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Nanocellulose Materials – Different Cellulose, Different Functionality

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Summary: Nanocelluloses combine in a very exciting manner important properties of cellulose with amazing features of nano-scale materials. With a view to the increasing discussion on the potential risks of nanoparticles and nanotechnology to human health and the environment, it is important to point out that the nanocellulose fibers are irreversibly networked in the supramolecular cellulose structure. This contribution assembles the current knowledge in research, development, and application in the field of nanocelluloses through examples. The topics combine selected results on nanocelluloses from bacteria and wood as well as the formation and *in situ* shaping of cellulose bodies, the coating of materials with nanosized cellulose networks/supports, and the preparation of nanocellulose composites as well as the use of bacterial cellulose as novel type of medical implants.

Keywords: bacterial cellulose; implant; nanocellulose materials; nanocomposites; wood nanocellulose

Introduction

Cellulose is a fascinating biopolymer, subject of intensive research and development, and a sustainable raw material for a large industry.[1] As polysaccharide formed by the repeated connection of D-glucose building blocks, cellulose is characterized by specific properties quite different from other natural and synthetic polymers: hydrophilicity, chirality, biodegradability, broad chemical modifying capacity, and its formation of versatile semicrystalline fibre morphologies.

Regarding origin, morphology, and processing different types of cellulose are available. As representative examples can be cited celluloses from wood, cotton, other plants, algae, and microorganisms, cellulose allomorphs like cellulose I and II, and value-added products as pulp as well as regenerated or microcrystalline cellulose. Structure, properties, and specific application fields of these cellulose types vary in the well-known cellulose profile.

In contrast, quite different celluloses and quite different functionalities result if the property-determining supramolecular structure of cellulose is formed as a nanofibre network. In this case, the increased ratio of the fibre surface leads to strong interactions with the surrounding components resulting, e.g., in the embedding of large amounts of water, strong interactions with other polymers and biomaterials including catalytic effects, and fixation of nanoparticles of different types.[2] Moreover, these celluloses show nanoporosity in solid state and transparency of its dispersions and composite materials. That means, celluloses of this type combine in a very exciting manner important properties of cellulose with amazing features of nano-scale materials.

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With a view to the increasing discussion on the potential risks of nanoparticles and nanotechnology to human health and the environment, e.g., in[3], it is important to point out that the nanocellulose fibres are networked in the supramolecular cellulose structure. That means they are fixed irreversibly.

The described quite different type of cellulose is named nanocellulose, i.e., if celluloses are composed of a nanosized fibre network and the nanofibre structure determines the product properties and functionality, such polymers are described as nanocelluloses.

To produce nanocelluloses there are two important but completely different ways: the bio-formation of cellulose by bacteria[1] and the disintegration of plant celluloses using shear forces in refiner techniques.[4] The bacterial cellulose is produced mainly by *Gluconacetobacter* strains as their biofilms formed in high yields up to 40% in relation to the carbon source, e.g., glucose. In principle, wood nanocelluloses can also be prepared by electro spinning from pulp solutions[2,5] as well as by TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl) oxidation of wood cellulose combined with the simultaneous introduction of carboxylate groups in the cellulose molecules.[6,7]

As reviewed 2006[8], nanocelluloses turn out more and more to be innovative polymers in research and application. Because of the extraordinary supramolecular structure and exceptional product characteristics as pure, high-molecular, and high-crystalline cellulosics with water content up to 99%, nanocelluloses require increasing attention as different celluloses with different functionalities and open up completely novel fields of cellulose application.

Such fields are, e.g., nanonporous hydrophilic membranes, nanoscaffold-based composite materials, and medical implants for repair of hard and soft tissue and as cardiovascular substitutes.[8]

The research and development on bacterial nanocellulose (BNC) attain special importance against the background of investigations on the white biotechnology of cellulose, i.e. the production of cellulose by application of microorganisms/fermentation as an alternative to cellulose isolation from plants. At the same time, the practical use of different bacterial biofilms gain in importance.[9]

In general due to its ubiquity in nature and the longstanding contact with people cellulose is emotionally respected as a safe and acceptable polymer well-known from paper, cotton, pharmaceuticals, and wound care. This background, the excellent features of cellulose as polymeric dextrose and porous fibre framework as well as its function as hydrophilic and biocompatible polymer are important arguments for a positive perspective of nanocelluloses as efficient biomaterials and technical products.

