High-Strength Epoxy Bacterial Cellulose Based Composites

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Bacterial cellulose offers an interesting potential as natural biodegradable alternative to glass and carbon fibers that are currently used in structural composite. In the present paper, bacterial cellulose produced by Gluconacetobacter Xylinus ATCC 23768 was used as reinforcement fiber to develop four new type composites. The composites were prepared using bacterial cellulose sheets and epoxy resin infused at 10, 15, 250 MPa. These materials were composed of 8 layers of BC pressed at 10 MPa, 8 layers of BC pressed at 15 MPa, 8 layers of BC pressed at 250 MPa and 28 layers of BC pressed at 10 MPa. The first three obtained materials were subject to uniaxial tensile tests, while the fourth material was subject to three-point flexural tests. By using this unique natural material and the resin infusion method it was possible to obtain a composite with the highest reported strength for bacterial cellulose based composites until now. The tensile strength revealed is of about 465 MPa and Young's modulus of about 60 GPa.

Keywords: bacterial cellulose, Acetobacter xylinum,Gluconacetobacter Xylinus Epoxy composite

Composite materials, one of the most versatile classes of engineering materials are frequently criticized because of their environmental impact. While their properties can be easily adjusted by changes in fiber volume fraction and fiber orientation as well as matrix phase, various types of commonly used composite materials arises environmental problems during production and after their intended life [1]. For example, a glass fiber reinforced transport pallet requires an energy input of 1400 MJ with a 73.1 Kg of carbon dioxide emission [2, 3]. A general solution to the current situation is the substitution of currently used compounds in composites, either the reinforcing fibers, resin system or both at the same time with renewable materials.

The theoretical solution is simple but in practice other renewable materials capable to substitute glass fiber or carbon fibers are not actually available. Although a vast amount of publications present new developments on polymers from renewable materials and biodegradable polymers and composites, few of them are capable to compete with glass and carbon fiber composites [4-6].

A possible candidate is bacterial cellulose (BC), a biomaterial produced by gram negative bacteria *Gluconacetobacter Xylinus*. A bacterial cellulose membrane is a three-dimensional reticular network of fine fibrils (2-4 nm in diameter) coalesced into a ribbon (100 nm width, 1-9 μm length) one-hundred times smaller than wood fibers. The bacterium is unique in its prolific synthesis of cellulose, producing a hydro form of cellulose with extensive hydrogen bonding within the reticulated network that can hold up to 700 times its dry weight in water. In dry stage, BC it has a crystallinity index above 70% while a separate fibril can have a theoretical Young's modulus of 173 GPa and tensile strength in the order of 2 GPa [7, 8]. These mechanical properties are based on a pure cellulose fiber and therefore, they are never reached in actual materials that consist of cellulose fibers. However, these values are quite similar to those exhibited by some types of glass and carbon fibers and the highest ever reported values for two-dimensional organic materials [8, 9]. To fully demonstrate the potential of bacterial cellulose, new types of cellulose based composites have been developed. In this sense, some research groups have taken on the difficult task of quantifying the properties of a series of BC composite materials. The studies revealed a Young's modulus of 18-28 GPa and a tensile strength of 260-425 MPa for the new developed composites [8, 10-12]. Despite the achieved result in terms of strength, none of the research groups have investigated the potential of bacterial cellulose as reinforcement fibers and epoxy resin as matrix.

The aim of this paper is to present the preparation and characterization of a new developed bacterial cellulose epoxy laminate composite, which could replace the existing glass or carbon fiber epoxy composites that are frequently used in aerospace industry. Because the properties of bacterial cellulose are influenced by microorganisms cultivation conditions and by the purification treatment of the BC pellicles, the paper is organized in two parts. The first part presents the experiments performed on cellulose cultivation, alkaline treatment and drying of BC membranes. The second part presents the BC-epoxy composite preparation. The obtained composites were morphologically characterized using scanning electron microscopy (SEM). Mechanical properties of the composites were determined using tensile tests.

Experimental part
Reagents
The chemicals used throughout this work were purchased from Carl Roth GmbH + Co. KG if not mentioned otherwise. The used epoxy resin was Hexion EPIKOTE™ Resin 04908 + EPIKURE Curing Agent 04908.

