

Chapter 2

Cellulose Based Rubber Nanocomposites

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Abstract This chapter gives an introduction on the general aspects of cellulose, natural rubber and their bionanocomposites. A brief literature review on what has been done so far on the cellulose, natural rubber nanocomposites research area is also included in this chapter. This chapter also describes the structure, properties and characterization of cellulose as a biobased nanomaterial in natural rubber.

Keywords Cellulose • Natural rubber • Bionanocomposites

2.1 General Introduction

Bionanocomposites are nanocomposite materials where a biobased nano particle is incorporated in a biobased matrix. In true bionanocomposites, both the reinforcing material such as a natural fiber and the matrix are biodegradable and have the potential to replace current petrochemical-based materials. They represent an important element of future waste disposal strategies. Cellulose and chitin are the most abundant biomaterials in nature; they are also inexpensive, biodegradable and renewable and are sources of two most commonly used biobased nanomaterials viz. nanocellulose and nanochitin. They obviously receive a great attention for non-food applications. The use of natural fibers instead of traditional reinforcement materials, such as carbon, talc and glass fibers, gives several advantages such as low density, low cost, good specific biodegradability, reduced tool wear and mechanical properties. A variety of plant fibers with high tensile strength can be used including kenaf, industrial hemp, flax, jute, sisal, coir etc. Advantages of bionanocomposites

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over traditional composites are increased flexibility, reduced weight, reduced cost, greater moldability, sound insulation and renewable nature.

2.2 Cellulose

Cellulose was discovered in 1838 by the French Chemist Anselme Payen, who isolated it from plant matter and determined its chemical formula [1, 2]. Cellulose was used to produce the first successful thermoplastic polymer named celluloid, manufactured by the Hyatt Company in 1870. Hermann Staudinger had given the polymer structure of cellulose in 1920. The compound was first synthesized in 1992, without the use of any biologically-derived enzymes [3]. Cellulose is the most abundant natural biopolymer and is readily available from renewable resources. It is made of repeat units of the monomer glucose. This is the same glucose which in our body metabolizes in order to live, but we cannot digest it in the form of cellulose.

2.2.1 Structure and Properties

Hierarchical structure and chemical structure of cellulose given in Figs. 2.1 and 2.2 respectively. From the figures, it can be seen that cellulose is a homopolymer of

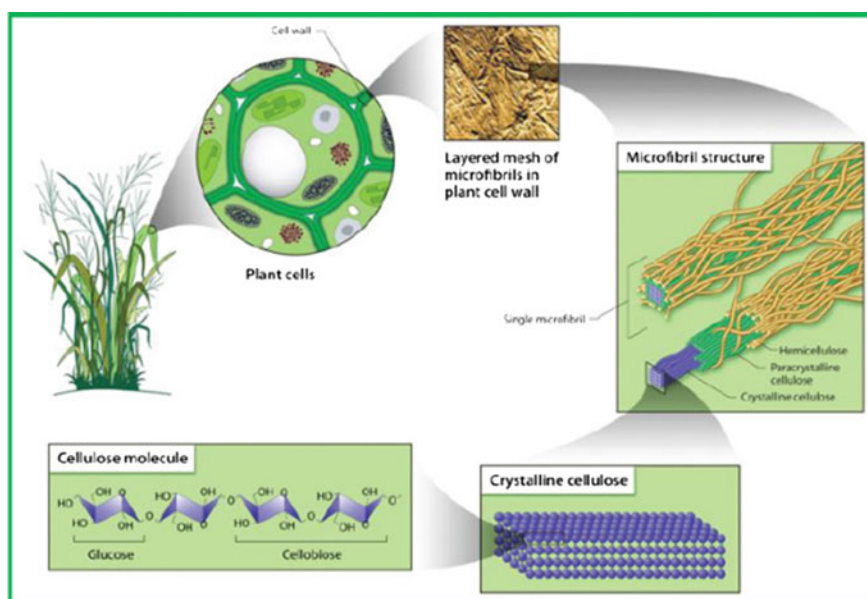


Fig. 2.1 Hierarchical structure of cellulose [9]

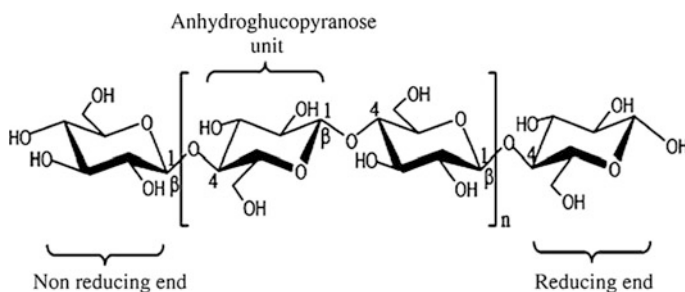


Fig. 2.2 Chemical structure of cellulose [10]

D-anhydroglucopyranose monomeric units connected through $\beta(1-4)$ glycosidic linkages. In general, it can be seen as a long chain polymer with D-glucose, a sugar, as its repeating units. Since the glucose units are 6 member rings within cellulose chain, they are called pyranoses. The glucose units in cellulose polymer are referred to as anhydroglucose units. Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide with linear chain of several hundred to over ten thousand $\beta(1-4)$ linked D-glucose units [1, 4]. Often in nature, cellulose is associated and mixed with other substances such as pectins, lignin, hemicelluloses, proteins and fats. Cellulose produced by plants, is found in two crystalline forms, cellulose I and cellulose II [5–8]. Among the four different crystalline polymorphs such as I, II, III, and IV, cellulose I is thermodynamically not stable while cellulose II is the most stable structure. Liquid ammonia treatment of cellulose I and cellulose II gives crystalline cellulose III form and the heating of cellulose III generates cellulose IV crystalline form. Recently a non crystalline form known as nematic ordered cellulose has been described. Highly ordered crystalline cellulose is produced from a solution in lithium dimethylacetamide.