Hydrogels were the first biomaterials rationally designed for human use. Up to now, they have moved forward at a dramatic pace. One part of the progress are hydrogels mimicking basic processes of living systems.[10] BNC as bio-formed natural hydrogel is a significant exponent of this process. Especially its great potential as tissuephil in vivo scaffold opens up new vistas for medical implants in hard and soft tissue repair.

During the last three years, an increasing activity in the field of nanocelluloses including further examples of practical application could be observed. In some cases information on BNC and its application are also described by the term ''biocellulose''. It is the aim of this contribution to assemble the current knowledge in research, development, and use of nanocellulose through examples. New frontiers are highlighted together with future strategies and perspectives of nanocelluloses.

Benefits of Bacterial Cellulose

Caused by its biotechnological production and its specific nano-scale structure BNC combines unique modes of processing,

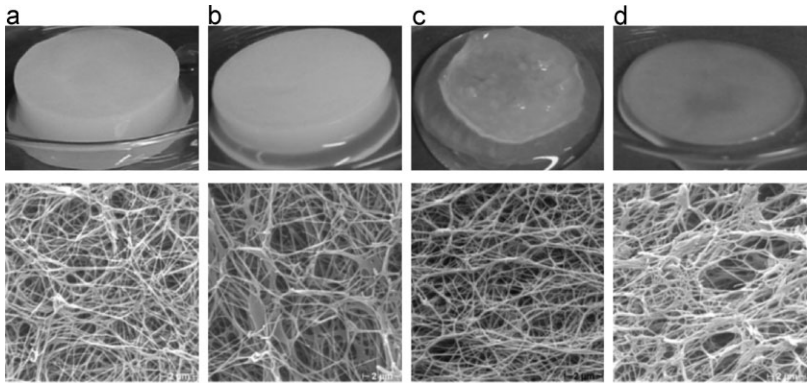

Figure 1.
Bacterial nanocellulose (BNC) and BNC network of various *Gluconacetobacter* strains. Scanning electron microscopy (SEM), magnification 10,000×: a – DSM 14666; b – ATCC 53582; c – ATCC 23769; d – ATCC 10245.

material formation, and product properties not accomplishable in case of plant celluloses and synthetic polymers. From this point of view the most important eight benefits of BNC can be evaluated as follows.

1. Control of supramolecular structure and properties during cultivation by choice of bacterial strain, carbon source in culture medium, types of additives during cultivation, and cultivation conditions.
2. Shaping of BNC materials during biosynthesis to produce fleeces, foils, patches, spheres, fibrils, or tubes, respectively.
3. Direct formation of cellulose bodies as hydrogels and as aerogels (after drying), respectively.
4. Surface cellulozation by thin layer cultivation resulting in coating of materials.
5. *In situ* composite formation using water soluble additives or dispersed particles.
6. Effective *post* modification/processing.
7. Specificity of the formed cellulose as nanofibre support useful, e.g., for particles, metals, and proteins.
8. Cellulose of high purity, high molecular weight, high crystallinity, controllable high water content, and high fibre stability as well as proven biocompatibility.

Control of Supramolecular Structure

An efficient opportunity to control the supramolecular structure of BNC results from the choice of the bacterial strain including its modification by bioactive agents and gene manipulation, respectively. As demonstrated in Figure 1 for the preparation of nanocellulose fleeces in static culture different bacteria strains form different fleeces regarding their thickness, consistence, and supramolecular network structure. By drying the native wet fleeces shape and structure can be considerably modified further on. By effective freeze and by critical point drying the original features will be retained to a large extend. Dewatering by hot pressing can be used to a stepwise ramming and drying of the fleeces. Typical examples for the control of BNC structure by carbon sources, *in situ* used additives, and by cultivation conditions are already given in.[8]

Shaping, Formation of Cellulose Bodies, and Surface Cellulozation during Biosynthesis

Shaping of polymer basis products to polymer materials is one of the most important procedure in polymer production and application. The main principles of shaping are thermoplastic techniques, sinter processes combined with elongation steps, shaping from solutions, and *in situ*

shaping. In case of synthetic polymers the thermoplastic forming is dominant followed by *in situ* techniques (e.g. emulsion polymerization). To produce cellulose materials from biomass the shaping from solutions (unmodified cellulose in *N*-methylmorpholine-*N*-oxide, xanthogenate process) is the only way caused by lack of thermoplastic behaviour of cellulose.