Microrganism culture
The microorganism used in this research was *Gluconacetobacter xylinus* DSM 2004, ATCC 23768, NCIB 7029 purchased from DSMZ - Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH.

Cultivation condition
The culture was performed in two steps. In the first step the inoculated medium was aerated for 72 h in an aeration
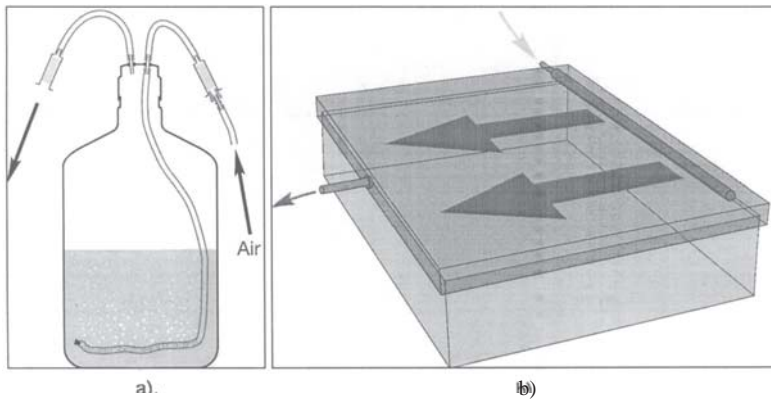
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Fig. 1.a) aeration barrel, b) cultivation tray with air flow
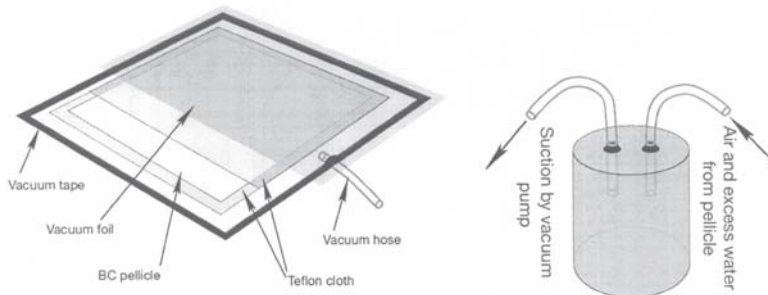

Fig. 2. Schematics of water removal setup

barrel as presented in figure 1 a) with a flow rate of 4 L/min of air. This step was performed to ensure the bacterium strain acclimatization to the cultivation medium.

The second step consisted in 240 h of static cultivation in special designed stainless steel trays with an area of 0.25 m^2. The trays were sealed off and air was supplied using a ventilation system as presented in figure 1 b).

Composition of culture media

The pH level of the media was adjusted to a 4.5 value, by citric acid addition in the second step of cultivation. The media consisted of glucose (50g/L), peptone (5g/L), yeast extract (5g/L), calcium carbonate (5g/L) and 3 mL of antifoam C emulsion, Sigma Life Science, A8011.

Purification of BC pellicle

The obtained BC pellicles were harvested after 240 h of static cultivation. Apart from cellulose, the pellicles contain a large amount of water, bacteria and other constituents of the medium, mostly high concentrations of gluconic acid. In order to obtain a pure BC pellicle, an alkaline treatment had to be performed. Pellicles of about 10 mm in thickness were immersed in a solution of 1M sodium hydroxide, placed in a pressure cooker and heated for 30 min at a temperature of 110°C to ensure sterilization. The pressure cooker was used for safety reasons. The solution was left to cool at room temperature and then the pellicle was immersed in fresh water in an Erlenmeyer flask. The Erlenmeyer flask was shaken regularly and water was refreshed until the *p*H reached a neutral value and pellicle changed color from brownish yellow to milky white, ensuring that the leftovers of the medium and bacteria were removed.

Drying the pellicles

The drying process was performed in two steps. In the first step the pellicles were vacuum squeezed and in second step they were mechanically pressed. First, the pellicles were placed between Teflon cloth and under a plastic bag connected to a vacuum pump. The water removal setup is presented in figure 2.