The $\beta(1-4)$ glycosidic linkage gives cellulose the linearity that results in a rigid rod-like molecule. This position makes them readily available for intramolecular and intra-strand hydrogen bonding. The hydrogen bonds cause the chains to group together in highly ordered crystal-like structure and hold the network flat. In the crystalline region of the cellulose, the extensive and strong inter-chain hydrogen bonds give the resultant fibers good strength and insolubility in solvents. This prevents cellulose from melting at elevated temperatures. Orderless regions, the chains are different and more available for hydrogen bonding to other molecules, example water. The cellulose structures can absorb large quantities of water and is thus very hygroscopic. As a result, cellulose swells, but does not dissolve in water. Cellulose is the structural component of the primary cell wall of green plants, many forms of algae. Some species of bacteria secretes it to form biofilms. About 33% of all plant matter is cellulose (the cellulose content of cotton is 90% and that of wood is 50%) [11]. In addition to cellulose, plant fibers contain different natural substances mainly hemicelluloses, lignin, pectins and waxes [12, 13].

Cellulose derived from plant is unpurified cellulose associated with other kinds of natural polymers like lignin and hemicellulose while bacterial cellulose (BC) is nearly purified cellulose. Cellulose is considered as a nearly inexhaustible raw material with fascinating structures and properties for the remarkable demand for environmentally friendly and biocompatible products. As is well known, cellulose is insoluble in many solvents, which leads to a limitation in its reactivity and processability for utilization. Natural cellulose fibers are gaining attention as a reinforcing phase in thermoplastic matrices [14–16]. Its low density, highly reduced wear of the processing machinery and relatively reactive surface may be mentioned as attractive properties, together with their low price and abundance. Nevertheless, such fibers are used only to a limited extent in industrial practice, this may be explained by very difficulties in achieving acceptable dispersion levels. The reinforcing ability of the cellulose whiskers lie in their high surface area and good mechanical properties [17, 18]. However, to obtain a significant increase in material properties the whiskers should be well separated and evenly distributed in the matrix material. Different processing methods aided with a variety of chemicals (compatibilizers, surfactants, etc.) have been explored to fulfill these requirements [19].

2.2.2 Preparation of Cellulose Nanofibers

Cellulose nanofibres (CNF) were obtained through mechanical fibrillation of bamboo pulp. The pulp was dispersed homogeneously in distilled water using a laboratory shear mixer. In this experiment fibrillation was done using contact mode grinding, where the final gap between the stones (from 0-point) was further decreased by 10 μm during the grinding. The grinding speed was approximately 3600 rpm and the total processing time was around 20 min.

Cellulose fibers are fibers that are still recognizable as being from a part of the original plant because they are only processed as much as needed to clean the fibers for use. For example, cotton fibers look like the soft fluffy cotton balls that they come from. Linen fibers look like the strong fibrous strands of the flax plant. All “natural” fibers go through a process where they are separated from the parts of the plant that are not used for the end product, usually through harvesting, separating from chaff, scouring, etc. these fibers are more larger than whiskers. The schematic representation of the cellulose fibre is shown in Fig. 2.3.

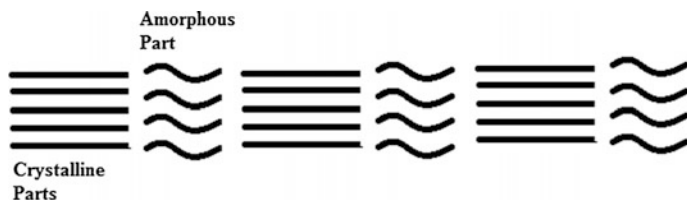


Fig. 2.3 Schematic representation of the nano cellulose fibre

2.2.3 Preparation of Cellulose Whiskers

The elementary crystallites are often referred to as cellulose nanowhiskers, whiskers, nanocrystals, nanofibers, microcrystallites, or microcrystals. Hereafter, they will be called “whiskers”. Currently, whiskers (diameter 20–40 nm) are being extensively investigated in both research and industry, because of the abundance and renewable nature of cellulose, and the outstanding mechanical properties of cellulose nanocrystals. Due to its high elastic modulus (134 GPa), these cellulose nanocrystals are suitable as reinforcement in nanocomposites [20]. Whiskers constitute a generic class of materials having mechanical strength equivalent to the binding forces of adjacent atoms. The resultant highly ordered structure produces not only high strength but also significant changes in electrical, optical, magnetic, ferromagnetic, dielectric, conductive, and even superconductive properties. The schematic representation of the nano cellulose whiskers is shown in Fig. 2.4

Very recently many scientists have prepared nanowhiskers from different sources such as kraft pulp [21], bacterial cells [22], sisal [23], ramie [24], cotton [25] wheat straw [25], bacterial cellulose [26, 27], sugar beet [28], as well as sea animals called tunicin [29, 30]. Typical procedures currently employed for the production of cellulose whiskers consist of subjecting pure cellulosic material to strong acid hydrolysis under strictly controlled conditions of temperature, agitation, and time. The amorphous regions are preferentially hydrolyzed, whereas crystalline regions remain intact under an acid attack because they have a higher resistance to acid attack than amorphous regions [31, 32]. The nature of the acid and the acid-to-cellulosic fibers ratio are also important parameters that affect the preparation of cellulose whiskers. The differences in the kinetic of hydrolysis between amorphous and crystalline regions produce the acid cleavage event. The hydrolysis carried out over the amorphous regions, produces rod-like crystals called “whiskers”. Acid hydrolysis of native cellulose induces a rapid decrease in its degree of polymerization (DP). The DP subsequently decreases much more slowly, even during different hydrolysis experiment times [33–35]. The suspension is subsequently diluted with water and washed with successive centrifugations method. Dialysis method against distilled water is then performed to remove any free acid molecules from the dispersion. Additional steps such as filtration [36], differential centrifugation [37], or ultracentrifugation (using a saccharose gradient) have been also reported [38]. These whiskers are homogeneous crystallites. This is confirmed



Fig. 2.4 Schematic representations of the nano cellulose whiskers

by X-ray crystal diffraction [39], electron microscopy with iodine-staining [39], small-angle X-ray diffraction [34] and neutron diffraction analyses [40].

The stability of these suspensions depends on the dimensions of the dispersed particles, their size polydispersity and surface charge. Different acids have been used as solvents for dissolution of cellulose. Sulfuric and hydrochloric acids have been extensively used for whisker preparation, but phosphoric and hydrobromic acids have also been reported for such purposes. When whiskers are prepared by hydrolysis in sulfuric acid, they tend to remain dispersed in water, due to the fact that sulfuric acid reacts with the surface hydroxyl groups of cellulose to yield charged surface sulfate esters that promote their dispersion.

