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BioM&M_2018

Experimental study on the actuation and fatigue behavior of the biopolymeric material Cottonid

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Abstract

Saving and reducing the consumption of electrical energy is one of the major future challenges for industry and society. It would be desirable, if an actuator autonomously responds to an environmental stimulus like humidity, temperature or light. In this study, the actuation and fatigue behavior of the macromolecular cellulose-based material Cottonid is characterized. It is hygroscopic and possesses process-related anisotropic mechanical properties, which makes it an efficient adaptive material for humidity-driven actuators. A quantitative and qualitative evaluation of the passive movements of Cottonid-based bilayer structures in reaction to humidity absorption and desorption was performed concerning parameters like angle of deflection and saturation. To assess direction-dependent fatigue performance, specimens were prepared in 0° and 90° according to cellulose micro fibril orientation and cyclically loaded in stepwise load increase tests. 0° specimens reached highest stresses at failure whereas 90° specimens showed a pronounced cyclic deformation behavior. Differences in damage development due to alternating micro fibril orientations could be visualized via computed tomography (CT), which leads to a profound understanding of biomechanics.

Selection and Peer-review under responsibility of 1st International Conference on Materials, Mimicking, Manufacturing from and for Bio Application (BioM&M).

Keywords: Humidity-driven movements; hygroscopicity; anisotropy; cellulose; micro fibril orientation; direction-dependent fatigue; autonomous actuators

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2214-7853
Selection and Peer-review under responsibility of 1st International Conference on Materials, Mimicking, Manufacturing from and for Bio Application (BioM&M).

1. Introduction

Through evolutionary selection, plants and animals developed structures and mechanisms adapted to their environment over time, which can be quite impressive, like the well-known lotus effect. In science, phenomena like this are used as a source of inspiration to transfer adaptive properties developed by nature into technical processes to create resource- and energy-efficient solutions. In this context, the way in which plants change their shape in response to environmental stimuli without an equivalent of muscles or metabolism came to the fore for a broad number of scientific fields, because of the possibility to generate motion without the use of an electrical energy source. In engineering, components and products primarily use electrical actuation devices like motors to transform electrical into mechanical energy and it would be desirable, if the device responds autonomously to a defined environmental trigger respectively stimulus, like temperature, humidity or light [1,2].

Generally, movements of plants occur over a wide range of sizes and scales, e.g. for biological purposes like seed dispersal, and were first revealed and described by Charles Darwin in the late 19th century. Focusing on humidity-driven actuation, there is a variety of examples of natural hygromorphs, which move passively in reaction to alterations in relative humidity. The movement has its origin on the molecular level and is a result of swelling and shrinking of the cellulose micro fibrils in reaction to increasing respectively decreasing humidity. The pine cone as natural role model for passive actuation, e.g. shows bending movements of its individual scales, which rely on their bilayered microstructure. A bionic transfer of this principle enables the development of functional materials respectively adaptive actuators in times of resource scarcity caused through environmental respectively social issues [3-13].

In this experimental study, the cellulose-based material Cottonid is characterized under medial and mechanical loading. Pretests revealed a pronounced humidity-driven swelling and shrinking behavior in comparison to wood, which lead to the assumption, that the chemical modification of the cellulose as well as the ability of fine-tuning the micro fibril orientation during manufacturing of Cottonid, are beneficial for passive, humidity-driven movements. This promotes Cottonid as an efficient material candidate in the context of smart stimuli responsive materials (SMRs).

1.1. Cottonid

To explain what Cottonid is, it is helpful to compare it to wood, e.g. beech wood, concerning its material category and its main molecular components. In contrast to wood, Cottonid is a modified biopolymeric material, which means, that its raw material cellulose is chemically treated during the manufacturing process to modify and improve the material properties. This enables to create a more homogenous and process-related microstructure, meaning a suitable arrangement of the cellulose micro fibrils, and to produce tailor-made properties over parameter variation. Furthermore, Cottonid is 100% cellulose-based without by-products like hemicellulose or lignin. The manufacturing process is based on the principles of parchmentizing known from the already in the late 19th century patented material vulcanized fiber. As raw material, unsized machine-made papers layers with a high percentage of α-cellulose are used. The cellulose can be derived from different sources, like cotton linters or wood pulp. Fig. 1. (a) shows a SEM micrograph of the raw paper, where the cellulose micro fibrils are clearly visible. To produce Cottonid, several sheets of this raw paper are fed into a continuous process and joint together over a chemical reaction, see Fig. 1. (b).

