may affect the properties of the prepared composites. Ke *et al.* [75] studied the effect of amylose content in starches on the mechanical properties. Four dry corn starches with different amylose content were blended with poly lactic acid at various starch/poly lactic acid ratios and characterized for morphology, mechanical properties and water absorption. Tensile strength and elongation of the blends decreased as starch content increased, but no significant difference was observed among the four starches at the same ratio of starch/poly lactic acid. The rate and extent of water absorption of starch/poly lactic acid blends increased with increasing starch. Blends made with high-amylose starches had lower water absorption than the blends with normal and waxy corn starches.

Starch can be used as a reinforcing or a matrix. Nanocomposite materials were obtained using glycerol plasticized starch as the matrix and a colloidal suspension of cellulose whiskers as the reinforcing phase. After mixing the raw materials and gelatinization of starch, the resulting suspension was cast and evaporated under vacuum. The composites were conditioned at various moisture contents in order to evaluate the effect of this parameter on the composite structure. The specific behavior of amylopectin chains located near the interface in the presence of cellulose probably led to a transcrystallization phenomenon of amylopectin on cellulose whiskers surface [76]. The reinforcing effect of whiskers strongly depended on the ability

of cellulose filler to form a rigid network, resulting from strong interactions between whiskers such as hydrogen bonds, and therefore on the moisture content. It was shown that increasing water content induced the crystallization of amylopectin chains and the accumulation of plasticizer in the cellulose/amylopectin interfacial zone [77]. Another approach is using latex of poly (hydroxyoctanoate) as a matrix and using a colloidal suspension of hydrolyzed starch or cellulose whiskers as natural and biodegradable filler. High-performance materials were obtained from these systems, preserving the natural character of poly (hydroxyoctanoate). Specific polymer-filler interactions and geometrical constraint due to the particle size of the latex have to be considered to account for the mechanical reinforcement effect of cellulose whiskers [78].

2. Preparation

2.1. Nanofibrill

A variety of techniques have been used to make nanostructures.

2.1.1. By mechanical fibrillation

The fibrillation of pulp fiber to obtain nano-order-unit web-like network structure, called microfibrillated cellulose, is obtained through a mechanical treatment of pulp fibers, consisting of refining and high pressure homogenizing processes. The refining process used is common in the paper industry, and is accomplished via a piece of equipment called a refiner. In a disk refiner, the dilute fiber suspension to be treated is forced through a gap between the rotor and stator disks, which have surfaces fitted with bars and grooves, against which the fibers are subjected to repeated cyclic stresses. This mechanical treatment brings about irreversible changes in the fibers, increasing their bonding potential by modification of their morphology and size. In the homogenization process, dilute slurries of cellulose fibers previously treated by refining are pumped at high pressure and fed through a spring high pressure loaded valve assembly. As this valve opens and closes in rapid succession, the fibers are subjected to a large pressure drop with shearing and impact forces. This combination of forces promotes a high degree of microfibrillation of the cellulose fibers, resulting in microfibrillated cellulose [79].



Figure 5. Homogenizer (Microfluidizer) used for the production of microfibrillated cellulose

The refining process is carried out prior to homogenization due to the fact that refining produces external fibrillation of fibers by gradually peeling off the external cell wall layers (P and S_1 layers) and exposing the S_2 layer and also causes internal fibrillation that loosens the fiber wall, preparing the pulp fibers for subsequent homogenization treatment [80].

Nakagaito *et al.* [81] studied how the degree of fibrillation of pulp fibers affects the mechanical properties of high strength cellulose composites. It was found that fibrillation solely of the surface of the fibers is not effective in improving composite strength, though there is a distinct point in the fibrillation stage at which an abrupt increase in the mechanical properties of composites occurs. In the range between 16 and 30 passes through refiner treatments, pulp fibers underwent a degree of fibrillation that resulted in a stepwise increment of mechanical properties, most strikingly in bending strength. This increase was attributed to the complete fibrillation of the bulk of the fibers. For additional high pressure homogenization-treated pulps, composite strength increased linearly against water retention values, which characterize the cellulose's exposed surface area, and reached maximum value at 14 passes through the homogenizer (Figure 5.).

2.1.2. By electrospinning of polymer

Electrospinning derived from electrostatic spinning. Electrospinning has been recognized as an

efficient technique for the fabrication of polymer nanofibers. Various polymers have been successfully electrospun into ultrafine fibers e.g. cellulose acetate. There are basically three components to fulfill the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process a high voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates, and is collected as an interconnected web of small fibers [82, 83]. One electrode is placed into the spinning solution/melt, the other is attached to the collector. The electric field is subjected to the end of the capillary tube that contains the solution fluid held by its surface tension. This induces a charge on the surface of the liquid. The potential difference depended on the properties of the spinning solution, such as polymer molecular weight and viscosity. When the distance between the spinneret and the collecting device was short, spun fibers tended to stick to the collecting device as well as to each other, due to incomplete solvent evaporation. Mutual charge repulsion and the contraction of the surface charges to the counter electrode cause a force directly opposite to the surface tension [84]. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone [85]. By further increasing in the electric field, a critical value is attained with which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to become very long and thin. Meanwhile, the solvent evaporates, leaving behind a charged polymer fiber. In the case of the melt the discharged jet solidifies when it travels in the air.

Most of the polymers were dissolved in some solvents before electrospinning. When the solid polymer or polymer pellet is completely dissolved in a proper amount of solvent that is held, for example, in a glass container, it becomes a fluid form called polymer solution. The polymer fluid is then introduced into the capillary tube for electrospinning. Both the dissolution and the electrospinning are essentially conducted at room temperature with atmosphere condition.

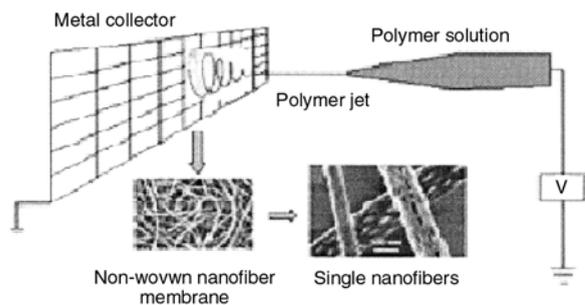


Figure 6. Schematic diagram to show polymer nanofibers by electrospinning.

Polymers, molten in high temperature, can also be made into nanofibers through electrospinning. Instead of a solution, the polymer melt is introduced into the capillary tube. However, different from the case of polymer solution, the electrospinning process for a polymer melt has to be performed in a vacuum condition [86–88]. Namely, the capillary tube, the traveling of the charged melt fluid jet and the metal collecting screen must be encapsulated within a vacuum. A schematic diagram to interpret electrospinning of polymer nanofibers is shown in Figure 6.

A polymer solution, such as cellulose acetate dissolved in 2:1 acetone: dimethyl acetamide was introduced into the electric field. The polymer filaments were formed, from the solution, between two electrodes bearing electrical charges of opposite polarity. One of the electrodes was placed into the solution and the other onto a collector. Once ejected out of metal spinnerets with a small hole, the charged solution jets evaporated to become fibers which were collected on the collector [89].

2.1.3. From sea animals

Colloidal suspensions of cellulose whiskers in water were prepared as following; the shells of the tunicates cut into small fragments and bleach by three successive treatments with sodium hypochlorite in dilute acetic acid. Heat the mixture to 70–80°C and keep at this temperature for 1 hour. After the third cycle, the tunicate mantles isolate via decanting, wash with ice water, and disintegrate in blender into an aqueous suspension (tunicate content ~3% w/w). The disintegrated mantles subsequently hydrolyze by adding concentrated sulfuric acid, heating the mixture to 80°C, and rigorous stirring at this temperature for 20 minute to yield a suspension of cellulose whiskers. After washing with water until the pH is neutral, adding water so

that the whisker concentration, suspension of cellulose whiskers will be obtained [90].

