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Nanocellulose Polymer Composites as Innovative Pool for (Bio)Material Development

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Summary: Using a "never-dried" procedure (according to Figure 4) shaped bacterial nanocellulose (BC, 1% cellulose, 99% water) has been modified by the formation of BC-polymer composites. For this purpose, acrylate and methacrylate monomers and methacrylate crosslinkers were photopolymerized inside an ethanol-swollen nanofiber network. Using the ethanol as solvent and as confirmed by model reactions the synthetic polymer (SP) part of the composites is constructed of crosslinked polymers (number of repeating units in the range of 500). As part of ongoing work on the development of (bio)materials from the innovative pool of BC composites these investigations are recently directed towards the creation of collagen-like materials. Thus, for these purposes, mainly water absorption capacity, strength, and elasticity have to be controlled, whilst still retaining essential features of BC like shape, nanofiber network, pore system, and proved biocompatibility. Using acrylic acid, 2-ethylhexyl acrylate, 2-hydroxyethyl methacrylate, N-vinyl pyrrolidone as acrylate monomers and triethylene glycol dimethacrylate and 1,4-butandiol dimethacrylate as crosslinkers of different concentrations either a filling of the pores or a coating of the fibers in the BC nanocomposites could be achieved. The small cellulose content of the composites significantly increases the water absorption value and the strength of the material as well as the ability of re-swelling in the case of fiber coated composites. Sample 12 is an optimized BC-SP composite regarding important properties of hyaline cartilage like Young's modulus in the range of 5–20 MPa using the well-known Simplex-method.

Keywords: bacterial nanocellulose; biomaterials; photopolymerization; poly(meth-)acrylates; polymer composites

Introduction

Nanocelluloses – Nanocellulose materials (NACEMAT)

"Nanocelluloses" like bacterial cellulose (BC) and mechanically disintegrated wood cellulose are composed of nano-sized fibers where the nanofiber structuring determines the properties of the product.[1] Materials based on this type of cellulosics become increasingly important and open an innovative pool for (bio)material development.

The bacterial synthesized cellulose is of special interest because of its unique specific structure and properties. This BC is quite different from plant celluloses and takes centre stage in our investigations. It is defined by high purity (free of hemicelluloses, lignin, and alien functionalities such as carbonyl- or carboxyl groups) and high degree of polymerization (up to 8000).

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Moreover, it is specifically characterized for its high crystallinity (80–90%) and a water-swollen nanofiber network (99% water). It is well known that BC is shaped during cultivation. Examples are layers of different thickness, thin foils, and – we have shown – various types of tubes.[2] Contrary to plant celluloses, BC can be used directly in its biogenously formed molecular, supramolecular, and morphological structure without damage to the nanofiber network and the corresponding pore system.

BC is produced by *Gluconacetobacter xylinus*, a rod shaped, aerobic, gram negative bacterium. It is synthesized in static culture as a white gelatinous material in the form of mechanically stable hydrogel pellicles on the surface of the culture medium. In 1886, A. J. Brown first reported that the pellicles were composed of pure cellulose.[3]

Shaped BC – Bacterial Synthesized Cellulose (BASYC®)

In the last 10 years, the formation of BC directly in the culture medium has been used to produce shaped soft tissue- and vessel substitutes as tubes (BASYC®).[2] First tests of BASYC® implants as cuffs for nerve suturing have shown a complete covering of the implant by connective tissue containing small capillaries outside, where no inflammation reaction occurred after 4 weeks. Based on these results, BASYC® was used as a vessel substitute in the carotid artery of the rat in subsequent studies. The internal surface of the BASYC® material became completely covered by an endothelial cell layer after a residence time of four weeks in the animal body.[4] Moreover, there was no thrombotic occlusion directly after operation ($N = 20$) and all interpositioned tubes had a patency rate of 100% even after one year of observation ($N = 5$).[1] These results confirm the "vitalization" of BC and the fundamental importance of the basic research for the development of medical devices as a new biomaterial.

A broadening of the innovative pool of cellulosic biomaterials towards substitution of supporting tissue (cartilage, bone), requires a distinct change of the BC hydrogel properties. Mainly water absorption capacity, strength, and elasticity have to be controlled and essential features of BC like shape, nanofiber network, pore system, and biocompatibility have to be retained.