Fig. 1. (a) SEM micrograph of raw paper; (b) Manufacturing process of Cottonid: 1. Parchmentizing, 2. Reaction and washing out, 3. Drying and planning; (c) SEM micrograph of Cottonid.

As catalyst, sulphuric acid or zinc chloride solution is used for a chemical modification of the cellulose, meaning etching of the micro fibril surfaces, to produce hydrate cellulose, which results in a chemical cross-linking between the single paper layers over hydrogen bonds, (1.). Therefore, Cottonid is more or less a laminated material and the amount of treated paper layers define the thickness of the end product. To avoid a further reaction after parchmentizing, the chemicals are washed out over several water baths, (2.) and finally the material gets planed and dried using roll mills, (3.). The resulting microstructure is shown in Fig. 1. (c). After the process, Cottonid has increased properties in comparison to its raw material paper. It has a woody nature and is resistant to elevated temperatures or chemical solutions. In addition, there are no residuals left over from the manufacturing process, which could harm the environment. The mechanical properties are comparable to some technical plastics. Furthermore, because of the directed manufacturing process of machine-made paper, Cottonid possesses anisotropic mechanical properties. It behaves like fiber-reinforced plastics, which show highest strengths in fiber direction and are weakest, when loaded perpendicular to it. So, dependent on the specimen in respect to manufacturing direction respectively cellulose micro fibril orientation, varying mechanical properties like ultimate tensile strength UTS can be detected for Cottonid [14-18].

This experimental study investigates interdependencies of the process-related anisotropy of Cottonid and its actuation and fatigue behavior. Medial as well as mechanical experiments were performed by varying parameters referring to the manufacturing process, like amount of paper layers respectively thickness of the material, chemical catalyst and loading direction in respect to cellulose micro fibril orientation. The aim is to draw a line between microstructure, humidity-responsiveness and mechanical strength of Cottonid, to characterize the material in the context of adaptive and autonomously moving structures [19-21].

2. Experimental procedure

2.1. Specimen preparation

Based on the anisotropic properties of Cottonid caused by the directed manufacturing process, specimens were prepared in 0° and 90° according to cellulose micro fibril orientation for a direction-dependent actuation and fatigue assessment, see Fig. 2. During the actuation experiments, a highly hydro-active Cottonid layer was combined with office paper (80 g/m^2) to create a bilayered structure (width w = 15 mm, length l = 30 mm). Thicknesses of active layers were $t_{active,sulph}$ = 0.5 mm and $t_{active,zinc}$ = 0.4 mm, see Fig. 2. (a), which results in a thickness ratio of approx. 0.2 of the bilayers. Because office paper is less reactive to humidity, swelling and shrinking of Cottonid results into a bending movement of the actuator, as described before for pine cone scales, which can be qualified and comparatively evaluated in an efficient and descriptive way. For mechanical testing, specimens Type 1B according to DIN EN ISO 527 were used, see Fig. 2. (b). Thickness was t = 8 mm.

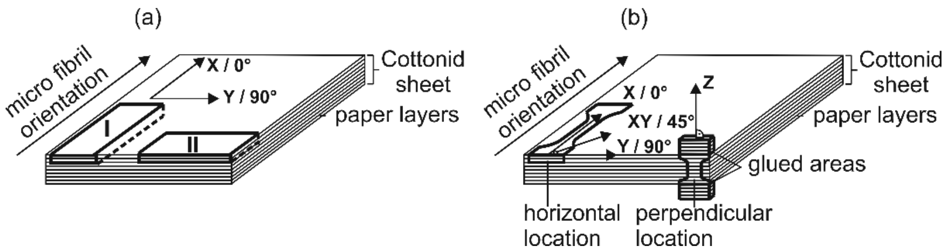

Fig. 2. Specimen preparation for (a) Actuation tests and (b) Fatigue tests [17].