The formation of cellulose by fermentation (bacterial cellulose) opens up new vistas for the *in situ* shaping of cellulose. This bio-shaping allows the production of flat materials (fleeces, foils, Figure 2a), hollow bodies (Figure 2b), spheres (Figure 2c), fibres, and coatings with high effectiveness simply during bacteria cultivation.

Flat products of different geometry are formed during the well-known static cultivation in liquid culture medium or in thin-layer cultivation on solid phases like agar, silicone, rubber, and different porous membranes. It is also well-known that size and thickness of the BNC fleeces and foils can be controlled by the type of strain, volume of culture medium, and cultivation time.[8] The use of a matrix in the static culture allows the formation of hollow bodies of different shape. As summarized in[8] a corresponding matrix-reservoir-technology leads to tubes suitable as vascular implants in medicine. Another method consists in the use of oxygen-permeable silicone hoses and the formation of tubular formed BNC around the tire-tube.[11]

Under agitated cultivation conditions (shaking, stirring) the BNC formation proceeds to spheres and fibrils controlled by type and intensity of agitation. This type of cultivation opens the possibility to produce BNC in commercial fermentation equipment. But there are some restrictions: only few *Gluconacetobacter* strains are adaptable (e.g. ATCC 53582), inhibition of BNC formation by share forces resulting in lower yields, spontaneous formation of bacteria mutations, and change of BNC structure and properties.[12]

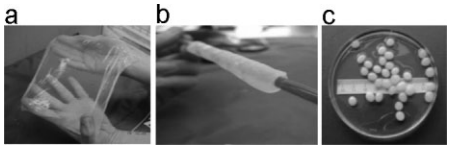

Figure 2.
Bio-shaped BNC hydrogel materials: a – foil (thickness 200 μm); b – tube as vessel implant (15 cm length, 6 mm inner diameter); c – spheres (2-3 mm diameter) produced by shaking rate of 80–100 rotations per minute.

The coating of material surfaces during biosynthesis of BNC is strongly affected by the type of the material and the surface properties. As demonstrated in our recent work, polymers like Teflon®, Dacron®, and polyamide as well as metals as aluminium and steel can be coated in a good manner. The toxicity of copper or copper blends inhibits the cellulose formation completely. Natural fibres, paper, and wood are very useful for an effective cellulozation. In case of nematic ordered surface areas a strong interaction between the nascent BNC nanofibres and these surface parts could be observed.[13,14] The deposition of the BNC follows the oriented molecular tracks and allows the regulated fabrication of 3D functional materials. By solid culture on honeycomb porous bodies honeycomb patterned BNC products could be prepared.[15]

In situ Composite Formation and post Modification as Nanofibre Support

The formation of composites with different partners like bioactive agents, natural polymers, synthetic monomers as well as polymers, metals and metal oxides meanwhile represent a large field of BNC investigation and development. Thereby, *in situ* as well as *post* modification procedures are used.[8] There are important examples of composites reinforced by BNC fibers, but also novel materials prepared by filling BNC with additives.

Because of its high Young's modulus up to 134 GPa[8] BNC has a high-capacity reinforcement agent potential for technical applications. Inspired by nature Juntaro et al.[16,17] and Pommet et al.[18] obtained a new class of very complex hierarchical