Ultrasonic treatments [41] have the potential to change the morphology of the whiskers formed. When hydrolysis is carried out under ultrasonic treatment, a combination of both sulfuric and hydrochloric acids during the hydrolysis appears to generate spherical cellulose nanocrystals instead of rod like nanocrystal which are the typical morphology of whiskers. These spherical cellulose nanocrystals show better thermal stability mainly because they possess fewer sulfate groups on their surfaces [42]. In order to obtain whiskers, the concentration of sulfuric acid in hydrolysis reactions has a typical value of 65 wt%. However, the temperature can range from room temperature to 70 °C and the corresponding hydrolysis time can be varied from 30 min to overnight depending on the temperature. Dong et al. [43] have investigated the influence of hydrolysis time on the length of cellulose whiskers and their surface charge. They reported a decrease in the whiskers length and an increase in their surface charge with prolonged hydrolysis time. Beck-Candanedo et al. [44] have investigated the reaction time and acid to pulp ratio on whiskers obtained by sulfuric acid hydrolysis of bleached softwood sulfite pulp. The results showed that shorter nanocrystals with narrow size polydispersity were produced at longer hydrolysis time.

2.2.4 Characterization of Cellulose Nanowhiskers

Geometrical characteristics of cellulose whiskers depend on the origin of cellulose microfibrils and on the conditions of the acid hydrolysis process such as time, temperature, and purity of materials. The length (L) and lateral dimension (D) of cotton whiskers were around 200 and 5 nm, respectively (ratio $L/D = 40$). The length and lateral dimension of tunicin whiskers were reported to be around 1000 and 15 nm, respectively (ratio $L/D = 67$).

Table 2.1 list the geometrical properties of several cellulose whiskers as well as the technique used for their study. However, AFM topography may show rounded cross sectional profiles in cases where other shapes are expected. For instance, AFM imaging of valonia whiskers showed different shape than the square shaped cross section observed under TEM images.

Terech et al. [45] reported the use of Small-angle (Neutron and X-ray) scattering techniques to determine the precise shape of tunicin whiskers. They demonstrated

Table 2.1 Geometrical characteristics, length and width, of cellulose nanocrystals from different origin [21–30]

Source	Length (nm)	Width (nm)	Technique
bacteria	100–1000	5–50	TEM
cotton	70–300	5–15	TEM, DDLS ^a , AFM
Cotton linter	25–500	6–70	FEG-SEM ^b , TEM, AFM
ramie	50–250	5–10	TEM.
sisal	100–500	3–6.5	TEM
tunicate	100–1160	8.8–28	SANS ^c , DDLS, TEM
valonia	>1000	10–20	TEM
Soft wood	100–200	3–5	TEM, AFM
Hard wood	140–150	4–5	AFM
MCC	35–270	3–48	TEM

^aDDLS Depolarized dynamic light scattering^bFEG-SEM Field emission gun scanning electron microscopy^cSANS Small angle neutron scattering

that the cross sectional shape of these rigid whiskers was rectangular with a calculated value close to $88 \times 182 \text{ \AA}$. In addition, cellulose samples can be characterized by its degree of crystallinity. The crystalline regions of cellulose are characterized by an orderly arrangement of molecule chains and are assessed from wide-angle X-ray scattering (WAXS) patterns or from the evaluation of a ^{13}C CP-MAS NMR spectrum. Tashiro and Kobayashi [46] calculated the three dimensional elastic constants for native and regenerated cellulose perfect crystal. The theoretical values of Young's modulus along the chain axis were 167.5 and 162.1 GPa, respectively. Sturcova et al. [47] reported measurements of the elastic modulus of tunicin whiskers using a Raman spectroscopy technique. The glass transition temperature (T_g) of cellulose reinforced composites is an important parameter which influences different properties of the resulting composite such as mechanical behavior, matrix chains dynamics and swelling behavior.

2.2.5 Nanocomposites of Cellulose Nanowhiskers

Natural cellulose fibers such as cotton, ramie, etc. have been used in the garment industry as blends. These blends have their own distinctive properties that are affected by the fiber sources, the proportion of fibers blended and the processing techniques. Mayer et al. [48] prepared blends with cellulose acetate and starch using a melt processing technique. The results showed that cellulose acetate/starch blends have acceptable properties for injection-molded applications and that they are biodegradable and nontoxic. Silk fibroin (*Bombyx mori*)/cellulose blend films have also been studied. The mechanical properties showed that both strength and elongation at break of silk fibroin films were improved by blending with cellulose [49].

Industrial thermoplastics manufacturing techniques have been explored to prepare natural fiber reinforced composites. Torres and Diaz [50] adapted conventional thermoplastic processing techniques such as extrusion, compression and rotational molding in order to manufacture natural fiber reinforced polymers. They used natural lignocellulosic fibers such as sisal, jute and cabuya to reinforce polyethylene and starch matrices [51–55]. Grande and Torres [55] have prepared lignocellulosic fiber reinforced composites using a single screw extruder. The polymer matrix employed was polyethylene. Jute and sisal were used as reinforcement with initial lengths varying from 5 to 10 mm. The results showed that at higher processing temperatures, the fibers were more aligned in the flow direction. In the extrusion process, one disadvantage is the presence of bubbles which affect the quality of the extruded rods. A way of controlling the formation of bubbles is by pretreating the fibers.

The main disadvantages of cellulose are their hydrophilic nature, high moisture absorption and limited thermal stability. The hydrophilic nature of lingo cellulosic fibers leads to poor interfacial adhesion and dispersion in olefinic thermoplastic matrix materials [56]. The high moisture absorption promotes dimensional instability of composites [57]. In order to avoid this issue, modification of cellulose fibers by esterification has been used. Torres et al. [58] have assessed the interfacial properties of lignocellulosic reinforced composites prepared with untreated fibers and with fibers treated with stearic acid. Interfacial shear strength was measured by a single fiber fragmentation test. The limited thermal stability determines low permissible temperatures of processing. The processing temperature for cellulose based reinforced composites is limited to around 200 °C, in higher temperature can be used for short periods of time [59]. Other properties such as thermal conductivity and water absorption have been studied in fiber reinforced composites. The cellulose based materials that are used as nanoreinforcements are cellulose nanocrystals (i.e. whiskers and nanospheres), nanofibrillated cellulose, regenerated cellulose nanoparticles and electrospun nanofibers. A wide range of polymer matrices have been used to form cellulose nanocomposites. Synthetic polymers such as polypropylene, poly(vinyl chloride) (PVC) [60], waterborne epoxy [61], waterborne polyurethane [62], polyurethane [63], poly-(styrene-co-butyl acrylate) [64], polysiloxanes [65], cellulose acetate butyrate [66, 67], poly(caprolactone) [68], poly(vinyl alcohol) [69] and poly(vinyl acetate) [70]. Different biopolymers such as soy protein [71], chitosan [72], regenerated cellulose [73], silk fibroin [74], poly(hydroxyoctanoate) [75] have also been used as matrices. Siqueira et al. [76] prepared cellulose nanocomposites to reinforce polycaprolactone (PCL) matrix. As reinforcement, they used two kinds of nanoscale fillers, nanowhiskers and microfibrillated cellulose, both extracted from sisal. They found significant differences according to the nature of the nanoparticle and amount of nanofillers used as reinforcement.