Modification of BC – Formation of Composites

Basic changes of BC supramolecular structure and properties can be achieved by variation of the bacterial strain.[5, 6] Similar effects can be observed after addition of water-soluble additives like carboxymethyl cellulose or methyl cellulose to the culture medium (in situ modification).[7–10]

To create collagen-like structures for the development of supporting tissues according to the previously defined targets the biotechnologically shaped BC has to be modified after biosynthesis (post modification) under mild and specific conditions. From this point of view, we have started investigations on the design of different types of nanocellulose polymer composites. Thus the formation of a network of synthetic polymers (SP) inside the fiber- and pore system of BC is a suitable way. The well-known combinations/composites of cellulose with synthetic polymers like reinforcement of SP with cellulose fibers, crystallites/whiskers, and grafting onto cellulose as well as blending cellulose derivatives with SP are not suitable for this purpose. Acrylates and methacrylates as monomers and methacrylate crosslinkers were chosen because of their availability, ease of polymerization, and the broad variability of structure and properties of the resulting polymers. A further important attribute of the corresponding polymers is their well-known applicability in operative medicine.

In this paper the preparation and characterization of representative composites of this type as well as the optimization

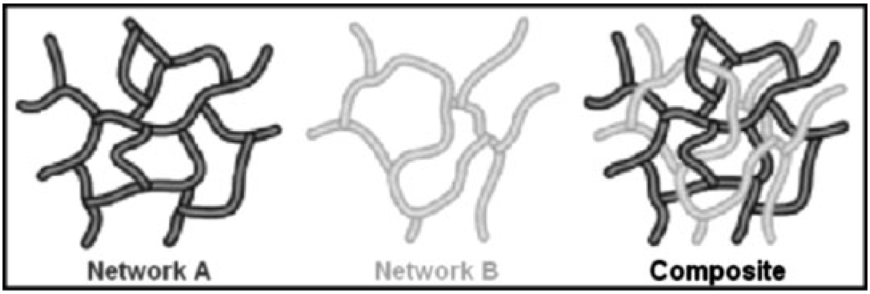

Figure 1.
Principle of composite formation. The synthetic polymer network (B) is formed inside the bacterial cellulose (network A). Scheme according to http://www.polymerics.de/technology/ipn_en.html.

of the collagen-like properties will be described.

Design of Collagen-like BC-SP Composites

In the following composites (Figure 1) BC acts as a biogene scaffold (network A) and therein the acrylates and methacrylates (Figure 2) have to be polymerized in the presence of a crosslinker (network B).

In preliminary investigations it could be shown that the photopolymerization of the monomers occurs directly in the shaped and never-dried BC (Figure 3a). This was found to be the best way to create the collagen-like nanocomposites. For the formation of the interpenetrating SP network the preservation of the original pore- and fiber structure (Figure 3b) by a spacer solvent is essential. But the water included during biosynthesis of BC has to be exchanged by ethanol or similar solvents because of the water-insolubility of the hydrophobic acrylates/methacrylates. These monomers are essential for the control of the properties of the aimed collagen-like materials, where the pore filling or fiber coating by the polymer depends on the monomer concentration in the solvent. In addition, the use of such solvents also ensures the homogeneous distribution of monomers and crosslinkers in the shaped BC sample.

In contrast, the use of freeze-dried BC leads to an inhomogeneous distribution of the liquid monomers even after dilution with solvents (incomplete re-swelling). Moreover, the classical thermal polymerization

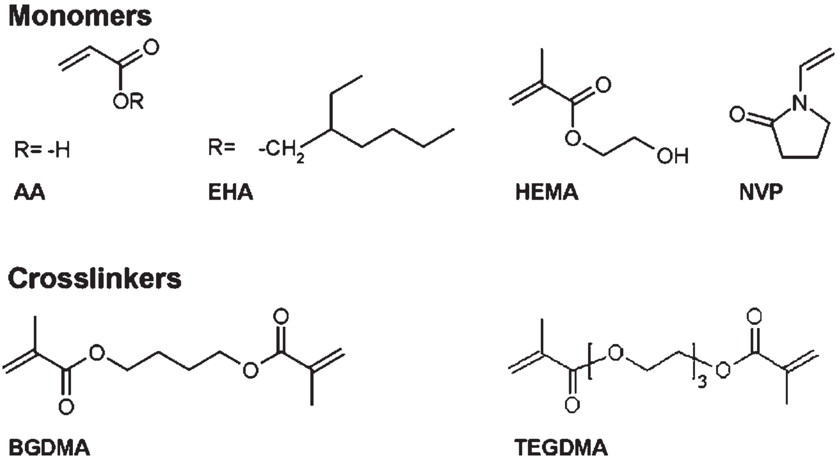

Figure 2.
Monomers and crosslinkers; AA–acrylic acid; EHA–2-ethylhexyl acrylate; HEMA–2-hydroxyethyl methacrylate; NVP–N-vinyl pyrrolidone; BGDMA-1,4-butanediol dimethacrylate; TEGDMA–triethylene glycol dimethacrylate.