''truly green'' composites, which are both derived from renewable resources and biodegradable. The argument of the authors is as follows: up to now, the main disadvantage of natural fibers as fillers is their low compatibility with many hydrophobic polymeric matrices inducing poor mechanical composite properties. Therefore, they introduced BNC as a nano-scale reinforcement by attaching it *in situ* to the surface of natural fibres like sisal and hemp. The strong inherence between BNC and the coated fibre surface is caused by the high self-affinity of cellulose through hydrogen bonding. In this sense, the originally quite smooth surface of sisal (Figure 3a) is covered by little BNC fibres (Figure 3b). After removing the natural fibre substrates like waxes and other organic compounds that form a protecting hydrophobic layer around the sisal fibre, the surface was completely covered with BNC (Figure 3c). After drying, the authors embedded these modified fibres into matrices of poly(L-lactid acid) (PLLA) and cellulose acetate butyrate, respectively. It could be shown that the BNC nanofibres improve the interaction between the primary fibres and the synthetic polymer matrix, which leads to enhanced mechanical properties and water resistance. In case of modified sisal reinforced PLLA the parallel strength increases by 44% and the off-axis composite strength by 68%.

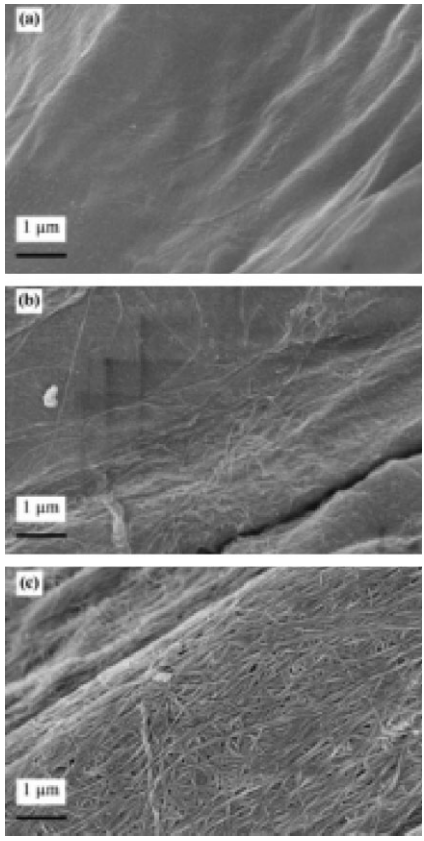

Figure 3.
SEM images of sisal fibre surfaces: a – natural sisal fibre; b – sisal fibre to which BNC was attached; c – acetone-treated sisal fibre after BNC coating.[18]

Yano et al.[19–21] and Nogi et al.[22] discovered that the nanofibre network of BNC has an extraordinary potential as reinforcement to obtain optically transparent and low thermal expansion materials. The produced BNC fibre-reinforced composite resin/compositions – using epoxy resin, phenolic resin, and acrylic resin – had a total light transmittance up to 86% and the thermal expansion coefficient of acrylic resin could be reduced to the half.

Yoon et al.[23] developed electrically conductive BNC by incorporation of carbon nanotubes (CNT). BNC pellicles were dipped into a dispersion of CNT in a surfactant solution for several hours. The authors investigated that unlike most studies on simple blends of CNT with polymeric materials the CNT were incorporated into BNC pellicles in the aqueous state and could be well-dispersed in the BNC, which acts as nano-scale support. Before drying the CNT-containing BNC, the surfactant was extracted by pure water. Field emission scanning electron microscopy (SEM) shows the homogeneous distribution of CNT in BNC without aggregation (Figure 4). This is one of the most important requirements for achieving an uniform conductivity all over the composite. It was found that the incorporation process is an useful method not only for dispersing CNT in an ultrafine fibrous network structure but also for enhancing the electrical conductivity of the polymeric membranes.

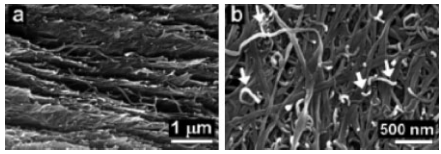

Figure 4.
Field emission SEM images of a – the fractured surface and b – the inner layer of the carbon nanotube (CNT)-incorporated BNC pellicle immersed in 0.05 wt% of CNT derpersion for 24 h; arrows show CNT.[23]

Evans et al.[24] generated electrically conductive BNC composites, too. These patented materials could be used to form electrodes for use in membrane electrode assemblies for fuel cells. Therefore, the BNC was modified *in situ* by incorporating electrically conductive carbonaceous material into the culture medium with *Gluconacetobacter hansenii*. Moreover, Koga[25] patented dye-sensitized solar cells on BNC-basis. Corresponding to Evans the bacteria are cultivated in presence of the dyes, electrolytes, oxidation-reduction agents, and semiconductor particles. The resulting composites are the basis for the mentioned solar cells. As further inorganic additive for *in situ* and *post* modification of BNC Yano et al.[26] have been used silica.