2.2. Characterization of passive humidity-driven movements

Experimental studies concerning the actuation behavior of Cottonid in reaction to alterations in relative humidity φ were performed in an alternating climate chamber (MKF 115, Binder GmbH, Tuttlingen, Germany) on Cottonid/paper bilayer actuators as described in subsection 2.1., fixed at one end. Deflection angle Δα was determined at the free end during a swelling time of t_s = 30 min in a testing atmosphere of T = 23 °C and φ = 95% r.H. The tests where instrumented with optical tracking and images were taken every 30 seconds with a waterproof camera placed in the climate chamber. The actuation behavior of 0° specimens was monitored from frontal view and of 90° specimens from lateral view respectively, because actuation performance will happen perpendicular to cellulose micro fibril orientation. The chemical catalyst, which was used for manufacturing of the Cottonid layer, was either a sulphuric acid (H_2SO_4) or a zinc chloride ($ZnCl_2$) solution, to assess influence of manufacturing parameters on the bending performance. Actuators were stored in a desiccator before the testing to ensure comparable material conditions.

2.3. Fatigue assessment

To investigate the fatigue behavior of Cottonid, load increase tests (LIT) were used, which exhibit the opportunity of resource-efficient estimation of the fatigue properties of various materials. This method has been successfully applied to composite structures in previous studies [22-24]. Here, LIT was applied for an evaluation of the influence of process-related anisotropy on the fatigue behavior of Cottonid. The tests were performed on a servo-hydraulic testing system (F_{max} = 63 kN, Schenk/Instron, Darmstadt, Germany) with a frequency f = 5 Hz and a sinusoidal load-time function. During LIT, specimens were subjected to a tension-tension load of R = 0.1 in 0° and 90° to manufacturing direction respectively cellulose micro fibril orientation. Load was increased stepwise with $\Delta\sigma_{max}$ = 5 MPa after $\Delta N = 10^4$ cycles starting at $\sigma_{max,start}$ = 5 MPa until failure, see Fig. 3. (a). To characterize the material's response to cyclic loading, dynamic Young's modulus E_{dyn} as well as change in temperature ΔT were taken as the relevant damage parameters based on research activities in the field of fiber-reinforced composites, see Fig. 3. (b) [25,26]. For the evaluation of deformation-induced changes in microstructure, the degradation of E_{dyn} was monitored during loading using a tactile extensometer with a gauge length of L_0 = 25 mm for strain measurements. E_{dyn} was calculated using secant modulus between (ε_{min}, σ_{min}) and (ε_{max}, σ_{max}). For temperature measurements, three thermocouples were mounted over the clamping length of the specimen to monitor temperature changes in the material during loading. Thermocouple 2 was mounted in the gauge length of the extensometer and directly corresponds to the strain measurements, see Fig. 3. (c).

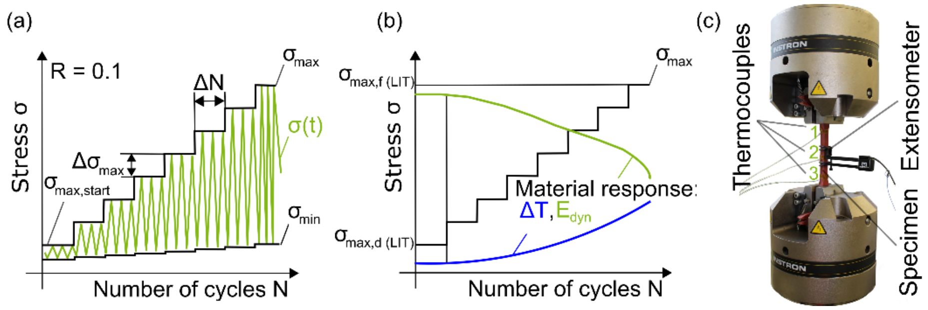

Fig. 3. (a) Scheme of load increase test (LIT); (b) Detection of material response during cyclic loading; (c) Instrumented specimen for LIT.

2.4. Structural Investigations

Accompanying to the actuation and fatigue tests, direction-dependent structural investigations were performed. Therefore, computed tomography images were collected with a 160 kV microfocus X-ray tube (Nikon, X TH 160, Alzenau, Germany) and reconstructed into 3D volumes via software VGStudio Max (Volume Graphics, edition 2.2). Structural changes due to mechanical loading were visualized over in situ mechanical tomographic investigations, using a tension/compression testing system (F_{max} = 5 kN, CT5000TEC, Deben UK Ldt., Suffolk, UK), which is integrable into CT. The testing principle is to capture the microstructure of Cottonid in the volume under defined tension loads and to compare it to the initial state.