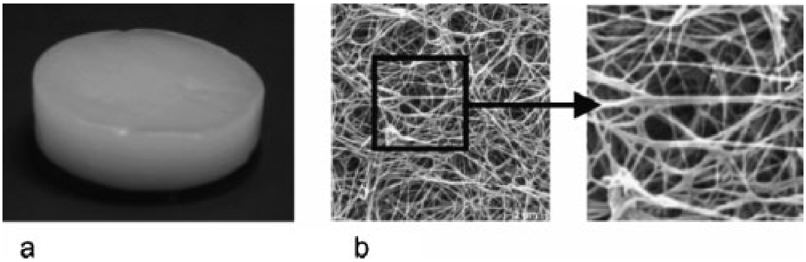

Figure 3.
BC (strain DSM 14666) as starting material for BC-SP composites; a – water-swollen and shaped sample; b – Scanning electron microscopy (SEM) image of the fiber network (magnification 10 000).

of acrylates and methacrylates in the ethanol-swollen network causes a distinct discharge of the monomers and/or polymers out of the BC sample and thus causing a drastic change of the original shape. A solvent exchange from water to n-propanol leads to the same observation.

These results demonstrate the need of a "never-dried" procedure for the preparation of shaped BC-SP composites in (bio) material development (Figure 4). The photopolymerization was carried out in presence of the photoinitiator Darocur 1116® (2-hydroxy-4'-isopropyl-2-methyl propiophenone) using a xenon flashlamp.

In radical polymerizations the presence of ethanol as solvent for monomers and crosslinkers is a challenge because of its polymer-precipitation properties influencing the resulting chain lengths of the polymer. Therefore a model reaction of a mixture of 2-ethylhexyl acrylate (EHA – 99 mol%) and triethylene glycol dimethacrylate (TEGDMA – 1 mol%) as crosslinker, and Darocur 1116® (1 wt% in relation to the monomer/crosslinker mixture) as initiator in ethanol without BC was investigated. The monomer/crosslinker concentration was incrementally increased up to 100% EHA/TEGDMA in steps of 10 wt%. It was observed that using

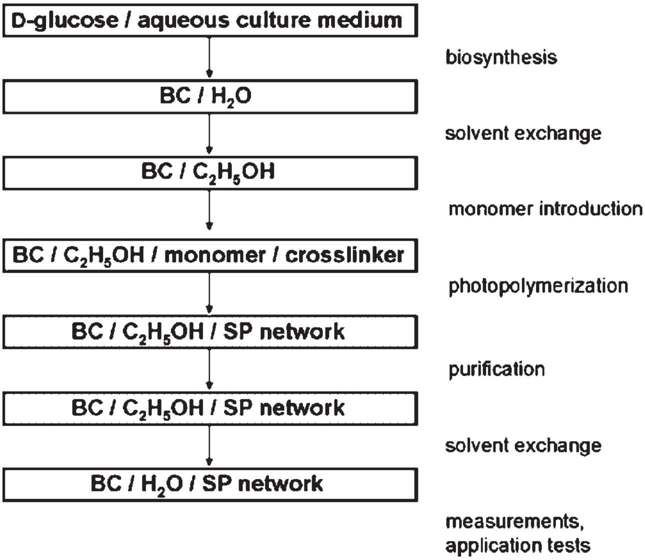

Figure 4.
Never-dried procedure for the preparation of BC-SP composites.

concentrations of 40 wt% acrylate/crosslinker solution in ethanol could produce dimensionally stable samples. A further increase of EHA/TEGDMA in the mixture leads to an enhanced strength of the products whilst still retaining the desirable flexibility. According to these results, the acrylate/crosslinker concentration for the BC-SP composite preparation was carried out in the range of 30–60 wt% in ethanol. This was possible because the composite partner BC stabilizes the viscous samples formed in the model reaction even when using concentrations lower than 40 wt% acrylate/crosslinker.

For determining the molecular weight (gel permeation chromatography, GPC) of the samples in ethanol, a model reaction was used without the addition of crosslinker. As expected the chain lengths of the poly(EHA) is drastically affected by the ethanol content (Figure 5). In case of the previously defined EHA/TEGDMA concentrations from 30–60 wt% the chain lengths are in the range of 200–500 repeating units. That means the SP part of the composites (crosslinker used) is built up by polymer networks of relatively low molecular weight polymer chains.