Using a never-dried procedure, Kramer et al.[27] modified shaped BNC with the aim of formation of BNC/synthetic polymer (SP) composites. Acrylate and methacrylate monomers and methacrylate crosslinkers (Figure 5a) well-known from medical applications were photopolymerized inside the ethanol-swollen BNC nanofibre network (Figure 5b-I). The result was a collagen-like material (Figure 5b-II) with control of water absorption capacity, strength, and elasticity. The essential features of the BNC, e.g., shape, nanofibre network, pore system, and proved biocompatibility were still remained. Using monomers of different concentrations either filling of the pores or coating of the fibres in the BNC composites were attained. An optimized BNC-SP composite showed characteristic properties of hyaline cartilage, e.g., Young's modulus of 5–20 MPa.

Laborie et al.[28] are engaged in integrating and property design in BNC nanocomposites using thermoplastics. By varying the growth conditions of the bacteria, chemical and thermal properties of the cellulose/thermoplastic nanocomposites can be effectively altered. The polyvinyl alcohol-BNC system as a new nanocomposite for biomedical applications is described by Millon et al.[29] and Wan et al.[30]. Polyvinyl alcohol itself is a hydrophilic biocompatible synthetic polymer with various characteristics desired for biomedical applications and can be transformed into a solid hydrogel by physical crosslinking useful as a cartilage-like implant.

Wood as Source of Nanocellulose

Although cellulose nanofibrils are still known since 1960s,[31,32] these nanostructured cellulose elements have gained in

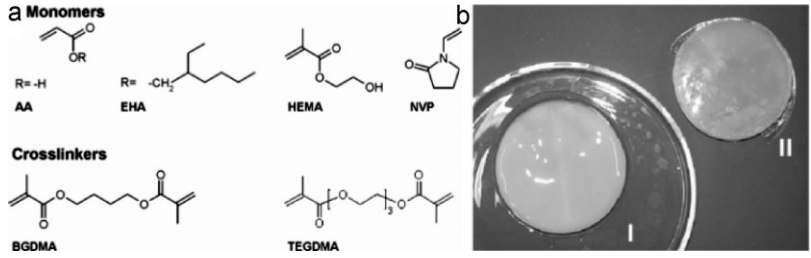

Figure 5.
a – monomers and crosslinkers: AA – acrylic acid; EHA – 2-ethylhexyl acrylate; HEMA – 2-hydroxyethyl methacrylate; NVP – N-vinyl pyrrolidone; BGDMA – 1,4-butanediol dimethacrylate; TEGDMA – triethylene glycol dimethacrylate; b – I – starting material: never-dried BNC pellicle (shaped in a glass tube matrix) after solvent exchange from water to ethanol and II – final BNC-synthetic polymer composite.

importance only in the last few years regarding the development of nanomaterials based on renewable resources.[33]

As a structural component in plants, cellulose is arranged as a system of fibrils embedded in a lignin matrix. A single fibril has a diameter of about five nm and a length of up to tens of micrometers.[34] In contrast to BNC that consists of pure nm-sized cellulose fibres[8] the isolation of pure cellulosic structures having dimensions in the range of 1–100 nm from wood and plants requires multi-stage disintegration processing.[35]

There are different terms describing nano-sized celluloses formed by such procedures.[36] The term ''fibril'' means long and thin pieces of cellulosic material, but the term ''nanofibre'' has become more commonly used in the last few years because it states more clearly that the functionality and the behaviour of nanocelluloses can differ from that of larger fibers. Generally, nanofibres represent the elemental assemblies of distinct polymer units. Very long and straight crystals of cellulose are called ''whiskers'', ''nanorods'', ''rod-like cellulose microcrystals'' or ''nanowires''. Nanofibers that remain attached together for at least a portion of their length are usually described as ''microfibrillar cellulose'' (MFC) and ''nanofibrillar cellulose'' (NFC). But also ''nanoscale fibrillated cellulose'' as well as ''cellulosic fibrillar fines'' are mentioned. The term ''cellulose aggregate fibrils'' has been used when the fibrils have not been completely separated from each other. For larger aggregate structures the term ''microcrystalline cellulose'' (MCC) has been used.