The cellulose whiskers having an average length of 1.2 mm and diameter of 90 μm . The incorporation of cellulose whiskers into the Soy protein isolated (SPI) matrix led to an improvement in the water resistance of SPI composites. The addition of cellulose whiskers promoted strong interactions between whiskers

and the SPI matrix. The effect of whiskers on the mechanical properties exceeded conventional predictions from traditional classical models applied to filler-reinforced nanocomposites such as the Halpin—Kardos model. Flandin et al. [77] prepared nanocomposites containing cellulose whiskers that were coated with a conductive polypyrrole. They measured their electrical properties and found strong interactions between fillers. Factors such as the nature of polymer matrix and the surface energy of the whiskers showed an influence on the formation of this network. Gea et al. [78] prepared biocomposites based on bacterial cellulose (BC) and apple and radish pulp. The bacterial cellulose films formed by a network of cellulose nanofibers were disintegrated to be used as reinforcement in order to produce biocomposites sheets with apple and radish pulp. This nanosize disintegrated BC fibers were blended with apple and radish pulp in the wet state and then hot pressed to produce paper-like sheets. The results showed that the organic matrices such as apple and radish pulp are heavily reinforced with BC. For pure apple and radish pulp, the Young's modulus was around 4.5 GPa while BC reinforced sheets reached values as high as 6.5 GPa. Nishino et al. [79] prepared “all-cellulose” composites, in which both the fibers and the matrix were cellulose. This composite was manufactured using a wet process by controlling the solubility of cellulose through pretreatment conditions. The cellulose self-reinforced composite showed excellent mechanical and thermal properties such that this composite can be used as an alternative of glass-fiber-reinforced composites. Fiber pretreatment enhances the molecular diffusion across the fiber-matrix interface, obtaining improved transverse mechanical properties of the composite.

Gindl and keckes [80] prepared cellulose based nanocomposite films with different ratio of cellulose I and II, The process consist of a partial dissolution of microcrystalline cellulose powder in lithium chloride/N,N-dimethylacetamide and film made by casting. This nanocomposite films were transparent to visible light and of high strength and stiffness with regard to comparable cellulosic materials and they are easily recyclable and biodegradable as well.

2.2.6 Manufacturing Techniques of Nanocellulose Based Composites

2.2.6.1 Casting-Evaporation Processing

Casting evaporation techniques have been extensively used to transfer cellulose whiskers from an aqueous dispersion into an organic polymer matrix. Nanocomposites films are formed via solution casting, allowing the solvent to evaporate. Two steps are used to prepare nanocomposites films. The first step consists of mixing an aqueous suspension of cellulose nanostructures with dispersed or solubilized polymer matrix. Homogeneous suspensions are obtained by magnetic stirring at room temperature or by using an autoclave reactor for mixing at high

temperatures. The suspensions are generally degassed under vacuum to remove air. Then, the mixture is casted on the Petri dish (e.g. Teflon or propylene dishes) and put in a drying oven under vacuum. An increase of temperature allows the solvent evaporation and the film formation.

2.2.6.2 Sol—Gel Processing [81, 82]

Sol—Gel processing is based on the formation of a three dimensional template of well individualized cellulose whiskers which is filled with a polymer. The first step in this process is the formation of a cellulose nanostructure template. This involves the formation of an aqueous cellulose nanostructures dispersion which is converted into a gel through solvent exchange with a water miscible solvent (e.g. acetone). In the second step, the cellulose nanostructures template is filled with a matrix polymer by immersing the gel into a polymer solution. This polymer solvent must be miscible with the gel solvent and does not disperse the cellulose nanostructures. Polymer solvent must be miscible with the gel solvent and does not disperse the cellulose nanostructures.

2.2.6.3 Melt Compounding Processing [83]

Very few studies have been reported concerning the processing of polysaccharide nanocrystal-reinforced nanocomposites by melt extrusion processing. The hydrophilic behavior of polysaccharides causes irreversible agglomeration during drying and aggregation in non-polar matrices because of the formation of additional hydrogen bonds between amorphous parts of the nanoparticles. In the preparation of cellulose whiskers reinforced poly lactic acid (PLA) nanocomposites by melt extrusion was carried out by pumping the suspension of nanocrystals into the polymer melt during the extrusion process. An attempt to use poly vinyl alcohol (PVA) as a compatibilizer to promote the dispersion of cellulose whiskers within the PLA matrix was reported [84]. Orts et al. [85] extruded starch plastics reinforced with cotton whiskers, which showed 5 times of increment Young's modulus relative to a control sample with no cellulose reinforcement. Organic acid chlorides-grafted cellulose whiskers were extruded with low density poly ethylene (LDPE) [86]. The homogeneity of the ensuing nanocomposite was found to increase with the length of the grafted chains.

2.2.6.4 Electrostatic Fiber Spinning (Electrospinning)

This method allows preparing fibers with diameters ranging from several micrometers down to 100 nm through the action of electrostatic forces. It uses a high electrostatic potential applied to a spinning liquid across a charged nozzle and

a grounded collector screen. In these conditions, a charged stream of the spinning liquid is ejected and ultimately a mat of non-woven fibers is collected on the collector. Electrospinning processes has been used to prepare nanocomposite fiber mats. In order to prepare nanocomposite fiber mats, mixtures containing the polymer solution and cellulose whiskers solution are placed in the appropriated electrospinning. Peresin et al. [87] have produced nanocomposite mats of poly (vinyl alcohol) (PVA) reinforced with cellulose nanocrystals using this electrospinning technique. Smooth nonwoven mats with homogeneous nanofibers were obtained. Park et al. [88] have also incorporated cellulose whiskers into nanofibers of polyethylene oxide (PEO) by the electrospinning process.