The photopolymerization of different types of acrylates and methacrylates inside the BC pore system using the never-dried procedure leads to flexible and stable products retaining the original BC shape without discharge of monomers. A typical example is shown in Figure 6. Monomer concentration of 60 wt% generates composites with completely filled BC pores. The application of about 30 wt% causes a coating of the BC fibers (see results of scanning electron microscopy (SEM) investigation in Figure 7).

In addition, this method allows for the purification of the composites (extraction of residual monomers and oligomers – see experimental) and the supply of the final product in a water-swollen state, ready for tests as biomaterial. Residual monomers and oligomers were detected by gas chromatography only in the first and second extract.

A typical example from literature preparing BC-acrylate composites is described by Choi and co-workers.[11] In contrast to the previously described procedure air-dried BC was used pre-activated by ultraviolet (UV) irradiation. Acrylic acid units have been grafted onto this BC. The resulting membranes show an acceding density by increasing UV irradiation time combined with an increasing ion-exchange capacity. The modified membranes exhibit excellent tensile strength due to the high crystallinity of BC.

Nogi et al. used nano-sized fibers like BC (free from light scattering in visible light) as reinforcement agents in optically transparent polymers. Dried BC sheets were

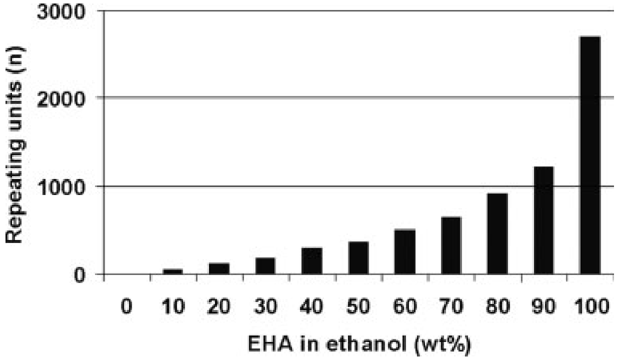

Figure 5.
Chain length (GPC measurements) of the products of EHA polymerization in ethanol as a model reaction without crosslinker.

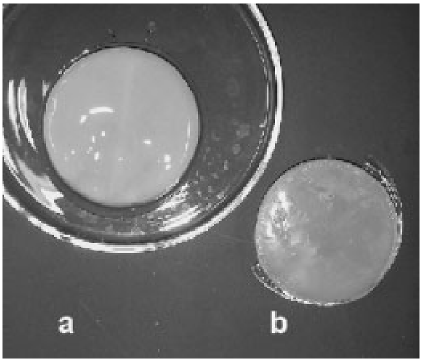

Figure 6.
a – Starting material: never-dried BC pellicle (shaped in a glass tube matrix) after solvent exchange from water to ethanol; b – final BC-SP composite sample 01.

impregnated with acrylic or epoxy resins and subsequently UV cured (two times pressed). Even with a high fiber content of 60–70 wt% the composites show a high degree of transparency of up to 80%.[12]

Characterization of the BC-SP Composites

SEM images of BC-SP composites show that the BC pore system (Figure 7b) of the ‘‘maximum filled’’ composites is homogeneously charged by the crosslinked SP (Figure 7a). In contrast, the bisection of the concentration of the monomer/crosslinker mixture (see Table 2) leads to a partially coating of the fibers (‘‘fiber coated’’ composites, Figure 7c). The pore system is accessible further on.

^{13}C-cross-polarization magic-angle spinning (CP/MAS) NMR characterization of selected composites resulted in clear determination of the small cellulose content in the products.

Water-swelling investigations of the maximum filled composites directly after photopolymerization showed the influence of the type of monomer on the water absorption value (WAV) (Figure 8). The composite WAV is very low in comparison to freeze-dried BC (60%), but hydrophilic monomers like acrylic acid (AA) (sample 01) allow higher water absorption than the hydrophobic EHA (sample 02). It is possible to influence the WAV by combination of hydrophilic and hydrophobic monomers as shown in sample 03 (EHA/2-hydroxyethyl methacrylate (HEMA)/N-vinyl pyrrolidone (NVP)). In all samples the BC showed higher water absorption of the composites in relation to samples of the corresponding SP without BC. This action of the nanocellulose is especially remarkable and important for the favored collagen-like properties because of the low cellulose content in the composites. As can be seen in Figure 8 the loss of residual amounts of ethanol in case of non-swellable samples causes a decrease of weight and therefore a seemingly ‘‘negative swelling’’ (see Experimental, WAV).

In cases of AA the composite formation in presence of water will be proved and the properties of the formed BC-p(AA)- hydrogel will be examined in further investigations.