Beside the nonuniform nomenclature of nanocellulose materials in the literature, they can be divided into three different kinds of nanocellulose derived from plants: nanocellulose crystals (whiskers)[37] but also spheres,[38] nanocellulose fibres and nanocellulose composites.[36,39,40]

There are different methods known for the isolation of nanosized whiskers and fibres from plant celluloses.[37,39] Cellulose whiskers could be produced by acidic hydrolysis, nanosized fibres by physical methods (e.g. steam explosion).[41,42] Beside this the electrospinning method[5] for the preparation of nanocellulose fibres is often discussed in the literature.[43] This method delivers fibres from a solution of cellulose/cellulose derivatives. But up to now, there are no methods known that deliver nanosized fibres in the rage of 1–100 nm.[43,44]

The 9th International Conference on Wood & Biofiber Plastic Composites 2007 in Madison, WI (USA), highlighted the recent strong activities regarding the development and application of wood nanocellulose in that field. M. Ankerfors et al.[45], STFI Packforsk, referred, e.g., on the manufacture and uses of nanocellulose and M. L. Auad et al.[46], Auburn University, on temperature induced shape memory behaviour of nanocellulose composites.

Nanocelluloses as composite additives are already on the market. ''Stress-free'' blank for fishing rods made with nanocellulose ''bio-fibre'' as reinforcement component are an typical example (Cabela's, USA). In Germany, Rettenmaier & Sons, offer Arbocel® (nanodispersed cellulose – NDC) for sale as a novel generation of ultra fine cellulose additives for paper and board. This nanocellulose from wood comes from industrial serial production as part of their ''fibres designed by nature'' portfolio.

Medical Applications of Bacterial Cellulose

Since long time, plant celluloses are well-known for external wound care. Therefore, it is obvious that one of the first applications of BNC in the medical field was its use as wound dressings. Thereby the described benefits of BNC open up new profiles as humidity source, 3D template for tissue growth, and as active component in wound healing. But in case of chronic wounds pure BNC shows no significant effect on the biochemical stage. Therefore, different

types of BNC-composites have been produced and investigated regarding this purpose. In contrast to plant celluloses BNC can also be incorporated into the living body. Therefore, the completely novel application field of cellulosic medical implants can be developed. Up to now, the presented results concern method and devices for soft and hard tissue repair and replacement, respectively. For the designing of biomaterials for wound care and implantation the main wound and tissue healing processes have to be in mind. The wound healing involves various cell types in soft tissue (e.g. granulocytes, lymphocytes, and plasma cells), extracellular matrix and different soluble compounds in the first period. In the cycle of soft tissue healing four steps are important: hemostasis, inflammation, granulation, and scarification. The most important point for this normal healing is the regular blood supply and no infection. In cases with complex disturbances of blood supply (chronic wounds, chronic ulcer) the biomaterial cannot restore the soft tissue defect. The common biomaterial device can only help against infection and mechanical influences. In the wound healing process of bone the healing period take longer as in the soft tissue layer. That means that different applications require different properties of BNC as medical device, especially as implant under function.

In case of BNC wound dressings[8] there was only low activity during the last three years. Czaja et al.[47] summarised the external application of BNC in medicine: temporary wound coverage, treatment of chronic wounds and burns as well as in cosmetics. At the moment only ''Suprasorb'' wound dressing from Lohmann & Rauscher is on the market. On the asian markets cosmetic products called ''bio cellulose'' represent further typical external applications.