2.2.6.5 Layer-by-Layer (LBL) Electrostatic Assembly

Layer-by-layer assembly (LBL) is able to produce nanometer-scale multi-layered materials in order to improve highly desirable properties including mechanical, chemical, electrical, thermal, magnetic and optical. Highly charged polyelectrolytes can produce charge reversal upon adsorption on the oppositely-charged substrate. In consequence, when the substrate is exposed to a second solution containing polyelectrolytes of opposite charges, an additional layer is adsorbed on the first layer, thereby forming a second layer. These steps can be repeated cyclically to form multilayer structures on a given substrate. The use of the LBL technique is expected to maximize the interaction between cellulose whiskers and a polar polymeric matrix. It also allows the incorporation of cellulose whiskers with a dense and homogeneous distribution in each layer. De Mesquita et al. [89] obtained a biodegradable cellulose nanocomposite from layer-by-layer (LBL) technique. This nanocomposite was composed of highly deacetylated chitosan and eucalyptus wood cellulose nanowhiskers. They claimed that the driving forces for the growth of the multilayered films were the hydrogen bonds and electrostatic interactions between the negatively charged sulfate groups on the whisker surface and the ammonium groups of chitosan. Their results showed that cellulose nanowhiskers adsorbed on each chitosan layer presented high density and homogeneous distribution and the average thickness of a single bilayer was found to be 7 nm. Podsiadlo et al. [90] reported the preparation of cellulose whiskers multilayer composites with a polycation, poly-(dimethyldiallylammonium chloride) (PDDA) using the LBL technique. The average thickness of a single bilayer was found to be 11 nm and the multilayer films revealed uniform coverage and densely packed cellulose crystal surface. Cranston et al. [91] reported the orientation of the cellulose nanocrystals layer adsorbed onto poly(allyl)amine hydrochloride (PAH) coated silicon surface after long exposure to a strong magnetic field.

2.2.6.6 Bottom-up Manufacture of Bacterial Cellulose Nanocomposites

Grande et al. [92] developed a technique for the production of self assembled bacterial cellulose nanocomposites. This technique is based on the natural bottom-up process found in the synthesis of bacterial cellulose (BC). For instance, BC-starch nanocomposites were prepared by this technique. Starch was gelatinized in different stages and formed a layer that covers cellulose nanofibrils. The BC-starch gel formed was hot pressed into sheets. As a consequence, starch was forced to further penetrate into the BC network. Nanocomposites produced by this technique showed a high volume fraction (around 90%) of a strong phase of BC nanofibers covered by a starch phase. This technique has the advantage to be extended for the addition of other materials into the BC network e.g. BC-hydroxyapatite nanocomposites [93]. Nanocomposites produced with this technique could have a variety of potential biomedical applications.

Zimmermann et al. [94] have used cellulose fibrils obtained from sulphite wood pulp to reinforce water soluble polymers such as polyvinyl alcohol (PVA) and hydroxypropyl cellulose (HPC). The mechanical properties of these nanocomposites were measured by tensile tests showing that the addition of fibrils increase the modulus of elasticity (E) up to three times and the tensile strength up to five times compared to the raw polymer. Zimmermann et al. [95] have determined the 'E' values and the hardness of cellulose/HPC nanocomposites using nanoindentation technique. The results showed that the E values measured by nanoindentation were from two to three times higher than the E values measured by means of tensile tests. Stauss et al. [96] have explained that differences between tensile test and indentation results are due to the fact that they do not test the same material volumes and regions.

2.2.7 Applications of Cellulose Based Blends, Composites and Nanocomposites

Natural cellulose fibers such as cotton, ramie, etc. have been used as blends for textile applications. High modulus regenerated cellulose fibers are produced on a commercial scale. For instance, Lyocell®, a high performance cellulosic fiber, has been used in many nonwoven applications because of its high strength, durability, absorbency, purity and biodegradability. Lyocell® fibers have been explored in blends. Chang et al. [97] prepared Lyocell® based blends. Poly (vinyl alcohol) (PVA), poly(acrylic acid-co-maleic acid) (PAM) and poly(vinyl alcohol-co-ethylene) (EVOH) were used as fillers in blends with lyocell produced through solution blending. The results showed that blends with PVA exhibit the best tensile properties. Thus, Lyocell® fibers have recently been used as reinforcement for thermoplastic fiber composites.

Bacterial cellulose has been used for the production of scaffolds for tissue engineering [98]. Andersson et al. [99] prepared engineered porous BC scaffolds by fermentation of *Acetobacter xylinum* in the presence of slightly fused wax particles with a diameter of 130–300 μm , which were then removed by extrusion. In this research, human chondrocytes were seeded onto the porous BC scaffolds and the results showed that cells entered the pores of the scaffolds and that they increasingly filled out the pores overtime. The proliferation of human chondrocytes within the porous BC was observed as well. Samir et al. [100] have studied the possibility to reinforce thin films of polymer electrolytes for lithium battery applications. They reinforced polyoxyethylene with tunicate whiskers. The results showed that the storage modulus and temperature stability was greatly improved, and the ionic conductivity was maintained. Yano et al. [101] obtained polymer resins reinforced with bacterial cellulose nanofibers. This flexible plastic composite maintains the transparency of the original resin even at high fiber contents (70 wt%). This composite has interesting technical properties such as low thermal expansion coefficients ($6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), mechanical strength 5 times higher than the one of engineered plastics (Young's modulus of 20 GPa and tensile strengths reaching 325 MPa) and high transparency. Bacterial cellulose has a wide range of potential biomedical applications such as wound dressing [102–104] artificial skin [105], dental implant, vascular grafos, coatings for cardiovascular stents, cranial stents, membranes for tissue-guided regeneration, controlled-drug release carriers, vascular prosthetic devices [106] and artificial blood vessels [107–109].

Cellulose nanofibers from different sources have showed remarkable characteristics as reinforcement material for optically transparent composites [110, 111]. Nystrom et al. [112] have produced a nanostructured high surface area electrode material for energy storage applications. The high surface area and good electronic conductivity of this composite made it suitable for use in electrochemically controlled ion-exchange [113–115] and ultrafast all polymer-based batteries. These investigations open up new possibilities for the production of environmentally friendly, up-scalable, cost efficient, and lightweight energy storage systems. Podsiadlo et al. [116] have prepared layer-by-layer assembled films of cellulose nanowires extracted from tunicate. These films showed strong antireflection properties due to porous architecture created by randomly-oriented overlapping nanowires. In addition to their antireflection properties, the remarkable mechanical properties of tunicate nanowires make films suitable for optical coatings.