2.1.4. From microcrystalline cellulose in organic solvent

The microcrystalline cellulose was swelled and partly separated to whiskers by chemical and ultrasonification treatments. Dimethyl acetamide with 0.5 wt% LiCl solution was used as swelling agent. The microcrystalline cellulose in LiCl/dimethyl acetamide was 10 wt% which was agitated using a magnetic stirrer for 12 hour at 70°C to swell the microcrystalline cellulose particles. The slightly swelled particles were then sonicated in an ultrasonic bath for 3 hours over a period of 5 days with long intervals between each sonication treatment, to separate cellulose nano whiskers [91].

2.1.5. By acid hydrolysis

Suspensions of nanocrystalline cellulose were prepared. Hydrolysis was carried out with sulfuric acid with constant stirring. Immediately following the acid hydrolysis, the suspension dilute 10-fold with deionized water to quench the reaction. The suspension centrifuges at 6000 rpm for 10 min to concentrate the cellulose and to remove excess aqueous acid. The resultant precipitate should be rinsed, recentrifuged, and dialyzed against water for 5 days until constant neutral pH [92].

2.1.6. From bacterial cellulose

Cellulose can be synthesized by some bacteria [31, 33]. For example, the cellulose was produced by static cultivation of *Acetobacter xylinum*, sub species BPR2001, in a fructose/CSL medium at 30°C [93]. The bacteria were grown in 400 ml Erlenmeyer flasks containing 100 ml of media. In order to remove the bacteria and to exchange remaining media, the produced cellulose pellicles were boiled in 1 M NaOH at 80°C for 1 hour followed by repetitive boiling in deionised water. To prevent drying and to avoid contamination, the washed cellulose was stored in diluted ethanol in a refrigerator.

The advantage in using bacterial cellulose as a model for plant cellulose lies in its high purity, fine fibrils (high surface area) [94], high tensile strength and water-holding capacity. So, bacterial cellulose

has been used as a reinforcing in nanocomposites [95].

2.2. Preparation of nanocomposite films

2.2.1. From regenerated cellulose

Microcrystalline cellulose powder is produced by acid hydrolysis of amorphous domains, which results in high crystallinity. Microcrystalline cellulose was activated for 6 hours in distilled H₂O at room temperature. Subsequently, the cellulose was dehydrated in ethanol, acetone, and N,N-dimethyl acetamide for 4 hours each. After decanting N,N-dimethyl acetamide from the dehydrated cellulose, LiCl/N,N-dimethyl acetamide solution was poured onto cellulose sample and stirred for 5 minutes. The solutions were then poured into Petri dish, and left at ambient atmosphere for 12 hour. After this time a 5–8 mm thick transparent gel had formed which was washed in distilled water and dehydrated between gently compressed sheets of paper. The final nanocomposite films were optically transparent and had a thickness between 0.2 and 0.5 mm [96].

2.2.2. By solution casting

For preparing solid polymer nanocomposite film, combine appropriate amounts of the nanoreinforcement's solution and dissolved polymer matrix.

Two processing conditions can be used to prepare the composites film from this mixture.

The mixture cast in a Petri dish and put in a drying oven under vacuum. The chosen temperature allows the solvent evaporation and the film formation (i. e. polymer particles coalescence). A so-called evaporated film is obtained and materials compression in mold under heating and pressure [92, 97].

The second route used to elaborate composite film, the mixture is first freeze-dried to allow water sublimation, and a compact soft powder is obtained. This powder then press under heating and pressure [62].

2.2.3. By extrusion

For mixing dry material with suspension solution; the composite materials will be compounded using a co-rotating twin-screw extruder with a gravimetric feeding system for dry materials and a peristaltic

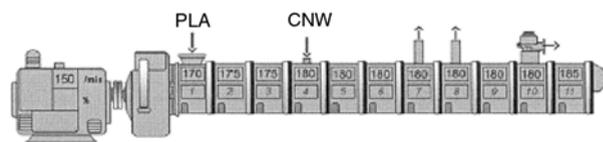


Figure 7. Schematic picture of the compounding process: feeding of poly (lactic acid) in zone 1, pumping of dispersed of cellulose whiskers in zone 4 and removal of the liquid using atmospheric and vacuum venting in zones 7, 8 and 10

pump for the cellulose whiskers suspension. Figure 7, shows a schematic picture of the compounding process.

For preparing nanocomposite film of poly (lactic acid)-malic anhydride-poly (ethylene glycol) reinforced with cellulose whiskers suspended in LiCl/dimethyl acetamide, poly (lactic acid) was fed in zone 1 and the cellulose whiskers suspension was pumped into the melted polymer at zone 4. The liquid phase was removed by atmospheric venting in zones 7 and 8 and by vacuum venting in zone 10. Both poly (lactic acid)-malic anhydride and poly (ethylene glycol) were premixed and fed in zone 1. The LiCl/dimethyl acetamide was removed by the venting system during the extrusion. The extruded materials were compression moulded to ~1.3 mm thickness.

The color on the samples was changed from transparent yellow to light brown which indicates thermal degradation. The color change and decreased mechanical properties indicates that the LiCl/dimethyl acetamide is not suitable as swelling-separation agent for cellulose whiskers if high temperature processing is used [91].

2.2.4. By electrostatic layer-by-layer

Electrostatic layer-by-layer self-assembled films have been exploited for the fabrication of sophisticated nanocomposite incorporated the linear polymer cellulose sulfate. In this method, a charged solid substrate is exposed to a solution of oppositely charged polyelectrolyte, followed by rinsing. The polymeric material adhering to the surface has more than the stoichiometric number of charges required for charge neutralization, thereby reversing the surface charge. This allows for easy adsorption of the next oppositely charged polyelectrolyte, also resulting in charge reversal. The amount of adsorbed polymer is self-limiting as a result of rinsing and allows for stepwise film growth [98, 99].

Resultant films and coatings show long-life stability as well as self-healing characteristics.

Structured layer-by-layer films have potential applications as antireflective coatings [100], waveguides, bio/optical sensors [101], separation technologies and drug delivery systems [102]. Conventionally, layer-by-layer assembly has employed solution-dipping (or dip-coating) in beakers of various sizes containing dilute aqueous polymer solutions. This inexpensive method works for most substrates independent of shape but has not always resulted in adequately homogeneous films. Alternatively, spin-coating is the most widely used technique for obtaining uniform films in lithography and other micromachining applications. The spin-coating process involves the acceleration of a liquid solution on a rotating substrate and is characterized by a balance of centrifugal forces (spin speed) and viscous forces (solution viscosity). Films created by this way have been found to be consistent and reproducible in thickness [103]. Nanocrystalline cellulose is amenable to sequential film growth by layer-by-layer assembly, as presented schematically in Figure 8.

Thin multilayered films incorporating polyelectrolyte layers such as poly (allylamine hydrochloride) and nanocrystalline cellulose layers were prepared by the electrostatic layer-by-layer methodology, as well as by a spin coating variant. Both techniques gave rise to smooth and stable thin films, as confirmed by atomic force microscopy surface morphology measurements as well as scanning electron microscopy investigations. Films prepared by spin-coating were substantially thicker than solution-dipped films. Thus both techniques are viable for producing structured nanocomposites, where the large aspect ratio cellulose units may serve to strengthen the elastic polymer matrix [93].



Figure 8. Schematic representation of the build-up of electrostatically adsorbed multilayered films. The polyelectrolyte, cationic poly(allylamine hydrochloride), is shown by the curved line and colloidal cellulose nanocrystals are represented by straight rods; counterions have been omitted for clarity

3. Characterization

Characterization of nanofibers and nanocomposites can be performed using different techniques such as transmission electron microscopy (TEM), X-ray and neutron diffraction, dynamic infrared spectroscopy, atomic force microscopy (AFM), differential scanning calorimetry (DSC), small angle neutron scattering (SANS), etc.