3. Results

3.1. Actuation behavior

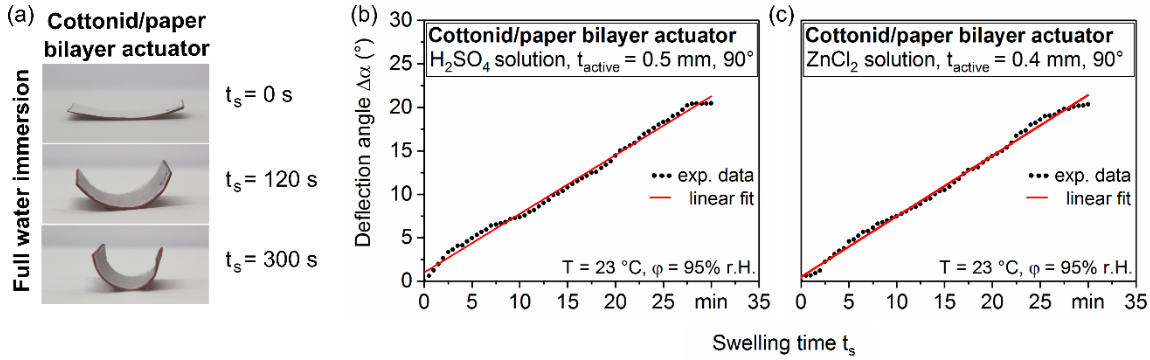

Fig. 4. (a) Cottonid/paper bilayer actuator fully immersed in water, swelling time t_s = 5 min; Plots of deflection angle Δα versus swelling time t_s = 30 min for (b) Sulphuric acid solution (H_2SO_4) and (c) Zinc chloride solution ($ZnCl_2$) as chemical catalyst during parchmentizing.

In Fig. 5. (a) the pronounced actuation behavior of a Cottonid/paper bilayer actuator is exemplary shown for direct water immersion and a swelling time of t_s = 300 s. Further, deflection angle Δα was plotted over swelling time t_s exemplary for 90° Cottonid/paper bilayer actuators. Testing parameters were T = 23 °C, φ = 95% r.H. and t_s = 30 min. In (b) results for H_2SO_4 solution and in (c) for $ZnCl_2$ solution as chemical catalysts during parchmentizing of Cottonid are shown. Deflection angles are $\Delta\alpha_{sulph}$ = 20.48° and $\Delta\alpha_{zinc}$ = 20.35°, which indicate a comparable rate of angular change of ~ 0.68 °/min of both bilayer typologies and do not verify an influence of the type of parchmentizing solution onto the actuation behavior of Cottonid. In addition, water absorption rate seems to be similar due to comparable slopes of the linear fits to the actuation curves of m ≈ 0.7. Saturation seems to occur at t_s ≈ 28 min, which has to be verified over long-term tests.

3.2. Fatigue

Fig. 5. illustrates LIT results for mechanical loading of Cottonid in 0° respectively 90° according to cellulose micro fibril orientation. The progression of maximum stress σ_{max} as controlled value as well as E_{dyn} and ΔT as measured values are plotted as functions of load cycles N. In addition, ΔT2 is plotted, representing the change in temperature in the gauge length of the specimen. For the investigations, a decrease of E_{dyn} respectively increase of ΔT2 during the mechanical loading was chosen as criterions for a material response onto cyclic loading. As can be seen in (a), for 0° specimens a linear decrease of E_{dyn} respectively increase of ΔT2 occurs in the seventh load step at $\sigma_{max,\mathbf{dI},\mathbf{0°}}$ = 35.0 MPa, defined as maximum stress at first response of the material during LIT. A second significant change in the measured values occurs in the load step right before failure at $\sigma_{max,\mathbf{dII},\mathbf{0°}}$ = 65.0 MPa. Here, for the first time a change in slope of E_{dyn} within one load step can be detected. Simultaneously, ΔT2 increases significantly up to 10 K, which finally results in failure of the specimen at a maximum stress at failure of $\sigma_{max,\mathbf{f},\mathbf{0°}}$ = 70.0 MPa and load cycles at failure of $N_{\mathbf{f},\mathbf{0°}}$ = 134,640. Reached values of $\sigma_{max,d}$ and $\sigma_{max,f}$ reveal, that Cottonid starts to respond onto cyclic loading at significantly lower loads than failure finally occurs. In comparison, Fig. 4. (b) shows an equivalent plot for LIT results for loading in 90° according to cellulose micro fibril orientation. In comparison to the previous results, it can be seen that $\sigma_{max,\mathbf{d},\mathbf{90°}}$ and $\sigma_{max,\mathbf{f},\mathbf{90°}}$ attain lower values. In the fourth load step at $\sigma_{max,\mathbf{dI},\mathbf{90°}}$ = 20.0 MPa the chosen criterion for material response was reached. Analogue to loading in 0°, a change in slope of E_{dyn} within one load step can be detected at $\sigma_{max,\mathbf{dII},\mathbf{90°}}$ = 40.0 MPa right before failure at $\sigma_{max,\mathbf{f},\mathbf{90°}}$ = 45.0 MPa ($N_{\mathbf{f},\mathbf{90°}}$ = 80,110). Fig. 5. (c) presents the normalized dynamic Young's modulus $E_{dyn}/E_{dyn,0}$ for both orientations. Loss of material's stiffness during LIT is comparable of about ~ 50%, although 90° specimens reach lower values of $\sigma_{max,d}$ and $\sigma_{max,f}$.