In addition, the application of the nanopaper-making strategy to cellulose/inorganic hybrids demonstrated the potential for “green” processing of new types of nanostructured functional materials. Bacterial cellulose (BC) membranes have been used as flexible substrates for the fabrication of Organic Light Emitting Diodes (OLED). Indium tin oxides were deposited onto the membrane using sputtering technique to improve conductive properties [117]. Van den Berg et al. [118] have prepared nanocomposites of semi conducting polymers reinforced with tunicate cellulose whiskers with a typical diameter or around 20 nm. The results showed that the nanocomposites synergistically combine the electronic characteristic of the conjugated polymers with the improved mechanical properties of the cellulose

scaffold. Other studies suggest that cellulose whisker can be used for electrical applications such as the creation of circuitry in a special kind of smart paper [119]. Shin and Exarhos [120] have prepared porous Titania by using a template process with cellulose nanocrystals. A colloid suspension of cellulose nanocrystals was added into titanium (IV) bis(ammonium lactate) dihydroxide (Tyzor-LA) to form a Tyzor-LA-cellulose nanocrystals composite. Cellulose nanofibrils are also used to prepare cellulose nanopaper structures of remarkable properties such as high toughness [121]. Large, flat, smooth and optically transparent cellulose nanopaper structures have been developed using several techniques.

References

1. R.L. Crawford, *Lignin biodegradation and transformation* (Wiley, New York, 1981). ISBN 0-471-05743-6
2. R. Young, *Cellulose structure modification and hydrolysis* (Wiley, New York, 1986). ISBN 0471827614
3. D. Klemm, H. Brigitte, F. Hans-Peter, B. Andreas, *ChemInform* **36**, 36 (2005)
4. D.M. Updegraff, *Anal. Biochem.* **32**, 420–424 (1969)
5. S. Kuga, R.M. Brown, *Carbohydr. Res.* **180**, 345–350 (1988)
6. K.R.Z. Andress, *J. Phys. Chem. B* **190**, 38 (1929)
7. Y. Habibi, L.A. Lucia, O.J. Rojas, *Chem. Rev.* **110**, 3479–3500 (2010)
8. H. Chanzy, Y. Nishiyama, P. Langan, *J. Am. Chem. Soc.* **121**(43), 9940–9946 (1999)
9. <http://www.treehugger.com/clean-technology/the-long-road-to-cellulosic-ethanol-zymetis-takes-another-stab-with-bacterial-enzyme-mixes.html>
10. <http://chemistry.about.com/od/factsstructures/ig/Chemical-Structures—C/Cellulose.htm>
11. E. Togawa, R.M. Brown, T.J. Kondo, *Biomaterials* **2**(4), 1324–1330 (2001)
12. A.K. Bledzki, S. Reihmane, J. Gassan, *J. Appl. Polym. Sci.* **59**, 1329–1336 (1996)
13. K.G. Satyanarayana, K. Sukumaran, P.S. Mukherjee, C.P. Pavitharan, *Cement Concr. Compos.* **12**, 117–136 (1990)
14. C. Klason, J. Kubat, H.E. Stromvall, *Int. J. Polym. Mater.* **11**(1), 9–38 (1985)
15. P. Zadorecki, A.J. Michell, *Polym. Compos.* **10**(2), 69–77 (1989)
16. D. Maldas, B.V. Kokta, R. Raj, G.C. Daneault, *Polymer* **29**(7), 1255–1265 (1988)
17. M. Grunert, T.W. Winter, *J. Polym. Environ.* **10**(1), 27–30 (2002)
18. K. Tashiro, M. Kobayashi, *Polymer* **32**(3), 454–463 (1991)
19. A.M.A.S. Samir, F. Alloin, A. Dufresne, *Biomacromolecules* **6**, 612–626 (2005)
20. I. Sakurada, Y. Nukushina, T. Ito, *J. Polym. Sci.* **57**, 651–660 (1962)
21. Rajalaxmi, Dash, F. Marcus, J.R. Arthur, *Carbohydr. Polym.* **91**, 2, 638–645 (2013)
22. M.S. Marta, A.A. Mohamed, M.L. Jose, C. Emo, G.W. Tina, F.W. Delilah, J.O. William, H. I. Syed, *Eur. Polym. J.* **13**, 61–70 (2013)
23. N.L.G. de Rodriguez, W. Thielemans, A.J. Dufresne, *Cellulose* **13**, 261–270 (2006)
24. M. El-Sakhawy, M. Hassan, *Carbohydr. Polym.* **67**, 1–10 (2007)
25. Jin, Gu, M.C. Jeffrey, Q.K. Edward, D.A. Douglas, *Carbohydr. Polym.* **92**, 2, 1809–1816 (2013)
26. D. Bondeson, A. Mathew, K. Oksman, *Cellulose* **13**, 171–180 (2006)
27. M. Stromme, A. Mihranyan, R. Ek, *Mater. Lett.* **57**, 569–572 (2002)
28. A. Dufresne, J.-Y. Cavallé, M.R. Vignon, *J. Appl. Polym. Sci.* **64**, 1185–11894 (1997)
29. M.D. James, F.C. Richard, E.G. Julie, J.E. Stephen, *Anal. Biochem.* **9**(1), 4707–4715 (2013)
30. V. Favier, R. Dendievel, G. Canova, J.-Y. Cavaille, P. Gilormini, *Acta Mater.* **45**, 1557–1565 (1997)