The same studies on fiber coated composites (sample 05 and 06) directly

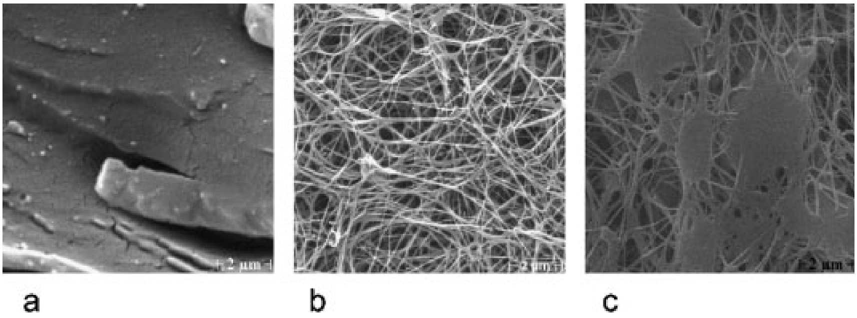

Figure 7.
SEM images (magnification 10 000) of freeze-dried BC-SP composites; a – sample 04 (maximum filled – 60 wt% monomer in ethanol); b – BC (DSM 14666); c – sample 06 (fiber coated – 30 wt% monomer in ethanol).

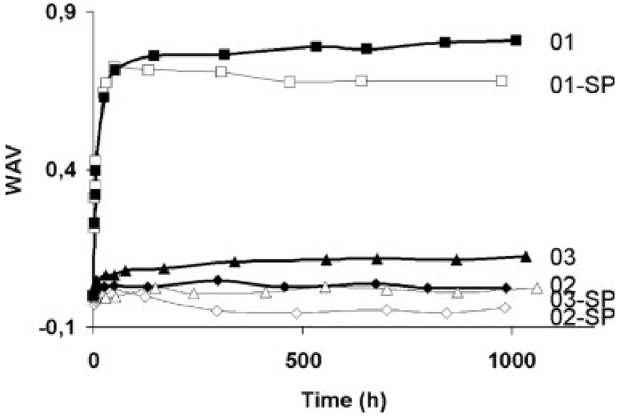

Figure 8.
Water absorptions values (WAV = m_w-m_d/m_d) of selected BC-SP composites and corresponding SP; m_w = mass of wet sample, m_d = mass of dry sample.

after preparation resulted in higher WAV in relation to the maximum filled samples. The specific feature of these composites consists in their ability of maintaining a complete shape and volume regeneration to pellicles after air drying to flat and wrinkled layers – the lower the amount of monomer the better the water absorption (Figure 9). It can be assumed that the partial fiber coating prevents the collapse of the pore system and allows the described re-swelling in water. In contrast, air-dried unmodified BC is not able to regenerate its shape and volume in the presence of water, mainly because of hornification.

Higher crosslinking of the SP composite partners causes a distinct decrease of re-swelling properties in all cases.

Certainly, the described photopolymerization of synthetic monomers inside of the cellulose pore system can be accompanied by partial grafting. However, because of

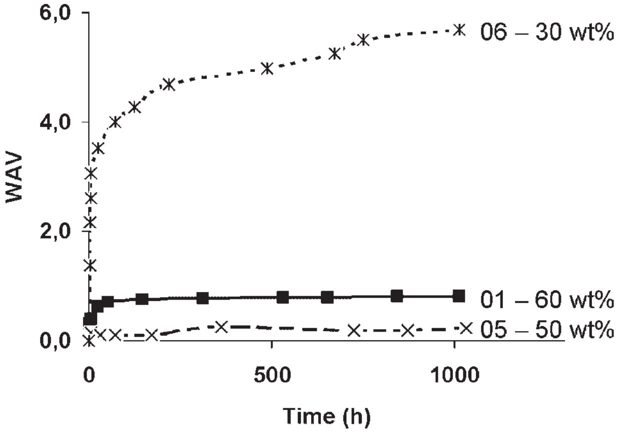

Figure 9.
Re-swelling of air-dried BC-SP composites of constant monomer composition with different monomer concentrations in ethanol.

the polymerization in presence of large amounts of ethanol this question is not simple to explain. It should be answered in further experiments whether the composites are real interpenetrating polymer networks (IPN) or partially grafted networks between BC and SP.

Regulated Modification of Collagen-Like Properties

As mentioned before, BC offers an innovative pool for the development of materials with specific properties. This will be illustrated by an example for supporting tissues (collagen-like materials such as hyaline cartilage). The above named maximum filled samples and further composites prepared corresponding to the subsequently introduced optimization method have been used for this purpose. The measurements were carried out in water-swollen states according to the never-dried procedure (see Experimental).