3.1. Nanoindentation techniques

Mechanical properties of materials have been commonly characterized using indentation techniques. Properties that are measured by indentation describe the deformation of the volume of material beneath the indenter (interaction volume). Deformation can be by several modes: elasticity, viscoelasticity, plasticity, creep, and fracture. These deformation modes are described by the following properties, respectively: elastic modulus, relaxation modulus, hardness, creep rate, and fracture toughness [2].

3.2. Microscopy characterization

Scanning electron microscopy (SEM) as well as atomic force microscopy (AFM) can be used for structure and morphologies determination of cellulose whiskers and their nanocomposites. From conventional bright-field transmission electron microscopy (TEM) it was possible to identify individual whiskers, which enabled determination of their sizes and shape. AFM overestimated the width of the whiskers due to the tip-broadening effect. Field emission SEM allowed for a quick examination giving an overview of the sample; however, the resolution was considered insufficient for detailed information.

By comparing TEM, Field emission scanning electron microscopy (FESEM) and AFM analysis of cellulose whiskers as in Figure 9, it is shown that; a) the whiskers did not differ significantly in contrast from the carbon film, b) it was difficult to clearly discern individual whiskers from agglomerated structures, and therefore an estimate of the width of the whiskers was not obtained while in, c) the structures differed from the needlelike shape as observed in TEM. The whiskers appeared significantly broader having a rounded shape. AFM could therefore be a powerful alternative to conventional

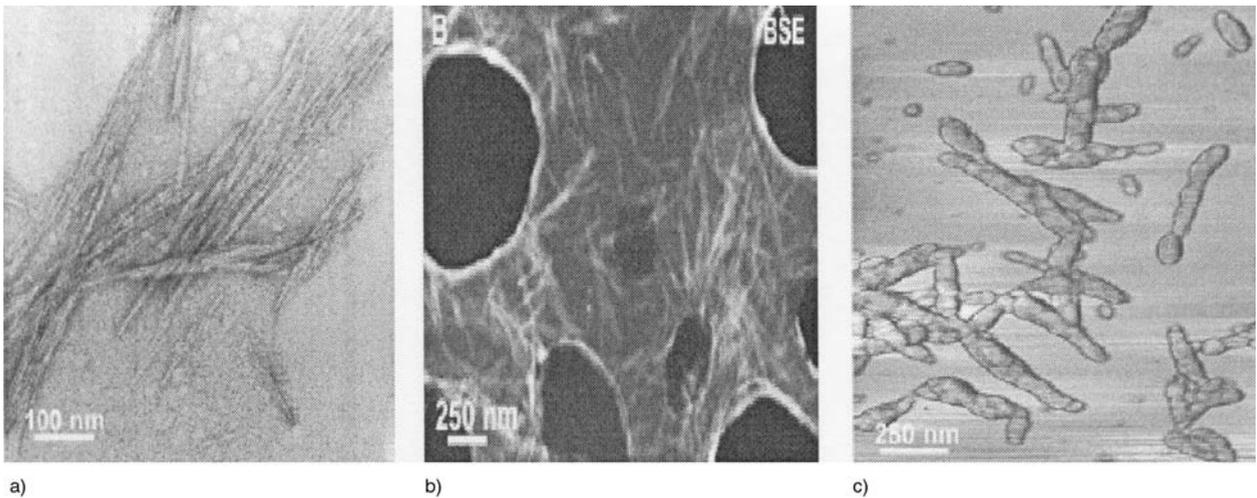


Figure 9. TEM, FESEM and AFM images of cellulose whiskers. a) Bright-field TEM image of stained cellulose whiskers on a porous carbon film, b) FESEM backscatter overview image of stained cellulose, c) AFM phase image of cellulose whiskers

bright-field transmission electron microscopy in such composite materials [104].

3.2.1. Small angle neutron scattering

Due to the sensitivity of this technique, this method was used for instance to investigate polymer layers grafted onto spherical particles with high specific area such as whisker, silica, latex particles or surfactants adsorbed onto ferrofluid particles [54, 105, 106].

3.3. X-ray diffractometry

The structural properties of the nanocomposite films can be characterized using X-ray diffraction like, the size of the cellulose crystallites [107] and crystallinity index [108].

3.4. Tensile tests

The nonlinear mechanical behavior of composites and unfilled matrix was analyzed using testing machine in tensile mode. The true strain ε was determined by the Equation (1):

$$\varepsilon = \ln \frac{L}{L_0} \quad (1)$$

where L and L_0 are the length of the specimen at the time of the test and the length at zero time, respectively.

The true stress σ was calculated by the Equation (2):

$$\sigma = \frac{F}{S} \quad (2)$$

where F is the applied load and S is the cross-sectional area at the time of the test.

From the stress-strain curves, the Young modulus (E) was determined from the slope of the low-strain region [21].

3.5. Electrical conductivity

For measuring ionic conductivities of ion-conducting solid polymer electrolytes or composites, the sample must be coated at their end with a silver paint to ensure a good electrical contact. Electrical conductivity measurements are performed at ambient temperature using several frequencies. The complex admittance is Y^* recorded versus time. From this admittance, the conductivity σ_c^* can be deduced by the Equation (3):

$$\sigma_c^* = Y^* \frac{L}{WT} = Y^* \frac{L^2}{V_0} \quad (3)$$

where W , L and T are the width, the length and the thickness of the sample during the test, and V_0 (the sample initial volume) = $L_0 \cdot T_0 \cdot W_0$ [58].

3.6. Transparency measurements

Transparency can be carried out using UV-visual spectrometry which gives the amount of light being transmitted through the nanocomposite films at different wavelengths [97].

3.7. Thermomechanical analysis

Thermomechanical measurements are performed using a thermomechanical analyzer. This analysis shows the temperature dependencies of a dynamic storage modulus [92].

3.8. Rheological behavior of suspensions

Rheological data could be collected with a rotating rheometer.

4. Applications

4.1. Cellulose–cellulose nanocomposites

Composite materials, typically glass fibers or carbon fibers embedded into epoxy resin or unsaturated polyester, show excellent mechanical and thermal properties; thus, they are widely used in various applications ranging from aerospace to vehicles to sports utensils [109]. However, these advantages cause environmental problems when disposing by incineration. Consequently, there are growing demands for environmentally friendly composites. Cellulose is the most abundant biomass resource and possesses excellent mechanical and thermal properties as mentioned before. Natural cellulose (cellulose I) also boasts an elastic modulus, E_1 , of 138 GPa for the crystalline regions in the direction parallel to the chain axis. This is comparable with the E_1 values of high performance synthetic fibers such as poly (phenylene terephthalamide) 130 GPa. In addition, the maximum macroscopic Young's modulus of natural plant cellulose (up to 128 GPa) is higher than those of aluminum (70 GPa) and glass fibers (76 GPa). The ultimate tensile strength of cellulose is estimated to be 17.8 GPa. This is 7 times higher than that of steel. Intrinsically, the very high elastic modulus and tensile strength (not specific modulus and specific strength) imply that cellulose possesses the potential to replace glass fiber, and it shows promise as a reinforcement fiber for composites where the density is not a concern. Current trends toward environmentally friendly composites focus on the use of cellulose fibers [110]. The interface between the fiber and the matrix often brings serious problems such as poor adhesion and water uptake by the composites. On the other hand, when the fiber and the matrix are composed of the same material,

some benefits relevant to recyclability, and a better adhesion at interface, can be expected [111].