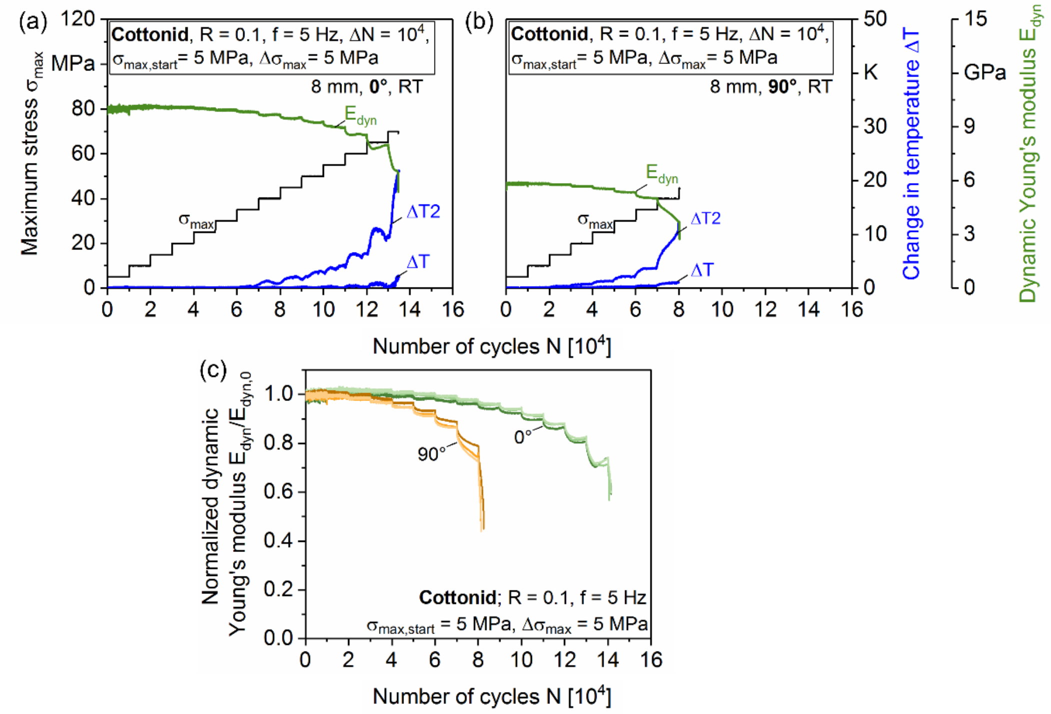

Fig. 5. Results of load increase test (LIT) on Cottonid in (a) 0° and (b) 90° to cellulose micro fibril orientation; (c) Normalized dynamic Young's modulus $E_{dyn}/E_{dyn,0}$ for 0° and 90°.

3.3. Structural investigations

By analyzing the material's volume over CT-scans, a high amount of voids can be detected in initial respectively unloaded state of the specimen, leading to the assumption of insufficient paper layer bonding during manufacturing. By increasing tension load, the amount of voids as well as their individual size itself increases. The results are shown exemplary for a 0° specimen and therefore a void development repsectively shift longitudinally in loading direction appears. So, a direction-dependent defect progression on the structural level can be detected, see Fig. 6.