Hyaline cartilage, the most common cartilage tissue in the human body, can be found, e.g., in the nose and the articular cartilage. This kind of cartilage is supplied with synovial fluid, renewed by a regular change between pressure and relief. Therefore, the modification of the Young's modulus was selected for the analysis of the collagen-like composites, while guaranteeing the material's capacity to absorb large amounts of water. A target Young's modulus between 5 and 20 MPa, similar to hyaline cartilage, was chosen based on our own measurements and on literature data, e.g., Martin et al.[13]

The analysis regarding a regulated property optimization of BC stood in the centre of our investigations. The intended modification of material properties was carried out using the Simplex-method as an experimental optimization procedure.[14] This method allows the identification of extreme values of target parameters, in our case the Young's modulus, while keeping the number of necessary experiments to a minimum. Therefore, a simplex was generated, which is an n-dimensional, convex, geometric figure that consists of (n+1) points. These points represent the number of necessary experiments. The three monomers HEMA, NVP, and EHA used for the production of the collagen-like materials were identified as the influencing parameters. 1 mol% TEGDMA as crosslinker was added in each case. During the experiments these parameters were varied in order to modify the Young's modulus.

The influences of the three parameters result in a considerable range of variation. In orientation and for classification three samples (04, 07, and 08; see Table 1) were taken. Sample 08 meets the requirements best and is therefore the origin for the creation of the start-simplex (sample 08, 09, 10, and 11; Table 1) as represented in Figure 10 (grey lines). The results of these experiments are the basis for the improvement shown as sample 12 (Table 1) in Figure 10 (black lines).

Table 1.
Composition of the Optimized BC-SP Composites According to Simplex-Method.

Step	Sample*	EHA	HEMA	NVP
		mol%		
Determination of the starting point	04	49	25	25
	07	25	49	25
	08	25	25	49
Calculation of runs and their realization	09	28	24	47
	10	24	28	47
	11	24	24	51
Calculation of new runs and their realization	12	27	22	50

* additional 1 mol% TEGDMA.

Table 2.
Mixture for the Formation of BC-SP Composites.

Sample	Monomer				Crosslinker		Concentration of ...	Initiator
	AA	EHA	HEMA	NVP	TEGDMA	BGDMA	monomer/crosslinker in ethanol	Darocur 1116®
	mol%						wt%	
01	99	—	—	—	—	1	60	1
02	—	99	—	—	—	1	60	1
03	—	49	25	25	—	1	60	1
04	—	49	25	25	1	—	60	1
05	—	49	25	25	1	—	50	1
06	—	49	25	25	1	—	30	1
07	—	25	49	25	1	—	60	1
08	—	25	25	49	1	—	60	1
09	—	28	24	47	1	—	60	1
10	—	24	28	47	1	—	60	1
11	—	24	24	51	1	—	60	1
12	—	27	22	50	1	—	60	1

The results of the measurements are illustrated in Figure 11a. The most diverging point was eliminated in the subsequent step. In the new simplex, the eliminated point was replaced with a new one, which was calculated by mirroring the suppressed point on the hyper-area created by the remaining points (shown in black lines in