This process allows the removing of water excess at low rates (about 10 to 15 min) and the fibers to rearrange without risk of pellicle tearing. The water excess was collected in a reservoir mounted before the vacuum pump. The pellicles resulted in smooth sheets from which more than 95% of the water was removed.

The squeezed pellicles were then mechanically pressed using a Joos laboratory press LAP 100 to remove out and evaporate the remaining moisture more rapidly. Since the vacuum-pressed pellicles are much thinner but still jelly-like, they are fragile and difficult to handle. The pellicles were therefore not taken out of the Teflon layers, but the entire stack was put in the mechanical press, also ensuring that the pellicles would not stick to the press. It is acknowledged that within reasonable bounds, the cellulose does not suffer any damage in strength or stiffness when different pressures are applied [12]. Practice proved that pressing the pellicles to a pressure of 0.3 MPa and heating them to 110°C for 10 min, followed by cooling to 40°C before releasing the pressure, results in dry and smooth sheets. It was essential to let the press cool down before opening it, since dry pellicles still deform due to thermal contraction.

Preparation of BC composites

In this research, two types of procedures were employed for the preparation of epoxy bacterial cellulose based composites. The first procedure was similar to the classic vacuum infusion procedure. This attempt to produce an epoxy-BC composite was made by stacking sheets of dry cellulose submerged in epoxy to avoid air insertion in the composite. The stack was then removed from epoxy and pressed using plastic foil and vacuum pressure. The obtained laminate was clearly not smooth and contained pockets of excess epoxy in the structure. During preliminary tensile testing, some layers completely delaminated. Under SEM examination in figure 3-1 and 3-2 the excess epoxy was clearly visible. The epoxy did manage to penetrate the sheets to such an extent that it adhered to the fibers, visible by the pieces of epoxy showing cellulose fibers attached to it, as one can see in figure 3-3 and 3-4.

The results obtained with this method were not suitable for structural test but they provided indispensable
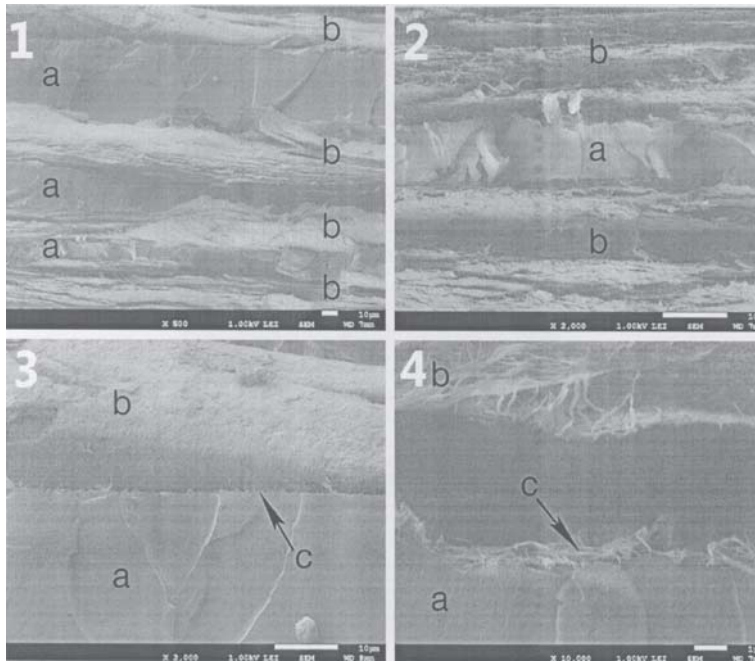
Fig. 3. SEM images of the BC-epoxy composites obtained in preliminary experiments: (1) Epoxy-BC composite (500x), view on surface of failure: layers of epoxy (a) and BC sheets (b) clearly visible; (2) Epoxy-BC composite (2000x), view on surface of failure, two sheets of BC (b) with epoxy in between clearly visible (a); (3) Epoxy-BC composite (2000x), view on surface of failure, showing separated layer of BC (b) from pocket of epoxy (a), visible cellulose fibers attached to the epoxy (c); (4): Epoxy-BC composite (10000x), view on surface of failure, showing separated layer of BC (b) from pocket of epoxy (a), visible cellulose fibers attached to the epoxy (c)
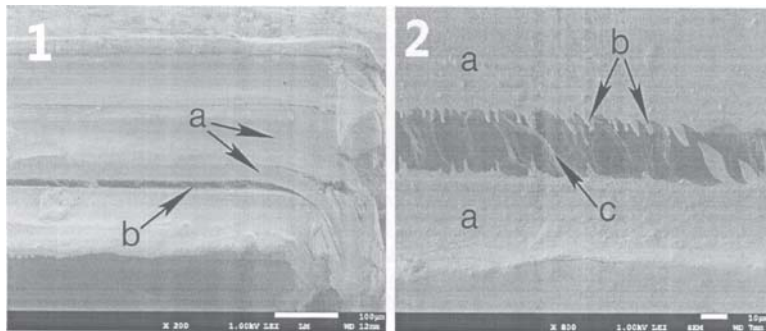