Wang et al.[48] described the formation of BNC dressings, artificial skins, and medical gauze by dropping a special culture medium step by step onto a membrane. By this method desired thickness and yield of BNC layer could be reached. The properties of BNC for the application as wet wound dressing strongly depend on the bacterial strain and on the drying procedure of the membrane. Therefore, the determination of network parameters by IR spectroscopy, gas permeability, and Young's modulus measurements are essential. From this point of view Clasen et al.[49] and Sultanova et al.[50] reported on the wound dressing potential of BNC produced by various bacterial strains. The resulting materials were different regarding network structure and physical properties. It could be shown that only one of the tested strains showed the capability to synthesize membranes that meet the requirements for an application as a wet wound dressing. Bacteriostatic effects of a ''neotype'' BNC wound dressing were compared by Zhao et al.[51] using four kinds of dressings containing neomycin and berberine. The BNC material showed the best effects on *Staphylococcus aureus* and *Escherichia coli*. Antimicrobial activity was achieved by formation and fixation of silver nanoparticles on BNC. By immersing BNC in silver nitrate solution the silver ions (Ag^+) were fixed on the cellulose nanofibres. Using sodium borohydride as reducing agent and silver nitrate in molar ratio of 100:1 well dispersed and regular spherical metallic silver nanoparticles (Ag^0) could be obtained (Figure 6c). Maneerung et al.[52] and Jung et al.[53] expected that this BNC composite hydrogels could be applied as wound dressings due to the antibacterial effect of the silver nanoparticles.

A wound dressing formed by incorporation of collagen type I into BNC showing a

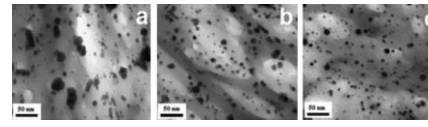

Figure 6.
Transmission electron microscopy (TEM) images of freeze-dried silver nanoparticle-saturated bacterial cellulose prepared from the $NaBH_4$:$AgNO_3$ molar ratio of a – 1:1; b – 10:1; c – 100:1.[52]

significant reduction of the amount of selected proteases and interleukins in the wound and possessing a distinct antioxidant capacity is described by Wiegand et al.[54] Sanchavanakit et al.[55] demonstrated a supporting of growth, spreading, and migration of human keratinocytes in wounds instead of human fibroblasts for the first time.

Jung et al.[56–58] developed composite films made of BNC and silk fibroin. Therefore, an aqueous silk fibroin solution was added to the BNC hydrogel. SEM investigations showed a well penetration of the fibroin between the individual BNC fibrils. Furthermore, the fibroin, which dissolves in pure state easily in water, did not dissolve in case of the silk fibroin-BNC composite. In dehydrated form the composite was very brittle, but in hydrated state the film became more flexible and tougher and the mechanical properties markedly increased. The authors announced this kind of composites as new potential biomaterial especially for the use as wound dressing or burn-healing hydrogel material.

In case of BNC use inside the body (implants) the field of grafts for cardiovascular diseases – illness no. 1 worldwide – is the most important application area. It is reported[59] that 250,000 patients in USA get cardiovascular grafts per year. Up to now, for these coronary bypasses (inner diameter < 6 mm) only autografts (*vena saphena* and *arteria mammaria*) can be used. Suitable artificial implant material for this purpose has not been developed yet.

As result of our ongoing research short micro vessel substitutes (e.g. 1.5 cm length and 0.7 mm inner diameter) – BASYC® – could be produced and investigated in microsurgical animal experiments.[60] For the use of BNC vessel substitutes in the cardiovascular field implantable tubes with an inner diameter of 3-5 mm and a length of more than 10 cm are needed. In the last years we could design such vessel implants (see Figure 2b, in ''Benefits of bacterial cellulose''). These bio-formed hydrogel tubes are characterized by mechanical stability, good surgical handling, and a smooth inner surface. As can be seen from confocal laserscanning microscopy (LSM) images (Figure 7) the smoothness of the inner surface of the BNC tube compared to that of common synthetic implant material is distinctly better. The higher roughness of polytetrafluoroethylene and polyester grafts is caused by their formation as filaments and expanded moulding, respectively.

We assume that the homogeneous inner surface structure of BASYC® causes the good result[60] regarding endothelization, low risk of thromboses and aneurysms. Therefore, tubular BNC materials cannot be produced by mechanical treatment of BNC fleeces. This manipulation results in distinct lesions of the surface. Schumann et al.[61] reported the positive results of the application of long BNC grafts in the porcine carotid artery (Figure 8).