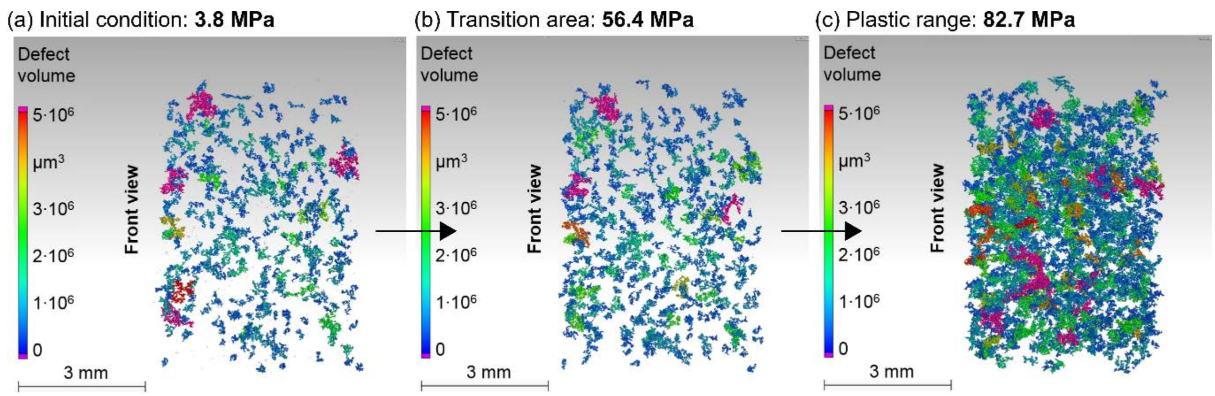

Fig. 6. In situ mechanical tomographic investigations in quasi-static range: (a) Initial state; (b) Transition area; (c) Plastic range.

4. Conclusions

An experimental study on the actuation and fatigue properties of Cottonid focusing the influence of its structural anisotropy was performed. The achieved results reveal first observations of process-related humidity-driven movements and significant differences concerning estimated fatigue strength depending on the location of the specimen respectively loading direction according to manufacturing direction. From the cross examination of the performed tests the following conclusions can be drawn:

1. The type of chemical catalyst (H_2SO_4/$ZnCl_2$ solution) used during parchmentizing does not influence the humidity-driven actuation behavior of Cottonid.
2. The fatigue properties of Cottonid are crucially influenced when varying loading direction according to manufacturing direction respectively cellulose micro fibril orientation. When loading 90° to micro fibril orientation, maximum stress at material response $\sigma_{max,\mathbf{d,90°}}$ as well as maximum stress at failure $\sigma_{max,\mathbf{f,90°}}$ show a decrease of about 40%, when compared against the averaged values of load increase tests in 0°.
3. Although results of fatigue tests in 90° according to micro fibril orientation showed lower values of maximum stress at material response $\sigma_{max,\mathbf{d,90°}}$ as well as maximum stress at failure $\sigma_{max,\mathbf{f,90°}}$ compared to 0°, the normalized dynamic Young's modulus $E_{dyn}/E_{dyn,0}$ revealed a comparable loss of stiffness of the specimens during loading of about 50%.
4. It could be shown, that Cottonid behaves like a fiber-reinforced composite concerning its mechanical properties and its deformation behavior, although it is 100% cellulose-based and does not have a fiber/matrix structure.
5. The structural investigations reveal a direction-dependent damage development when applying mechanical load, caused by the structural anisotropy, which manifests in an increase of void volume. This leads to the assumption of interdependencies between void development and loss of material stiffness during mechanical loading.

The drawn conclusions have to be statistically validated in further investigations. In the next steps of the project, structural optimization of Cottonid over manufacturing parameter variation shall be performed to achieve tailor-made actuation and fatigue properties. The aim is to create a suitable arrangement of the cellulose micro fibrils, for example to produce local anisotropic swelling and shrinking, in the sense of qualifying Cottonid as a hygro-active functional material in the field of bioarchitecture.

Acknowledgements

We thank the German Science Foundation (DFG) for funding the related research project "Biomechanical qualification of the structurally optimized functional material Cottonid as an adaptive element" (WA 1672 / 23; ZO 113 / 22).

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