Fig. 4. SEM images of epoxy-BC composite made using mechanical press: (1): Epoxy-BC composite (200x), (2) Epoxy-BC (800x), view on the side of the specimen, showing delamination caused by a cut made for observation. The layers on both sides (a) are difficult to distinguish because the edge of the specimen is covered with epoxy; (b) epoxy is on the side of the specimen, torn at the delamination, (c) are fibers torn from the layers
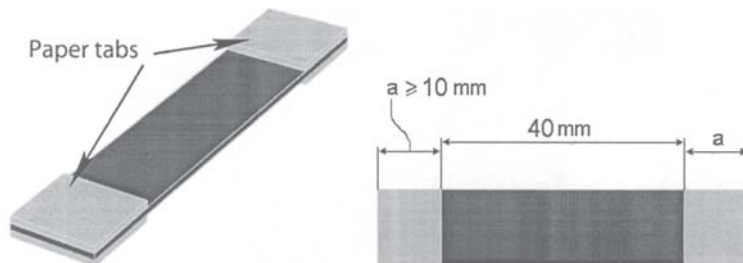

Fig. 5. Rectangular specimen with paper tabs

knowledge on the BC interaction with epoxy resin. Based on this data, the second procedure involved high pressure applied in order to force the resin to penetrate the BC sheets. In this procedure, sheets of cellulose were taped on a surface to prohibit pellicle shifting caused by the exerted pressure. The sheets were then laminated using a brush and the stack was covered in plastic foil and pressed mechanically. A SEM image, presented in figure 4-1, showed that excess epoxy existing between the smooth layers of BC was removed using this approach. A delamination occurred while preparing the small sample for SEM image, which showed that fibers were torn from the layers (fig. 4-2).

This demonstrates that fibers in the sheet failed before the bonding between fibers of adjacent layers, proving sufficient penetration of the epoxy and proper bonding to the BC. Four types of composites were produced based on this method as follows: the first one using 8 layers of BC pressed at 10 MPa, second one using 8 layers of BC pressed at 15 MPa, third one using 8 layers of BC pressed at 250 MPa and the fourth one using 28 layers of BC pressed at 10 MPa. From each of these composite materials were prepared 12 test samples with different dimensions as presented in table 1.

Tensile test

Samples obtained from the first three composite materials were subjected to tensile tests using a Zwick 1455 machine at a strain rate of 1 mm/min over a spam of 40 mm. As guideline the standard tests method for tensile properties of polymers matrix composites materials D 3039/D 3039M-07 was used. The only deviation from the standard was the use of paper tabs for the sample grip area, as one can see in figure 5.

Flexural tests

Three-point flexural test is a more common method for testing brittle materials that fail under relative small strains (less than 5%). To obtain more accurate results on the values of mechanical properties of BC-epoxy composites, the forth material (with 0.50 mm thickness pressed at 10 MPa), was subjected to three-point flexural tests (Standard ASTM D790-03) performed with the Zwick 1455 test machine using a three-point flexural bench.