Intensive investigations on preparation, characterization, and application experi-

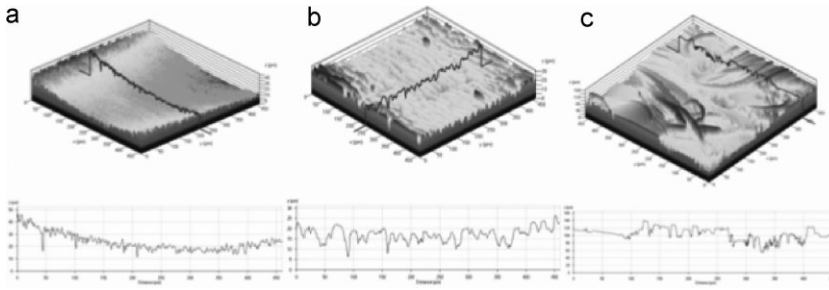

Figure 7.
Confocal laserscanning microscopy (LSM) images of the inner surface of a – BASYC®; b – polytetrafluoroethylene; c – polyester.

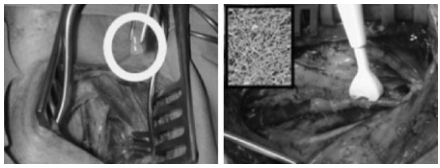

Figure 8.
a – Intraoperative situs of the carotid artery, BC tube in the forceps; b – BC graft implanted in the porcine carotid artery (7-0 prolene). Patency was subsequently controlled by flow measurement. The small picture is showing the ultrafine network structure of cellulose in the tube. The matrix did not contain cells and required no preclotting.[61]

ments of BNC tubes are also reported by Helenius et al.[62] and Bodin et al.[63]

As part of investigations on bone repair Hutchens et al.[64] demonstrated by combination of hydroxyapatite and BNC that BNC provides a template for the ordered formation of calcium-deficient hydroxyapatite (CDHAP), the natural mineral component of bone. An application as bone graft seems promising because CDHAP promotes bone colonization when implanted in osseous defects and degrades over time to be replaced by new bone. The bioactivity of CDHAP and the biocompatibility of BNC substantiate these composites as a new potential orthopedic biomaterial. The composites were formed by alternating incubation cycles of BNC pellicles with calcium and phosphate solutions. X-ray diffractometry confirmed that CDHAP was present in the composites and the pattern was very close to that of bone apatite. SEM images showed the apatite grown into discreet CDHAP clusters (Figure 9a) which seemed to be caused by the distinct arrangement of BNC molecules. The single clusters are composed of nanosized crystallites with high surface area (Figure 9b–d). On this growing field further results are presented by Wan et al.[65] and Hong et al.[66]

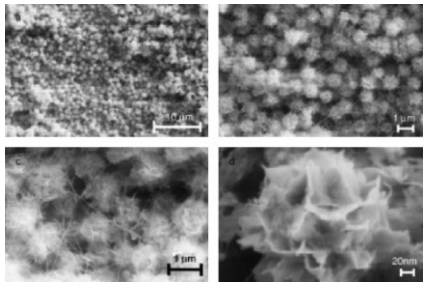

Figure 9.
SEM images of BNC-hydroxyapatite (HAP) composite (BNC-53% HAP) at a – 1,000×; b – 5,000×; c – 10,000×; d – 50,000×.[64]

Conclusion

The presented and exemplified benefits of bacterial nanocellulose (BNC) open up new application fields, vistas, and finally new markets for the biopolymer cellulose. The recently most important examples concern the formation and *in situ* shaping of cellulose bodies, the coating of materials with nanosized cellulose networks/supports, and the use of BNC as novel type of medical implants. Hugh challenges for the next years are deeper insights into the mechanisms controlling the supramolecular cellulose structure formation by bacteria, their use for tailoring the nanofibre network structure according to the application fields, and the production of BNC including shaped as well as composite materials in larger quantity and on a commercial level. Moreover, the BNC implants have been developed to such a level that clinical trials can be started in the next year.

Wood nanocelluloses benefit at this stage from their producibility from the inexhaustible cellulose source of plants and are subject of strong activity in research and development. Composite materials using wood cellulose nanofibres are on the market.

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