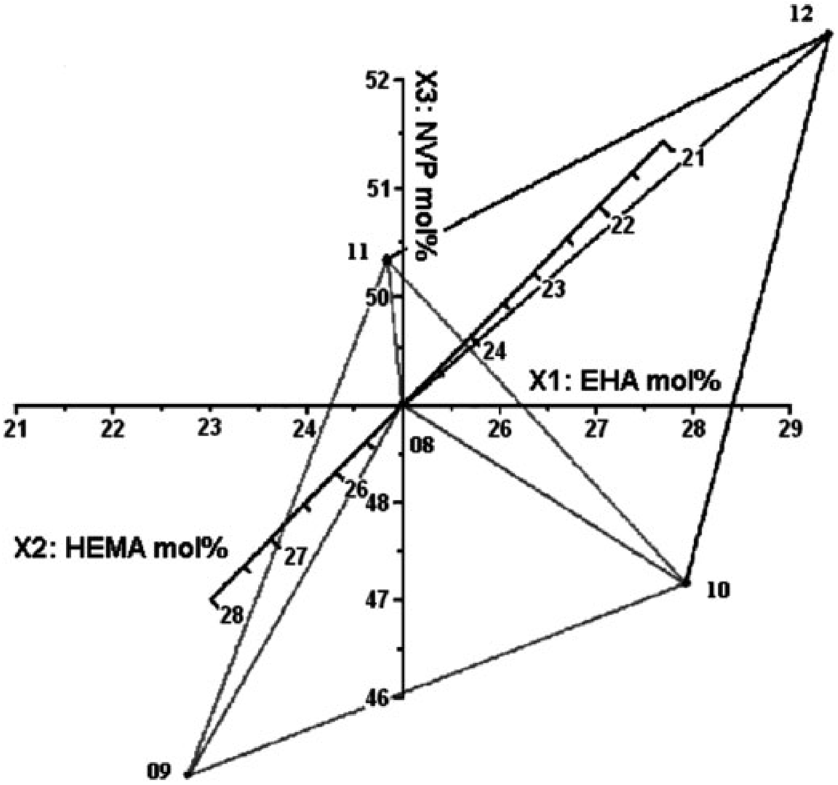

Figure 10.
Graphical representation of the experimental symplex-algorithm. Start-simplex (samples 08, 09, 10, and 11; grey lines) and the improvement (simplex 08, 10, 11, and 12; black lines).

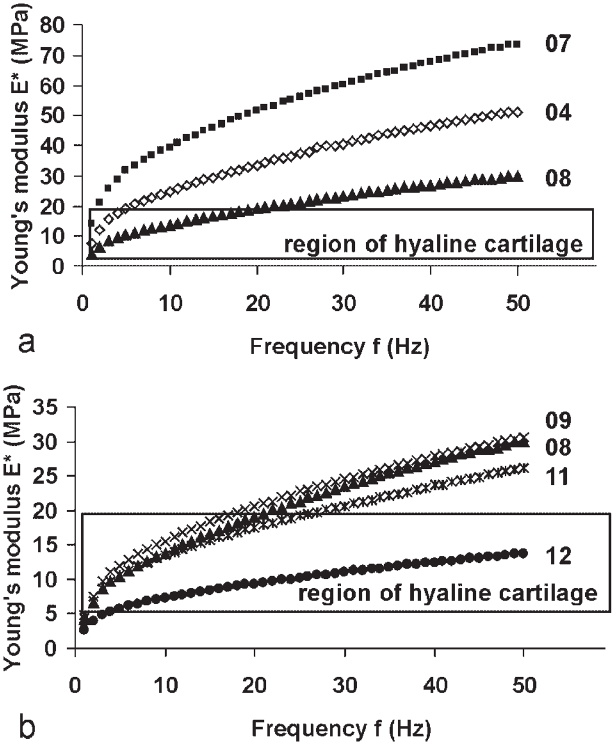

Figure 11.

Young's moduli of BC-SP composites prepared from BC and a mixture of monomers (EHA, HEMA, NVP) and TEGDMA and application of the Simplex-method (see text); a – first step: determination of the starting point; b – test realization of the last run calculated by Simplex-method.

Figure 10). After some repetitions of this procedure, the desired results were achieved (see Table 1). They are illustrated in Figure 11b.

It should be highlighted that the small cellulose part of these composites causes a drastic increase of the product strength. All samples of corresponding SP without BC are even too brittle for the measurement of the Young's modulus.

Experimental Part

Materials

Acrylic acid (AA), 2-ethylhexyl acrylate (EHA), 2-hydroxyethyl methacrylate (HEMA) and N-vinyl pyrrolidone (NVP) as monomers, 1,4-butanediol dimethacrylate (BGDMA) and triethylene glycole dimethacrylate (TEGDMA) as crosslinkers, the photoinitiator 2-hydroxy-4′-isopropyl-2-methyl propiophenone (Darocur 1116®) as well as the initiator azobisisobutyronitrile (AIBN) were used as received.

Cultivation Conditions of BC

The bacterium *Gluconacetobacter xylinus* (strain collection of the Institute of Organic and Macromolecular Chemistry Jena, deposited at Deutsche Sammlung für Mikroorganismen und Zellkulturen Braunschweig – strain DSM 14666) was cultivated as static culture at 28 °C for 14 d in Erlenmeyer flasks containing Hestrin-Schramm medium.[15] 20 ml of this medium were inoculated with 1 ml of a 12 d old liquid preculture. The steam sterilization of the culture liquid was carried out in a pressure cooker at 117 °C for 20 min.

The BC pellicles were taken from the culture medium, washed with distilled water, treated with boiling 0.1 N aqueous sodium hydroxide for 30 min, and washed with distilled water to a neutral reaction of the rinsing agent.