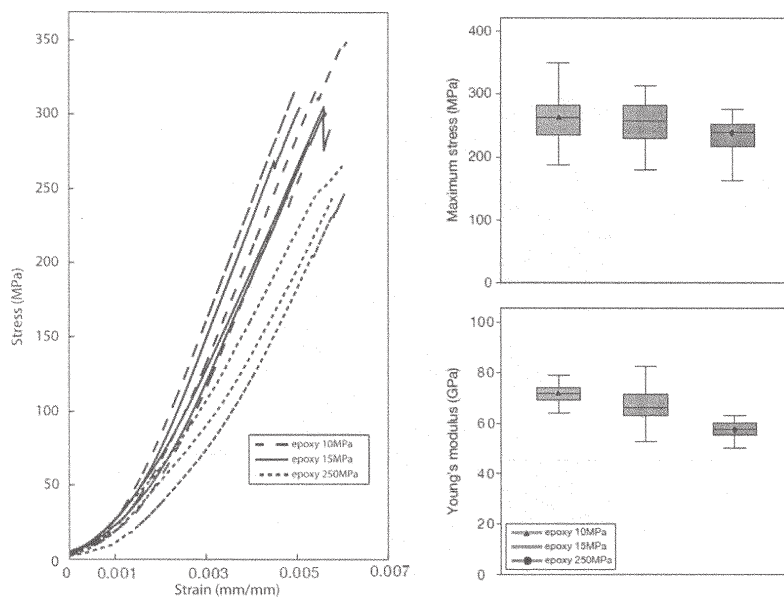| Test samples	Length	Width	Thickness	Nr. of BC sheets
Epoxy-BC at 10MPa	40 mm	15 mm	0.16 mm	8
Epoxy-BC at 15MPa	40 mm	15 mm	0.16 mm	8
Epoxy-BC at 250MPa	40 mm	15 mm	0.16 mm	8
Epoxy-BC at 10MPa	40 mm	10 mm	0.5 mm	28

Table 1
TEST SAMPLE DIMENSIONS

Fig. 6. Examples of stress-strain curves obtained from tensile test for BC-Epoxy composites and the Young's modulus, maximum strength reported for all the samples
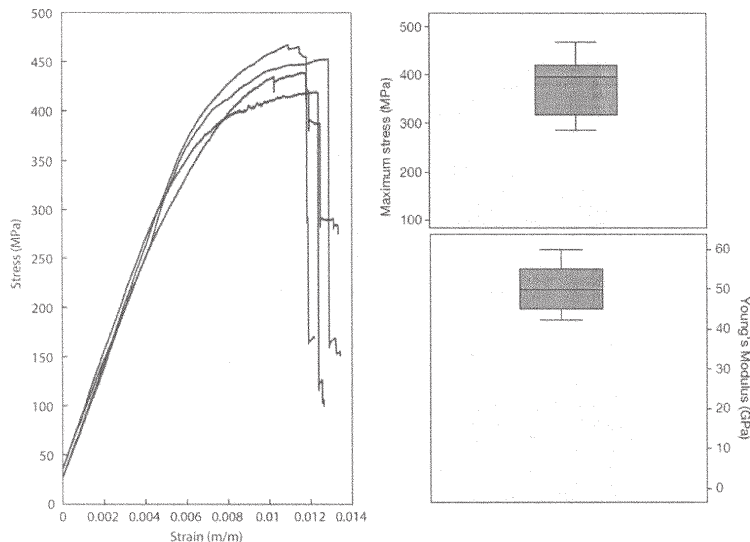
Fig. 7. Examples of stress-strain curves obtained from flexural test for BC-Epoxy composites and the Young's modulus, maximum strength reported for all the samples

Results and discussions

The results of the tensile tests are presented in figure 6. To keep the results visible, the stress-strain diagram presents just the three most relevant results obtained for each tested material. However, the maximum stress and Young's modulus presents a summation of all tested samples.

Figure 7 displays the results of the three-point flexural tests. Also in this case, the stress-strain diagram presents just a set of results for each tested material, but the maximum stress and Young's modulus are presents a summation of all tested samples.