Cellulose is well known not to melt, but shows thermal degradation at high temperature. Therefore, to process cellulose, a wet process should be employed. Consequently, cellulose/cellulose composite was manufactured by the wet process using LiCl/N,N-dimethyl acetamide as cellulose solvent and by controlling the solubility of cellulose through pretreatment conditions. This composite is totally composed of sustainable cellulosic resources, so it can be biodegradable after service. Cellulose self-reinforced composite, possessed excellent mechanical and thermal properties during use as well as transparent to visible light. This composite can be used as an alternative of the glass-fiber-reinforced composite. By choosing the pretreatment condition to the fiber, the transverse mechanical properties of the composite can be also enhanced through the molecular diffusion across the interface between the fiber and the matrix [92, 111].

The ratio of cellulose I and II affects the properties of the resulting nanocomposites. So, cellulose-based nanocomposite films with different ratios of cellulose I and II were produced by partial dissolution of microcrystalline cellulose powder in LiCl/N,N-dimethyl acetamide and subsequent film casting. The films are isotropic, transparent to visible light, highly crystalline, and contain different amounts of un-dissolved cellulose I crystallites as a filler. By varying the cellulose I and II ratio, the mechanical performance of the nanocomposites can be tuned depending on the composition. Also, the nanocomposites clearly surpass the mechanical properties of most comparable cellulosic materials, their greatest advantage being the fact that they are fully biobased and biodegradable, but also of relatively high strength [92].

4.2. Nanocomposites from cellulose derivatives

The chemical modification of dissolving-grade wood pulp fibers with a variety of acids and anhydrides represents longstanding industrial practice. Cellulose ethers and cellulose esters are used for a wide variety of products in the food, household products, health care, textile, and many other industries. Esters with short alkyl chains (acetate or propionate) form solvent-soluble, spinnable fibers;

esters with bulky substituents (butyrate, hexanoate, and higher) are progressively more thermally deformable under pressure. Such cellulose ester powders in the presence of different plasticizers and additives are extruded to produce various grades of commercial cellulose plastics in palletized form [112, 113]. Among biopolymeric materials, cellulose and cellulose derivatives enjoy widespread use and remain the single largest biopolymer. In multiphase polymer materials, cellulose may find application in both polymeric blends and as fibers in reinforced polymeric composites. Recently, composite materials based on cellulose derivatives have been the subject of intense research.

Polymer nanocomposites are one of the important application areas for nanotechnology, as well as naturally derived organic nanophase materials are of special interest in the case of polymer nanocomposites. Nanocomposites have been successfully fabricated from cellulose acetate, triethyl citrate plasticizer, and organically modified clay Cloisite 30B with and without maleic anhydride grafted cellulose acetate butyrate as a compatibilizer. The cellulosic plastic with cellulose acetate/triethyl citrate (80/20 wt%) was used as the polymer matrix for nanocomposite fabrication. Cellulosic plastic-based nanocomposites obtained using increased pre-plasticizing times showed better exfoliated structures. In the system containing compatibilizer, the minimum retention time required for obtaining almost completely exfoliated hybrid nanocomposites was shorter than in the system without compatibilizer [114–118].

Cellulose diacetate films incorporated with small amount of montmorillonite nanoclay ($\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$) were prepared from methylene chloride/ethanol (9:1 wt/wt) casting solutions. The various nanoclays were incorporated into the cellulose structure in order to enhance the mechanical properties as well as thermal stability of cellulose. The plasticizers used were: dibutyl phthalate, diethyl phthalate, poly (ethylene glycol). The films were completely transparent in the composition range of 10 to 30 w/w plasticizers and 1 to 7 w/w montmorillonite nanoclay. The strength of films decreased with the increase in the plasticizer content. All the films gave a single glass transition temperature, T_g , which decreased sharply from 180°C of the original cellulose diacetate to approx-

imately 95°C according to the content and kind of plasticizer [119, 120]. When the plasticizer was added into the cellulose diacetate film up to 30 wt%, the Young's modulus of film was decreased from 1930 MPa to 1131 MPa but was increased from 1731 MPa to 2272 MPa when the montmorillonite nanofiller was added into the film up to 7 wt%. The mechanical properties of cellulose diacetate films were decreased by addition of plasticizer but strengthened by the incorporation of montmorillonite nanofiller. Also, nanocomposites were synthesized using cellulose acetate bioplastic, citrate based plasticizer and organically modified clay nanofillers. Transmission electron microscopy revealed the existence of intercalated clay dispersed throughout the cellulose acetate matrix. The intercalated reinforcements resulted in enhancements of the composite tensile strength, tensile modulus, and coefficient of thermal expansion. The composite tensile strength of cellulose acetate increased approximately 38% after incorporating 5 wt% clay. The tensile modulus was also enhanced as much as 33% [121].

Biodegradable cellulose acetate/layered silicate grafted poly(ϵ -caprolactone) nanocomposites were prepared by in situ polymerization of ϵ -caprolactone in the presence of cellulose acetate and organically modified layered silicate [122].

Nearly monodisperse nanoparticles have been synthesized based on a naturally occurring polymer of hydroxypropyl cellulose. The hydroxypropyl cellulose nanoparticle assembly in water has been further stabilized by covalently bonding neighboring particles to form a three-dimensional network. This network contains a large amount of water similar to a conventional bulk gel [123]. From morphology analysis of hydroxypropyl cellulose fibril reinforced nanocomposites using nanoindentation. It was observed that hydroxypropyl cellulose composite with a fibril showed lighter and darker structures that can be explained by a contrast of crystalline fibril areas and the amorphous polymer matrix. The direct use of aqueous fibril suspensions for the compounding with hydroxypropyl cellulose was found to be an effective method of dispersing the fibrils within the polymer matrix. The results show a homogeneous distribution of cellulose fibrils at higher magnifications [124].

Another less studied form of cellulose, microcrystalline cellulose, which is used in the production of pharmaceutical tablets as binding material and

compatibility enhancer. Borges *et al.* [125] produced and characterized composites based on a cellulose derivative, 2-hydroxypropylcellulose used as matrix and reinforced with microcrystalline cellulose fibers. As both the matrix and Avicel fibers have free hydroxyl groups in the anhydroglucose units, they proposed a new way of elaborating these natural composites through the direct coupling between the fibers and the matrix. Different diisocyanates were used as coupling agents and the obtained composites presented improved mechanical properties as the result of a better fiber-matrix adhesion. In addition, the fibers concentration in the composite material used up to 30 w/w%. This means that, the inclusion of fibers in a hydroxypropylcellulose matrix produces composites with superior mechanical properties.

Carboxymethyl cellulose is a polyelectrolyte derived from natural materials. It has been extensively studied as a hydrogel polymer. The effect of nano-sized fillers on the properties of carboxymethyl cellulose-based composites is of interest in the development of novel or improved applications for hydrogel polymers in general and carboxymethyl cellulose in particular. The composite material composed of carboxymethyl cellulose, microcrystalline cellulose or cellulose nanocrystals, with glycerol as a plasticizer was prepared. Cellulose nanocrystals improved the strength and stiffness of the resulting composite compared to microcrystalline cellulose. In addition, a simple heat treatment was found to render the nanocomposite water resistant [126].

Ethyl cellulose/montmorillonite nanocomposite film plasticized with environmental-friendly plasticizer epoxidized soybean oil was prepared by melt process using Haake mixer. The addition of 10 wt% epoxidized soybean oil causes a decrease of T_g from 81 to 61°C. When the plasticizer was added into the ethyl cellulose films, the mechanical properties of ethyl cellulose films was decreased, however the addition of montmorillonite into the ethyl cellulose films or the ring opening reaction of epoxidized soybean oil plasticizer cause enhancement of mechanical properties [127].