31. M.N. Anglès, A. Dufresne, *Macromolecules* **34**, 2921–2931 (2001)
32. M.M. Ruiz, J.Y. Cavaille, A. Dufresne, J.F. Gerard, C. Graillat, *Compos Interface* **7**, 117–131 (2000)
33. O.A. Battista, S. Coppick, J.A. Howsmon, F.F. Morehead, W.A. Sisson, *Ind. Eng. Chem.* **48**, 333–335 (1956)
34. T. Yachi, J. Hayashi, M. Takai, Y.J. Shimizu, *Appl. Polym. Sci. Polym. Symp.* **37**, 325–343 (1983)
35. H. Hakansson, P. Ahlgren, *Cellulose* **12**, 177–183 (2005)
36. S. Elazzouzi-Hafraoui, Y. Nishiyama, J.L. Putaux, L. Heux, F. Dubreuil, C. Rochas, *Biomacromolecules* **9**, 57–65 (2008)
37. W. Bai, J. Holbery, K.A. Li, *Cellulose* **16**, 455–465 (2009)
38. M.M. De Souza Lima, Borsali, R. Langmuir **18**, 992–996 (2002)
39. J. Schurz, K. John, *Cellul. Chem. Technol.* **9**, 493–501 (1975)
40. Y. Nishiyama, U.J. Kim, D.Y. Kim, K.S. Katsumata, R.P. May, P. Langan, *Biomacromolecules* **4**, 1013–1017 (2003)
41. N. Wang, E. Ding, R. Cheng, *Langmuir* **24**, 5–11 (2008)
42. N. Wang, E. Ding, R. Cheng, *Polymer* **48**, 3486–3493 (2007)
43. X.M. Dong, J.F. Revol, D.G. Gray, *Cellulose* **5**, 19–32 (1998)
44. S. Beck-Candanedo, M. Roman, D.G. Gray, *Biomacromolecules* **6**, 1048–1054 (2005)
45. P. Terech, L. Chazeau, J.-Y. Cavaille, *Macromolecules* **32**, 1872–1875 (1999)
46. K. Tashiro, M. Kobayashi, *Polymer* **32**, 1516–1526 (1991)
47. A. Sturcova, G.R. Davies, S.J. Eichhorn, *Biomacromolecules* **6**, 1055–1060 (2005)
48. J.M. Mayer, G.R. Elion, C.M. Buchanan, B.K. Sullivan, S.D. Pratt, D.L. Kaplan, *Macromol. Sci. Part A* **32**, 775–785 (1995)
49. G. Freddi, M. Romano, M.R. Masafra, M. Tsukada, *J. Appl. Polym. Sci.* **56**, 1537–1545 (1995)
50. F.G. Torres, R.M. Diaz, *Polym. Compos.* **12**, 705–719 (2004)
51. F.G. Torres, R. Flores, J.F. Dienstmaier, O.A. Quintana, *Polym. Compos.* **13**, 753–764 (2005)
52. F.G. Torres, O.H. Arroyo, C. Gomez, *Thermoplast. Compos. Mater.* **20**, 207–223 (2007)
53. F.G. Torres, C.L. Aragon, *Polym. Test.* **25**, 568–577 (2006)
54. F.G. Torres, O.H. Arroyo, C. Grande, E. Esparza, *Int. J. Polym. Mater.* **55**, 1115–1132 (2006)
55. C. Grande, F.G. Torres, *Adv. Polym. Technol.* **24**, 145–156 (2005)
56. J.A. Youngquist, *For. Prod. J.* **45**, 25–30 (1995)
57. A.R. Sanadi, D.F. Caulfield, R.M. Rowell, *Plast. Eng.* **4**, 27–30 (1994)
58. F.G. Torres, M.L. Cubillas, *Polym. Test.* **24**, 694–698 (2005)
59. A.R. Sanadi, D.F. Caulfield, R.E. Jacobson, R.M. Rowell, *Ind. Eng. Chem. Res.* **34**, 1889–1896 (1995)
60. L. Chazeau, J.Y. Cavaille, G. Canova, R. Dendievel, B. Bouterin, *J. Appl. Polym. Sci.* **71**, 1797–1808 (1999)
61. M. Matos-Ruiz, J.-Y. Cavaille, A. Dufresne, C. Graillat, J.-F. Gerard, *Macromol. Symp.* **169**, 211–222 (2001)
62. X. Cao, Y. Habibi, L.A. Lucia, *Mater. Chem.* **19**, 7137–7145 (2009)
63. N.E. Marcovich, M.L. Auad, N.E. Bellesi, S.R. Nutt, M.I. Aranguren, *Mater. Res.* **21**, 870–881 (2006)
64. F. Favier, H. Chanzy, J.-Y. Cavaille, *Macromolecules* **28**, 6365–6367 (1995)
65. M. Grunnert, W.T. Winter, *Polym. Mater. Sci. Eng.* **82**, 232–233 (2000)
66. M. Grunnert, W.T. Winter, *J. Polym. Environ.* **10**, 27–30 (2002)
67. L. Petersson, A.P. Mathew, K.J. Oksman, *Appl. Polym. Sci.* **2009**, 112 (2001)
68. Y. Habibi, A.-L. Goffin, N. Schiltz, E. Duquesne, P. Dubois, A. Dufresne, *J. Mater. Chem.* **18**, 5002–5010 (2008)
69. S.A. Paralikar, J. Simonsen, J. Lombardi, *J. Membr. Sci.* **320**, 248–258 (2008)