The most significant difference between the results of flexural test and tensile tests is that the material undergoes plastic deformation just during the flexural test, but the Young's modulus does not vary so much between the two tests. Moreover, the stress-strain curves in flexural tests resemble to the ones stated in literature [13]. Since flexural test is more common and reliable for brittle materials and deflection can be measured more accurately, it seems that the cause of difference between the two types of tests is mainly due to crack propagation during the tensile test. Practice proved that creating BC composites in a common

composite laboratory resulted in dust accumulation on the BC pellicles that lead to material defects. Considering also the method employed for sample cutting, these defects were the main causes which led to crack formation and propagation in the sample during tensile test. However, if we examine further the results, other differences are visible as well. It is acknowledged that the first linear part of the curve during the flexural test is caused by the bending and stretching of the interatomic bonds, following Hooke's law. Next, the curve levels off, caused by the uncoiling of the molecules. Finally, the yield point is also the point of failure, because the structure does not allow for much slippage between the molecules. The material therefore, cannot strain further plastically and fails instantly. The yield strength is equal to the ultimate strength. Usually, the same rules applies also for the curves resulted from tensile test, but the obtained curves in the current tensile test are not linearly at the beginning of the tests because of the use of paper tabs. The tabs are often used in thin film testing, where the lower Young's modulus of the films dominates the test results and the influence of the tabs is not visible.

During tests, it was observed that the samples with paper tabs were often not gripped properly and shifted in
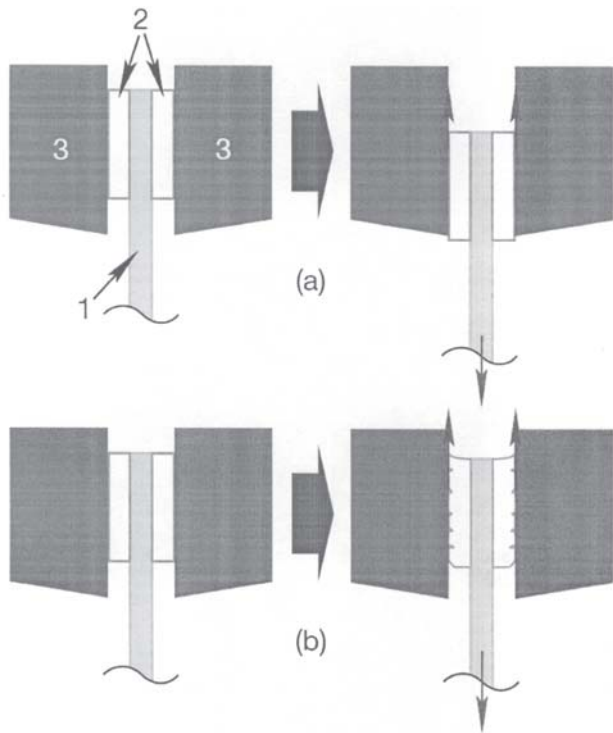
Fig. 8. Top end of BC-composite specimen (1), covered by paper tabs (2) in clamps (3); 8a) slipping of the specimen, 8b) initial partial gripping of the paper, tearing the surface of the tabs.

the clamps (fig. 8 a). Eventually, the clamps grip and the tensile force can build up, but during the initial gripping, it showed that the paper is gripped on some spots of the surface of the paper before others; distorting and tearing the surface to some extent (fig. 8 b). These two effects might be the cause of the first non-linear part or the curves and the slightly difference in Young's modulus between the two test. However failure occurred at the end of the near linear part of the curve in tensile tests because of cracks propagation resulting in failure before the actual ultimate strength.

Conclusions

Bacterial cellulose sheets were used as reinforcing fibers in the production of a new type of composite. The used resin matrix of the compost was epoxy type Hexion EPIKOTE™ Resin 04908 + EPIKURE Curing Agent 04908 which was mechanically infused in the bacterial cellulose at 10, 15, and 250 MPa. Both uniaxial tensile and three-point flexural tests were performed. The results revealed a tensile strength of about 465 MPa and a Young's modulus of about 60 GPa. Although higher values than those previous exposed were observed in Young's modulus, those values were credited to a series of measuring errors or material defects. For the Young's modulus, only the values validated by both tensile and three-bending tests and confirmed on

at least three test samples were considered and reported as results. However, these results are rather qualitative than quantitative and highlight the potential of BC-epoxy composite as an alternative material for structural use. More accurate tests must be performed on samples with a thickness higher than 3 mm to demonstrate the true potential of BC-epoxy composite as a material for structural use.

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