The reaction of dissolving-grade wood pulp fibers with a mixed *p*-toluenesulfonic/hexanoic acid anhydride system and a titanium (IV) isopropoxide catalyzed system under non-swelling reaction conditions produces fibers that represent biphasic cellulose derivatives. Transparent or semitransparent

composite sheets can be formed in which the thermoplastic cellulose hexanoate phase is consolidated into a continuous matrix reinforced with discontinuous cellulose I domains. The cellulose I component also varies with the extent of modification, and it provides for biodegradability and reinforcement (i. e., high modulus). Although no precise dimensions can be determined for the respective phase domains, the low solubility of the products and the decrease in the crystal size of cellulose I suggest that they are on the nanometer scale. There are differences in some properties based on the difference in the distribution of subsistent between the materials generated by toluenesulfonic/hexanoic acid anhydride and the titanium (IV) isopropoxide catalyzed systems [107].

4.3. Cellulose–inorganic nanocomposites

The integration of polymers and inorganic materials is an attractive field in materials science. Unfortunately, because of the differences in their individual intermolecular interaction forces, the interfacial incompatibility between inorganic and organic polymers often causes failures in the preparation of these composites. The lack of affinity and hydrophobic polymers make it difficult for a homogeneous mixture to be achieved. Tourmaline, from single-halose tourmaline, a mixed stone, is a naturally complex group of hydrous silicate minerals containing Li, Al, B, and Si and various quantities of alkalis (K and Na) and metals (Fe, Mg, and Mn). It is the principle boron-containing mineral in the crust and has its genesis in both igneous (principally pegmatites) and metamorphic rocks. Its structural formula is $\text{Na}(\text{Li}, \text{Al})_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$. Tourmaline forms hexagonal and prismatic crystals and possesses as antibacterial activity. On the other hand, the NaOH/thiourea aqueous system is hydrophilic, so it can be expected to disperse hydrophilic tourmaline nanoparticles. By using NaOH/thiourea aqueous solutions as cosolvents of cellulose and nanoparticles provides a simple, cheap, and pollution-free way of preparing such composite materials. By this way Dong *et al.* [128] prepared cellulose/tourmaline nanocomposites films via a casting method through coagulation with CaCl_2 and HCl aqueous solutions. Results indicated that adhesion between regenerated cellulose and filled nanocrystals can occur, and the dispersion of nanocrystals in cellulose is homoge-

neous but the induction of tourmaline breaks the partial intermolecular hydrogen bonds of cellulose, and this result in a reduction of the thermal stability of the composite films but composite films with tourmaline exhibit satisfying antibacterial action against *Staphylococcus aureus*. So, using NaOH/thiourea aqueous solutions as cosolvents of cellulose and nanoparticles provides a simple, cheap, and pollution-free way of preparing composite materials.

Suber *et al.* [129] study the synthesis and the comparative structural and morphological study of iron oxide nanoparticles in polystyrene-based ion-exchange resins and cellulose. The results show that the matrix influences the iron oxide particle size; the average size is about 7 nm in the resins and 25 nm in the cellulose. In the resins, particles are present inside the pores and as aggregates on the surface of the resin beads, whereas in the cellulose they are present on the surface and in the swollen network of the microfibers constituting the single fibers.

4.4. Starch nanocomposites

A number of researchers have presented work in the field of starch nanocomposites. Park *et al.* [131] reported on the preparation and properties of gelatinized starch/montmorillonite clay nanocomposites using both naturally occurring sodium montmorillonite and a number of alkyl ammonium modified clays. X-ray diffraction and transmission electron microscopy showed an intercalated structure for the starch/sodium montmorillonite, however the modified clays appeared either unchanged or agglomerated in structure [130]. Also they found that the unmodified sodium montmorillonite/starch nanocomposite also exhibited the greatest increase in modulus of all the clays used. Park *et al.* [132] also investigated the formation of montmorillonite-reinforced glycerol/plasticized thermoplastic starch. Scanning electron microscopy showed well-dispersed montmorillonite platelets. The Fourier-Transformed Infrared spectra indicated cooperation existed between montmorillonite and starch molecules and hydrogen bonds that formed between the reactive hydroxyl groups of montmorillonite and the hydroxyl groups of starch molecules. The mechanical and thermal properties of the starch nanocomposites formed showed significant improvements. Wilhelm *et al.* [133] have also investigated the for-

mation of starch/clay nanocomposites, using a Ca²⁺ hectorite (Mg₆Si₈O₂₀(OH)₄·nH₂O). Solution cast starch/clay nanocomposites showed no X-ray diffraction due to the first basal spacing, indicating almost total exfoliation in the starch matrix. Although this was a good result, starch does require some kind of plasticizer to reduce the brittleness of the starches. When glycerol was added by itself to the clay, the interplanar distance increased. Fischer *et al.* [134, 135] also investigated starch/clay nanocomposites and a number of experimental pathways were investigated, including the dispersion of Na⁺ montmorillonite clay in water, followed by blending in an extruder at a temperature of 85–105°C with a premixed powder of potato starch, glycerol and water. The resulting material appeared to be fully exfoliated and exhibited a reduction in hydrophilicity, and improved stiffness, strength and toughness.

The natural smectite clays, montmorillonite and hectorite, readily formed nanocomposites with thermoplastic starch which prepared by melt-processing of starch and glycerol [136]. In all cases, clay increased the elastic modulus of thermoplastic starch. The moduli of treated-hectorite and kaolinite composites were very similar at similar clay loadings and were lower than the nanocomposites, for nanocomposites, montmorillonite generally provided a slightly greater improvement in the modulus than untreated hectorite [137]. Another group of starch-based nanocomposites is those that are blended with biodegradable polyesters. McGlashan and Halley studied the dispersion of nanoclays in a number of different biodegradable starch/polyester blend formulations. The crystallization temperature of the nanocomposite blends was found to be significantly lower than the base blend, probably due to the clay platelets inhibiting order, and hence crystallization, of the starch and polyester. The best dispersions were found in the 30 wt% starch blends [138]. Kalambur and Rizvi [139] also investigated starch nanocomposites blends and successfully made starch/polylactic acid blends in the presence of montmorillonite nanoclay (Al₄Si₈O₂₀(OH)₄·nH₂O). By study the thermal stability of nanocomposites of starch/clay it is found that there is no significant effect of clay on the thermal degradation of starch, whereas a significant increase in thermal stability was observed when nanocomposites of thermoplastic starch and unmod-

ified montmorillonite was prepared by melt intercalation method even at 5% filler content. Thus, the preparation method might have an effect on the properties. Composites have been prepared by solution method after drying of starch and clay at 110°C. All composites show highest weight loss at 296°C. It was assumed that thermal degradation was influenced by hydroxyl group exposure, clay dispersion and reassociation of starch chains where clay dispersion was more important than others [140]. However, hydrophobic poly (lactic acid) and hydrophilic starch are thermodynamically immiscible, leading to poor adhesion between the two components, and hence poor and irreproducible performance. Various compatibilizers and additives have been investigated to improve the interfacial interactions of these blends. Wang *et al.* [141, 142] used methylenediphenyl diisocyanate to improve the interface and studied a blend of 55/45 w/w mixture of poly (lactic acid) and dried wheat starch in an intensive mixer with or without a low level of methylenediphenyl diisocyanate. Blends with methylenediphenyl diisocyanate had enhanced mechanical properties that could be explained by the in situ formation of a block copolymer acting as a compatibilizer. Scanning electron microscopy showed reduced interfacial tension between the two phases. The presence of methylenediphenyl diisocyanate also enhanced the mechanical properties of the blend at temperatures above T_g . Water uptake by the poly (lactic acid)/ starch blends with and without methylenediphenyl diisocyanate did not differ. Wang *et al.* [143] also studied the effect of starch moisture content on the interfacial interaction of an equal-weight blend of wheat starch and poly (lactic acid) containing 0.5% methylenediphenyl diisocyanate by weight. Starch moisture (10–20%) had a negative effect on the interfacial bonding between starch and poly (lactic acid). The tensile strength and elongation of the blend both decreased as starch moisture content increased. In blends of poly (lactic acid) /starch using dioctyl maleate as a compatibilizer markedly improved the tensile strength of the blend, even at low concentrations (below 5%). When dioctyl maleate functioned as a plasticizer at concentrations over 5%, significant enhancement in elongation was observed. Compatibilization and plasticization took place simultaneously according to the blends [144]. With dioctyl maleate as a polymeric plasticizer, thermal loss in the blends was not significant. Water absorption of

poly (lactic acid)/starch blends increased with dioctyl maleate concentration. Other compatibilizers were also studied for the starch/poly (lactic acid) blends, such as poly (vinyl alcohol) [145] and poly(hydroxyester ether) [146] it was added to a starch and poly (lactic acid) blend (50/50, w/w) to enhance compatibility and improve mechanical properties.