BC-SP Composite Standard Preparation (see also Figure 4)

The BC pellicles prepared as previously described were used for solvent exchange. This was carried out three times by dipping BC in ethanol for 24 h. The resulting ethanol-swollen BC pellicles were impregnated by storage in the mixture of acrylates/methacrylates, crosslinkers, and initiator for seven days (composition is shown in Table 2). The soaked pellicles were taken from the solution and placed in a glass vessel with the top cover as the polymerization reactor. Argon was passed through this reactor using a small cannula before polymerization.

The composites were synthesized by photopolymerization using a Dentacolor XS® (see below) under the conditions shown in Table 3.

This regime was necessary because of the heat development in the first part of the polymerization and the cooling of the lamp in the second part.

For purification the samples were washed by dipping in ethanol for 24 h (three times). The solvent exchange from ethanol to water was carried out three times by dipping BC in water for 24 h.

In case of SEM, WAV and Young's modulus measurements the samples were used the ethanol-swollen state.

Table 3.
Regime of BC-SP Composite Formation.

Number of irradiation cycles	Time of...	
	irradiation (s)	interruption (s)
12	10	50
6	90	300
2	180	600
turn the upside of the composite down		
4	180	600

Model Reactions

A: 99 mol% EHA, 1 mol% TEGDMA, 1 wt% Darocur 1116®
B: 100 mol% EHA, 1 wt% Darocur 1116®

In both cases the monomer concentration of the mixtures was increased up to 100% EHA and EHA/crosslinker, respectively, in steps of 10 wt%. The samples were photopolymerized using the regime shown in Table 4.

Photopolymerization

The photopolymerization was carried out in a Dentacolor XS® from Kulzer (wavelength 320–520 nm). The different procedures of polymerization described in Tables 3 and 4 result from the smaller sample volume of the model reactions.

SEM

The measurement was carried out with a DSM 940 A (Carl-Zeiss, Oberkochen). The cross section of the freeze-dried samples was sputtered with gold before measurement.

GPC

The measurement was carried out with a Jasco equipment (pump 980, UV-detector 975 (254 nm), refractometer 930, and three columns of various pore sizes (PSS Mainz - 10^3 Å, 10^4 Å, 10^6 Å)) at a flow rate of 1 ml/min. The mobile phase used was tetrahydrofurane and polystyrene as a standard. Samples were used without special preparation.

WAV

The maximum filled composites and the corresponding SP samples were not treated in a special way before measurement. That means that residual ethanol is included. The fiber coated samples were air-dried before measurement. Calculation of the water

Table 4.
Regime of Sample Formation.

Number of irradiation cycles	Time of...	
	irradiation (s)	interruption (s)
6	10	50
3	90	300
3	180	600

absorption: $WAV = m_w - m_d/m_d$ (m_w = mass of wet sample, m_d = mass of dry sample).

Young's Modulus

The measurement was carried out with an Explexor 500 N (Gabo Qualimeter, Ahlden) in an air-conditioned room at a temperature of 21.6 °C ± 0.7 °C. The prismatic samples were swollen in an isotonic aqueous solution (Ringer's solution) before measurement. The Young's modulus was determined within a range of frequency from 1 up to 50 Hz. The considered cross section for the evaluation of the Young's modulus shows a standard deviation of ±2.5 mm^2.

Conclusion

One important part of the current activities in the commercial application of BC is the development of nanocellulose materials called NACEMAT. Beside unmodified BC the formation of different types of composites offers a growing potential in technical and also in biomedical applications. The preparation of such BC materials can be realized either as in situ- or as post modification. In the latter case the biogeneous shape of the BC hydrogel can be retained in relation to the aimed application. Additionally the original fiber network can be present in the final product or disintegrated. As mentioned before, nanocellulose is not only produced by bacteria, it can also be produced from the nearly inexhaustible feedstock wood. Therefore, techniques are used where the cell wall is disintegrated by a controlled mechanical treatment.[16–18] Similar to BC, this wood nanocellulose has an amazing water storage capacity.

Nakagaito and co-workers formed nanocellulose composites with phenolic resins starting from disintegrated wood as well as from BC. Bending strength (370 MPa) and Young's modulus (19 GPa) of the wood based composites were lower than the BC reinforced resins (425 MPa, 28 GPa).[17, 19] Composites based on disintegrated BC, which is more similar to the wood product showed bending strengths and Young's moduli similar to wood-based composites. The high values of the BC-based materials seem really due to the extraordinary network structure of BC, up to now only producible by nature.

In agreement with the trend in nanocellulose composites our further investigations are directed to the formation of functionalized BC composites, the testing of selected BC-SP composites as part of the ongoing animal experiments and their evaluation as biomaterial including the use of the Simplex-method to optimize more than one composite property in parallel (e.g. abrasion). Moreover, the qualification of such composites for technical applications will be investigated.

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