70. M. Roohani, Y. Habibi, N.M. Belgacem, G. Ebrahim, A.N. Karimi, A. Dufresne, *Eur. Polym. J.* **44**, 2489–2498 (2008)
71. Y. Wang, X. Cao, L. Zhang, *Macromol. Biosci.* **6**, 524–531 (2006)
72. Q. Li, J. Zhou, L. Zhang, *J. Polym. Sci. Part B: Polym. Phys.* **47**, 1069–1077 (2009)
73. H. Qi, J. Cai, L. Zhang, S. Kuga, *Biomacromolecules* **10**, 1597–1602 (2009)
74. Y. Noshiki, Y. Nishiyama, M. Wada, S. Kuga, J. Magoshi, *Appl. Polym. Sci.* **86**, 3425–3429 (2002)
75. A. Dufresne, *Compos. Interface* **7**, 53–67 (2000)
76. G. Siqueira, A.J. de Menezes, A. Curvelo, A. Dufresne, *Polymer* **50**, 4552–4563 (2009)
77. L. Flandin, G. Bidan, Y. Brechet, J.Y. Cavaille, *Polym. Compos.* **21**, 165–174 (2000)
78. S. Gea, F.G. Torres, O.P. Troncoso, C.T. Reynolds, F. Vilasecca, M. Iguchi, T. Peijs, *Int. Polym. Proc.* **5**, 497–501 (2007)
79. T. Nishino, I. Matsuda, K. Hirao, *Macromolecules* **37**, 7683–7687 (2004)
80. W. Gindl, J. Keckes, *Polymer* **46**, 10221–10225 (2005)
81. J.R. Capadona, O. van den Berg, L.A. Capadona, M. Schroeter, S.J. Rowan, D.J. Tyler, C. Weder, *Nat. Nanotechnol.* **2**, 765–769 (2007)
82. J.R. Capadona, K. Shanmuganathan, D.J. Tyler, S.J. Rowan, C. Weder, *Science* **319**, 1370–1374 (2008)
83. J. Araki, S. Kuga, *Langmuir* **17**, 4493–4496 (2001)
84. M. Roman, W.T. Winter, *Biomacromolecules* **5**, 1671–1677 (2004)
85. W.J. Orts, J. Shey, S.H. Imam, G.M. Glenn, M.E. Guttman, J.F. Revol, *Polym. Environ.* **13**, 301–306 (2005)
86. J. Araki, M. Wada, S. Kuga, *Langmuir* **17**, 21–27 (2001)
87. M.S. Peresin, Y. Habibi, J.O. Zoppe, J.J. Pawlak, O.J. Rojas, *Biomacromolecules* **11**, 674–681 (2010)
88. W. Park, M. Kang, H.-S. Kim, H.-J. Jin, *Macromol. Symp.* **240**, 289–294 (2007)
89. J.P. De Mesquita, C.L. Donnici, F.V. Pereira, *Biomacromolecules* **11**, 473–480 (2010)
90. P. Podsiadlo, S.Y. Choi, B. Shim, J. Lee, M. Cuddihy, N.A. Kotov, *Biomacromolecules* **6**, 2914–2918 (2005)
91. E.D. Cranston, D.G. Gray, *Sci. Technol. Adv. Mater.* **7**, 319–321 (2006)
92. C.J. Grande, F.G. Torres, C.M. Gomez, O.P. Troncoso, J. Canet-Ferrer, J. Martínez-Pastor, *Mater. Sci. Eng. C* **29**, 1098–1104 (2009)
93. C.J. Grande, F.G. Torres, C.M. Gomez, O.P. Troncoso, J. Canet-Ferrer, Martínez-Pastor, *Polym. Compos.* **16**, 181–185 (2008)
94. T. Zimmermann, E. Pöhler, T. Geiger, *Adv. Eng. Mater.* **6**, 754–761 (2004)
95. T. Zimmermann, E. Pöhler, P. Schwaller, *Adv. Eng. Mater.* **7**, 1156–1161 (2005)
96. S. Stauss, P. Schwaller, J.-L. Bucaille, E. Blank, J. Michler, *Microelectron. Eng.* **67**, 818–825 (2003)
97. J.-H. Chang, S.W. Nam, S.-W. Jang, *Appl. Polym. Sci.* **106**, 2970–2977 (2007)
98. A. Svensson, E. Nicklasson, T. Harrah, B. Panilaitis, D.L. Kaplan, M. Brittberg, P. Gatenholm, *Biomaterials* **26**, 419–431 (2005)
99. J. Andersson, H. Stenhamre, H. Bäckdahl, P. Gatenholm, *Biomed. Mater. Res. Part A* **94**, 1124–1132 (2010)
100. M.A.S. Samir, F. Alloin, J.-Y. Sanchez, A. Dufresne, *Macromolecules* **37**, 4839–4844 (2004)
101. H. Yano, J. Sugiyama, A.N. Nakagaito, M. Nogi, T. Matsuura, M. Hikita, K. Handa, *Adv. Mater.* **17**, 153–155 (2005)
102. W. Czaja, A. Krystynowicz, S. Bielecki, R.M. Brown Jr., *Biomacromolecules* **27**, 145–151 (2006)
103. W.K. Czaja, D.J. Young, M. Kawecki, R.M. Brown Jr., *Biomacromolecules* **8**, 1–12 (2007)
104. D. Cienchanska, *Fibres. Text. East. Eur.* **12**, 69–72 (2004)
105. R. Jonas, L.F. Farah, *Polym. Degrad. Stab.* **59**, 101–106 (1998)
106. P.A. Charpentier, A. Maguire, W. Wan, *Appl. Surf. Sci.* **252**, 6360–6367 (2006)
107. D. Klemm, D. Schumann, U. Udhardt, S. Marsch, *Prog. Polym. Sci.* **26**, 1561–1603 (2001)

108. H. Backdahl, G. Helenius, A. Bodin, U. Nannmark, B.R. Johansson, B. Risberg, P. Gatenholm, *Biomacromolecules* **27**, 2141–2149 (2006)
109. W.K. Wan, J.L. Hutter, L. Millon, G. Guhadós, *ACS Symp. Ser.* **938**, 221–241 (2006)
110. S. Iwamoto, A.N. Nakagaito, H. Yano, M. Nogi, *Appl. Phys. A*, **81**, 1109–1112 (2005)
111. S. Ifuku, M. Nogi, K. Abe, K. Handa, F. Nakatsubo, H. Yano, *Biomacromolecules* **8**, 1973–1978 (2007)
112. G. Nystrom, A. Razaq, M. Stromme, L. Nyholm, A. Mihranyan, *Nano Lett.* **9**, 3635–3639 (2009)
113. A. Razaq, A. Mihranyan, K. Welch, L. Nyholm, M. Strømme, *J. Phys. Chem. Part B* **113**, 426–433 (2009)
114. K. Gelin, A. Mihranyan, A. Razaq, L. Nyholm, M. Strømme, *Electron. Acta* **54**, 3394–3401 (2009)
115. M. Stromme, G. Frenning, A. Razaq, K. Gelin, L. Nyholm, A. Mihranyan, *Phys. Chem. Part B* **113**, 4582–4589 (2009)
116. P. Podsiadlo, L. Sui, Y. Elkasabi, P. Burgardt, J. Lee, A. Miryala, W. Kusumaatmaja, M. Carman, M. Shtein, J. Kieffer, J. Lahann, N. Kotov, *Langmuir* **23**, 7901–7906 (2007)
117. C. Legnani, C. Vilani, V.L. Calil, H.S. Barud, W.G. Quirino, C.A. Achete, S.J.L. Ribeiro, M. Cremona, *Thin Solid Films* **517**, 1016–1020 (2008)
118. O. Van den Berg, M. Schroeter, J.R. Capadona, C. Weder, *Mater. Chem.* **17**, 2746–2753 (2007)
119. M. Agarwal, Y. Lvov, K. Varahramyan, *Nanomaterials* **17**, 5319–5325 (2006)
120. Y. Shin, G.J. Exarhos, *Mater. Lett.* **61**, 2594–2597 (2007)
121. E. Dujardin, M. Blaseby, S. Mann, *Mater. Chem.* **13**, 696–699 (2003)

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