4.5. Reinforcing agent for polymer electrolytes for lithium batteries application

Ion-conducting solid polymer electrolytes have attracted considerable interest, because of their potential application in rechargeable batteries, fuel cells, light-emitting electrochemical cells, electrochromics, and many other electrochemical devices [147–149]. Cellulose crystallites in the form of microcrystalline cellulose are currently utilized widely industrially. In the nanocomposite field, cellulose whiskers can be used as mechanical reinforcing agents of low-thickness polymer electrolytes for lithium batteries application but, the filler content is generally relatively low, below 10 wt%, avoiding significant decrease of the ionic conductivity. Nanocomposite polymer electrolytes based on high-molecular weight poly (oxy ethylene) were prepared from high aspect ratio cellulose nanocrystalline whiskers and lithium trifluoromethyl sulfonyl imide. The main effect of whisker is thermal stabilization of the modulus of composites above the melting point of the poly (oxy ethylene)/lithium trifluoro methyl sulfonyl imide complexes. The filler provides a high reinforcing effect, while a high level of ionic conductivity is retained with respect to unfilled polymer electrolytes. So the ionic conductivity was quite consistent with the specifications of lithium batteries [150, 151].

To study the effect of cellulose whiskers on mechanical properties of nanocomposite an aqueous suspension of high aspect ratio rod-like cellulosic particles composed of tunicin whiskers and a poly (oxy ethylene) aqueous solution casted in a Petri dish. After water evaporation a solid composite film was obtained, the mechanical behavior of tunicin whiskers/poly (oxy ethylene) nanocomposites was evaluated in the linear range over a broad temperature range from dynamic mechanical analysis. The main effect of the filler was a thermal sta-

bilization of the storage modulus for the composites above the melting temperature of the poly (oxy ethylene) matrix. It was shown that the formation of the cellulosic network through inter-whiskers hydrogen bonds, assumed to be responsible for the high mechanical properties of the composites, was not affected by the matrix crystallization process and filler/poly (oxy ethylene) interactions [152]. The incorporation of liquid compounds like plasticizers into the polymer electrolytes improves the ionic conduction. It generally results from the decrease of glass transition temperature of the complex, the reduction of crystallinity, the increase of salt dissociation capability and the rise of charge carrier diffusions. However, a decrease in mechanical strength of the resulting polymer electrolytes is predictable. Different plasticizers were used to enhance the conductivity. Plasticizers generally consist of low molecular weight organic molecules like propylene carbonate, ethylene carbonate, dimethyl carbonate, dioctyl phthalate, etc. An efficient plasticizer must display several properties: miscibility with poly (oxy ethylene), low viscosity, low volatility, electrochemical stability and high capability to solvate lithium salts. Low molecular weight poly (ethylene glycols) have chemical structure similar to that of poly (oxy ethylene), are thermally stable and can solvate lithium salts. To obtain new nanocomposite polymer electrolytes with both improved mechanical properties and improved conductivities, Azizi *et al.* [153] studied, poly (oxy ethylene)-lithium trifluoromethyl sulfonyl imide-based polymer electrolyte with tetra(ethylene) glycol dimethyl ether as plasticizer and cellulose whiskers as nanometric filler. The plasticizer induces both a loss of mechanical stiffness in the rubbery state of poly (oxy ethylene) and an increase of the ionic conductivity of the electrolyte. For salt-free systems and polymer electrolytes based on poly (oxy ethylene), a high reinforcing effect was observed above T_g of poly (oxy ethylene) when adding a low amount of tunicin whiskers. In addition, the filler provides a thermal stabilization effect of the material above the melting of poly (oxy ethylene). Both phenomena were ascribed to the formation of a rigid cellulosic network within the matrix as well as the conduction performances were similar for unplasticized and unfilled electrolytes on the one hand and plasticized filled systems on the other hand. Therefore, the later allows

conciliating good ionic conductivities and high mechanical performances.

The processing of a composite polymer electrolyte from an aqueous suspension of cellulose whiskers is not easy to consider since water can react with the negative electrode and reduce the battery cycle life. On the other hand, cellulose whiskers are very difficult to disperse in a polymeric matrix as they have a large surface area and possess large hydrogen forces among themselves. It can lead to the formation of strongly bound aggregates. A surfactant can be used to disperse cellulose whiskers in a non-polar solvent [39, 54] like toluene. However, the large amount of surfactant necessary to maintain the stability of the suspension, due to the high specific area of the filler, prevents the use of this technique for composites processing in organic solvents. Another way is the surface chemical modification of cellulose whiskers to disperse cellulose whiskers in organic solvents [56] but, the mechanical performances of the resulting composites strongly decrease after chemical modification. Azizi *et al.* [21] prepared nanocomposite film reinforced with tunicin whiskers from a *N,N*-dimethylformamide as an organic solvent without a surfactant addition or a chemical surface modification. Both the high value of the dielectric constant of dimethyl formamide and the medium wettability of tunicin whiskers were supposed to control the stability of the suspension. The nanocomposite materials were prepared by UV cross-linking; with thermally stable photoinitiator, 4-(2-hydroxyethoxy)-phenyl-(2-hydroxy-2-propyl) ketone, using an unsaturated polyether as matrix.

Cross-linking is one of the most common methods used to disrupt polymer crystallinity and to ensure mechanical properties. It is classically performed to provide both low-temperature conductivity and high-temperature mechanical stability. In comparing the behavior of weakly cross-linked poly ether α,ω -dihydroxyoligo(oxyethylene) filled with tunicin whiskers suspended in *N,N*-dimethylformamide and the one of unfilled materials exhibiting different cross-linking density. The cellulosic nanofiller provided a much higher reinforcing effect at high temperature than the cross-linking process, a photoinitiator, 4-(2-hydroxyethoxy) phenyl-(2-hydroxy-2-propyl) ketone used as cross-linking agent. In addition, nanocomposite electrolytes display a higher ionic conductivity on the whole temperature range due to the high crosslinking density that

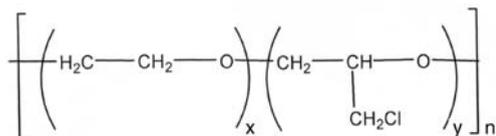


Figure 10. Chemical structure of ethylene oxide-epichlorohydrin copolymer

should be used for unfilled electrolytes in order to ensure satisfactory mechanical properties. It was also shown that tunicin whiskers seem to have no effect on the conduction mechanism of the polymer electrolyte. Therefore, the used cross-linked nanocomposite polymer electrolytes allow conciliating both higher ionic conductivities and higher mechanical performances [154]. Lithium perchlorate-doped nanocomposites of ethylene oxide-epichlorohydrin copolymers and cellulose whiskers can readily be produced by solution casting tetrahydrofuran/water mixtures comprising the components and subsequent compression molding of the resulting nanocomposites. Films of these materials display substantially improved mechanical properties, when compared to the not reinforced lithium perchlorate/ethylene oxide-epichlorohydrin (Figure 10), and their electrical conductivities experience comparably small reductions [90].

High performance solid lithium-conducting nanocomposite polymer electrolytes based on poly (oxyethylene) were prepared from high aspect ratio cellulosic whiskers and lithium trifluoro methane sulfonyl imide. The filler provided a high reinforcing effect while a high level of ionic conductivity was retained with respect to the unfilled polymer electrolytes [155, 156].

4.6. In biomedical

From a biological viewpoint, almost all of the human tissues and organs are deposited in nanofibrous forms or structures. Examples include: bone, dentin, collagen, cartilage, and skin. All of them are characterized by well organized hierarchical fibrous structures. In biomedical applications, for soft tissue replacement a developed material that will not only display similar mechanical properties as the tissue it is replacing, but also shows improved life span, biocompatibility, nonthrombogenic, and low degree of calcification needed. Hydrophilic bacterial cellulose fibers of an average diameter of 50 nm are produced by the bacterium *Acetobacter xylinum*, using a fermentation process.

They can be used in combination with poly (vinyl alcohol) to form biocompatible nanocomposites. Millon *et al.* [157] prepared poly (vinyl alcohol)/bacterial cellulose nanocomposites and they found that, the resulting nanocomposites possess a broad range of mechanical properties and can be made with mechanical properties similar to that of cardiovascular tissues, such as aorta and heart valve leaflets.

Silk fibroin-microcrystalline cellulose (cellulose whisker) composite films with varied compositions were prepared by casting mixed aqueous solution/suspensions of the two components. Silk fibroin was dissolved in lithium thiocyanate followed by dialysis; a cellulose whisker suspension was prepared by sulfuric acid hydrolysis of tunicate cellulose. Composite films showed improved mechanical strength at 20–30 wt% fibroin content, with breaking strength and ultimate strain about five times those of the constituent materials. From the observed shift in the infrared absorption bands of amide I and amide II of fibroin, the anomaly in the mechanical strength is considered to arise from the contact of fibroin with the highly ordered surface of cellulose whiskers. This phenomenon is not practicable for producing bulk materials because of the lengthy procedure of solubilization and dialysis involved, but may be useful in biomedical applications such as for cell culture media and implant materials, since both components are chemically inert and known to be compatible with living tissues [158]. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$)-bacterial cellulose as a novel class of nanocomposites were prepared by Wan *et al.* [159, 160]. The structure characterizing reveals that the crystallite sizes of the hydroxyapatite crystals are nano-sized and their crystallinities are low. The Fourier-Transformed Infrared spectroscopy results show that hydroxyapatite crystals are formed when the phosphorylated and CaCl_2 -treated bacterial cellulose fibers are soaked in a 1.5 simulated body fluid the hydroxyapatite crystals are partially substituted with carbonate, resembling natural bones. The nanocomposites containing hydroxyapatite with structural features close to those of biological apatites are attractive for applications as artificial bones. From the scheme, it is believed that the non-ionic hydroxyl groups on the unphosphorylated bacterial cellulose may firstly bind the calcium ions

through ionic-dipolar interaction, and then hydroxyapatite crystals grow around these trapped ions. The process is schematically displayed in Figure 11a. However, a different process is involved for the phosphorylated bacterial cellulose. As shown in Figure 11b, esterification takes place during phosphorylation and thus anionic phosphate groups are bonded to the cellulose chain through strong covalent bonds. The negatively charged phosphate groups are capable of trapping calcium ions, forming calcium phosphate complexes that act as nuclei of hydroxyapatite and hydroxyapatite grows by further complexation with phosphate ions in SBF as shown in Figure 11c. Note that the bonding between the calcium ions and bacterial cellulose chain is via strong ionic bonds for the phosphorylated bacterial cellulose while the calcium ions complexation with nonionic hydroxyl groups proceeds via ionic-dipolar interaction for the unphosphorylated bacterial cellulose (Figure 11a). An organic-mineral composite of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) nanoparticles and

carboxymethyl cellulose is synthesized via coprecipitation from a solution containing CaCl_2 , aqueous ammonia, $(\text{NH}_4)_2\text{HPO}_4$, and carboxymethyl cellulose. The hydroxyapatite nanoparticles are shown to form agglomerates about 200 nm in size. The interaction between the nanoparticles and carboxymethyl cellulose macromolecules leads to the formation of a pore structure potentially attractive for biomedical applications [161].

4.7. In papers industry

The pulp and paper industry is a materials industry. It provides materials for use in communications, packaging, consumer products, and other products. The intersection of wood fiber-based materials with nano-materials provides nearly unlimited opportunities for the pulp and paper industry to develop new products with enhanced functionality and greater value. Paper in itself provides an excellent platform for developing nano-material fiber composites for use in higher value printing, barrier packaging, and intelligent communications media. TiO_2 /cellulose nanocomposites were prepared through the titanyl sulphate hydrolysis in acidic medium in the presence of cellulosic fibers in specific experimental conditions, the cellulose fibers promote the nucleation and growth of TiO_2 particles, yielding hybrid materials containing up to 46% TiO_2 . Two series of paper handsheets having distinct TiO_2 content have been prepared, one from a selected hybrid composition and the other from mixtures of commercial TiO_2 and cellulose fibers. Comparative optical studies performed on the paper handsheets revealed a much higher opacity for the synthetic sample [162].

The pore structure of the cell wall of the never-dried pulp fibers has been identified as a general micropackaging or encapsulation system for a broad range of both organic and inorganic chemicals [163–166] these substances are entrapped in the cellulosic fiber matrix during the collapse of the cell wall pores as the pulp is dried [167]. Fahmy *et al.* [168] used sucrose as the nanoadditive to the mercerized non-dried cotton linter fibers. Relative to the sucrose-free paper, the sucrose-containing counterparts exhibit greater breaking length and remarkably high water uptake up to a sucrose content of 8–15% w/w.

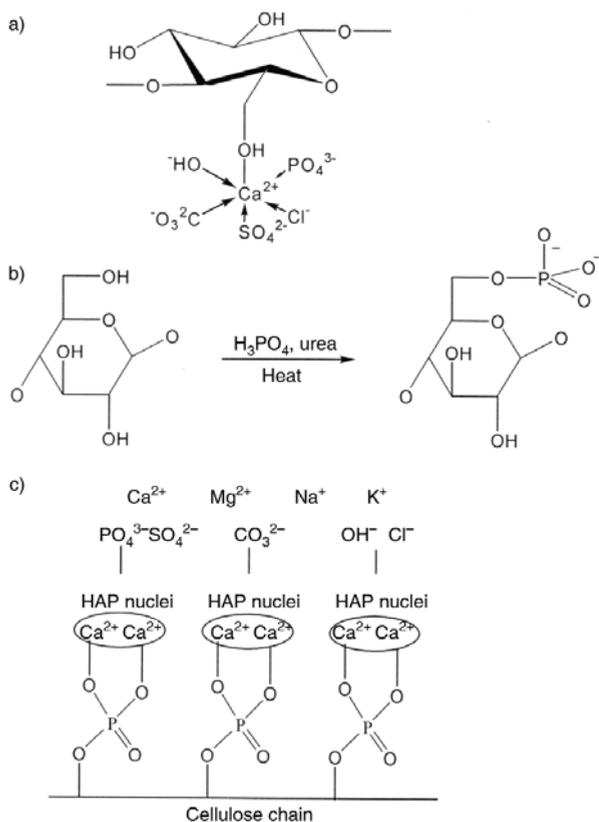


Figure 11. Schematic diagrams of various interaction processes. a) Hydroxyapatite growth on unphosphorylated bacterial cellulose, b) Phosphorylation of bacterial cellulose, c) Hydroxyapatite growth on phosphorylated bacterial cellulose (HPA = Hydroxyapatite)

4.8. In packing

In cellulose-based base material (e.g., copier paper or packing); a cellulose particles in nano-size range can be obtained from starting product containing cellulose (e.g., wood) by mixing with water; the mixture is heated, so that the product containing cellulose is hydrolyzed; the mixture then undergoes a shearing process giving base material and the base material is added to another solid- or liquid material-containing fiber substances [169]. On the other hand, biodegradable polymers such as starch [170, 171] poly (lactide) [172, 173] and poly (ϵ -caprolactone) [174–176] have attracted considerable attention in the packaging industry. In addition poly (lactic acid) is biodegradable thermoplastic polyester produced from L-lactic acid, which is derived from the fermentation of corn starch. Poly (lactic acid) is becoming increasingly popular as a biodegradable engineering plastic owing to its high mechanical strength and easy processability compared to other biopolymers [177]. It has gained enormous attention as a replacement for conventional synthetic packaging materials in the last decade [178] but the problem is the amount of transmitter light through the poly (lactic acid) sheet, for reducing this transmitter light, bentonite a layered silicate and microcrystalline cellulose chosen as nanoreinforcement for poly (lactic acid).

By comparing the mechanical, thermal and barrier properties of two different types of biopolymer based nanocomposites such as, bentonite a layered silicate and microcrystalline cellulose. The polymer matrix used was poly (lactic acid), a common available biopolymer. The bentonite nanocomposite showed great improvements in both tensile modulus and yield strength, while the microcrystalline cellulose nanocomposite only showed tendencies to improve the yield strength. There are a few factors that will help to explain these differences. First of all, the bentonite added to the poly (lactic acid)/bentonite material has theoretically twice the surface area of the added swelled microcrystalline cellulose. A larger surface area will allow 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 poly (lactic acid) and will therefore have better interaction with the poly (lactic acid) matrix. Good interaction

between the reinforcing phase and the matrix in a composite will allow for good stress transfer to take place in the composite. This gives rise to large improvements in the mechanical properties of the weaker matrix.

Also these two nanoreinforcements would affect poly (lactic acid) as a packaging material. The results showed a reduction in the oxygen permeability for the bentonite nanocomposite, but not for the microcrystalline cellulose nanocomposite. The amount of light being transmitted through the nanocomposites was reduced compared to pure poly (lactic acid) indicating that both nanoreinforcements were not fully exfoliated. [97].

4.9. Nanotechnology and wood as a building materials

Half of the wood products now used in construction are engineered wood composites. Nanotechnology will result in a unique next generation of wood-based products that have hyper-performance and superior serviceability when used in severe environments. They will have strength properties now only seen with carbon-based composites materials, and they will be both durable while in service and biodegradable after their useable service-life. Nanotechnology will also promote the development of intelligent wood- and biocomposite products with an array of nanosensors built in. Building functionality onto lignocellulosic surfaces at the nanoscale could open new opportunities for such things as self-sterilizing surfaces, internal self-repair and electronic lignocellulosic devices. The high strength of nanofibrillar cellulose together with its potential economic advantages will offer the opportunity to make lighter weight, strong materials with greater durability [5]. However, as in all markets, technology and shifting demographics give rise to hanging market demands. Materials and products used in housing construction are not immune to such changes. Because a home or a commercial building is typically the largest purchase a family will make and one of the larger investments a corporation will make, consumers want structures that maintain their value over time and are safe and secure, healthy, comfortable, long-lasting (durable), low maintenance, affordable (lower in cost and providing more value for the dollar), easily adaptable to new and modified architectural designs, and allow for personalized customization, have smart system

capabilities, and reduce costs for heating and air conditioning.

Wood-based construction materials function extremely well under a variety of end-use conditions. Under wet conditions, however, they can be prone to decay, mold, mildew, and insect attack. Wood can be protected from biodeterioration by treatments using toxic chemicals or by maintaining low moisture content in wood. Achieving control of moisture is a major opportunity for nanotechnology to aid in preventing biodeterioration of wood and wood-based materials. New non- or low-toxicity nanomaterials such as nanodimensional zinc oxide, silver, titanium dioxide, and even possibly clays might be used as either preservative treatments or moisture barriers. In addition, resistance to fire might be enhanced by use of nanodimensional materials like titanium dioxide and clays.

Composites allow an array of disparate materials with greatly differing properties to be engineered into products matched to end-user needs and performance requirements. For example, future nanocomposite construction materials may use combinations of wood, wood fiber, plastics, steel, and concrete. To achieve this, it will be necessary to be able to make hydrophilic materials compatible with hydrophobic materials such as wood and plastics [179].

5. Conclusions

Nanotechnology presents a tool to extend structural performance and serviceability by orders of magnitude. Nanotechnology will allow engineers and scientists to manipulate and systematically eliminate the formation of random defects that now dictate the properties, performance, and serviceability of biocomposites as known today. This new ability to minimize and eliminate naturally occurring and human-made internal defects will allow realizing the true potential of biomaterials. Nanotechnology will help the ability of manipulate and control fiber-to-fiber bonding at a microscopic level, and it will also offer an opportunity to control nanofibrillar bonding at the nanoscale. Nanocomposites will be the new frontier. So, understanding the synthesis-structure-property relationship of nanocomposites is vital for the development of advanced polymer nanocomposites with enhanced mechanical strength, stiffness and toughness for structural engineering applications.

In the nanocomposite field, cellulose whiskers can be used as mechanical reinforcing agents of low-thickness polymer electrolytes for lithium batteries application but, the filler content is generally relatively low, below 10 wt%, avoiding significant decrease of the ionic conductivity. But using aqueous suspension of cellulose whiskers is not easy to consider since water can react with the negative electrode and reduce the battery cycle life. On the other hand, a surfactant can be used to disperse cellulose whiskers in a nonpolar solvent like toluene. However, the large amount of surfactant necessary to maintain the stability of the suspension, due to the high specific area of the filler, prevents the use of this technique for composites processing in organic solvents. Another way is the surface chemical modification of cellulose whiskers to disperse cellulose whiskers in organic solvents but, the mechanical performances of the resulting composites strongly decrease after chemical modification. Nanocomposites reinforced with cellulose whisker suspended in organic solvent without surfactant addition or surface modification lead to high ionic conductivities and high mechanical performances.

Wood can be protected from biodeterioration by treatments using toxic chemicals or by maintaining low moisture content in wood. Achieving control of moisture is a major opportunity for nanotechnology to aid in preventing biodeterioration of wood and woodbased materials. New non- or low-toxicity nanomaterials such as nanodimensional zinc oxide, silver, titanium dioxide, and even possibly clays might be used as either preservative treatments or moisture barriers. In addition, resistance to fire might be enhanced by use of nanodimensional materials like titanium dioxide and clays.

Future nanocomposite construction materials may use combinations of wood, wood fiber, plastics, steel, and concrete. To achieve this, it will be necessary to be able to make hydrophilic materials compatible with hydrophobic materials such as wood and plastics.

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ABSTRACT Nanotechnology has applications across most economic sectors and allows the development of new enabling science. The ability to see materials down to nanoscale dimensions and to control how materials are constructed at the nanoscale is providing the opportunity to develop new materials and products in previously unimagined ways. This review covers the academic and industrial aspects of the preparation, characterization, material properties, crystallization behavior; melt rheology, and processing of polymer/cellulose or cellulose/cellulose nanocomposites. Cellulosic materials have a gr Download Citation on ResearchGate | Nanotechnology and its applications in lignocellulosic composites, a mini review | Nanotechnology has applications across most economic sectors and allows the development of new enabling science. The ability to see materials down to nanoscale dimensions and to control how materials are constructed at the nanoscale is providing the opportunity to develop new...Â Compared with plant cellulose, bacterial cellulose has found many applications in the biomedical field as tissue engineering materials due to their good biocompatibility, mechanical properties similar to those of hard and soft tissue and easy fabrication into a variety of shapes with adjustable interconnected porosity.