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Keywords: thickener, thixotropy, rheology, gel, water dispersion, bacterial cellulose

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Bacterial cellulose as polysaccharide possessing outstanding chemical purity and a unique structure compared with wood cellulose, attracts great attention as a hydrocolloid system. It was shown, that at intense mechanical action on a neat bacterial cellulose film in presence of water, the gel-like dispersions are obtained. They retain stability in time (at least, up to several months) and temperature (at least, up to 60 °C) without macro-phase separation on aqueous and cellulose phases. The main indicator of the stability is constant viscosity values in time, as well as fulfilling the Arrhenius dependence for temperature dependence of viscosity. Flow curves of diluted dispersions (BC content less than 1.23%) show strong non-Newtonian behavior over the entire range of shear rates. It is similar with dispersions of micro- and nanocrystalline cellulose, but the absolute viscosity value is much higher in the case of BC due to more long fibrils forming more dense entanglements network than in other cases. Measuring the viscosity in increase and decrease shear rate modes indicate an existence of hysteresis loop, i.e., thixotropic behavior with time lag for recovering the structural network. MCC and NCC dispersions even at cellulose content more than 5% do not demonstrate such behavior. According to oscillatory measurements, viscoelastic behavior of dispersions corresponds to gel-like systems with almost total independence of moduli on frequency and essentially higher values of the storage modulus compared with the loss modulus.

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Article

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Abstract: Bacterial cellulose as polysaccharide possessing outstanding chemical purity and a unique structure compared with wood cellulose, attracts great attention as a hydrocolloid system. It was shown, that at intense mechanical action on a neat bacterial cellulose film in presence of water, the gel-like dispersions are obtained. They retain stability in time (at least, up to several months) and temperature (at least, up to 60 °C) without macro-phase separation on aqueous and cellulose phases. The main indicator of the stability is constant viscosity values in time, as well as fulfilling the Arrhenius dependence for temperature dependence of viscosity. Flow curves of diluted dispersions (BC content less than 1.23%) show strong non-Newtonian behavior over the entire range of shear rates. It is similar with dispersions of micro- and nanocrystalline cellulose, but the absolute viscosity value is much higher in the case of BC due to more long fibrils forming more dense entanglements network than in other cases. Measuring the viscosity in increase and decrease shear rate modes indicate an existence of hysteresis loop, i.e., thixotropic behavior with time lag for recovering the structural network. MCC and NCC dispersions even at cellulose content more than 5% do not demonstrate such behavior. According to oscillatory measurements, viscoelastic behavior of dispersions corresponds to gel-like systems with almost total independence of moduli on frequency and essentially higher values of the storage modulus compared with the loss modulus.

Keywords: bacterial cellulose; water dispersion; gel; rheology; thixotropy; thickener

1. Introduction

Bacterial cellulose (BC) is a fibrous structural nanomaterial produced by certain bacteria in the form of exopolysaccharide in the course of its vital activity [1]. At the moment, a large list of bacterial strains capable to produce cellulose is known [2], but the most studied and commonly applied and used in the industry is the strain of *Gluconacetobacter* or *Komagataeibacter* (after reclassification) [3–7].

The process of BC synthesis is well studied. There are many papers where this process in various nutrient media is described in detail [8–10]. Biosynthesis of bacterial cellulose is a complex series of biochemical reactions, including a large number of key enzymes, which controlling the yield of cellulose. Many types of *Gluconacetobacter* can utilize a variety of carbon sources, such as glycerin, hexoses, pyruvate, dihydroxyacetone and dicarboxylic acids. However, the polysaccharide chains are synthesized from glucose only. The synthesis of bacterial cellulose proceeds in two main stages: (1) the formation of 1,4- β -glycosidic bonds between glucose monomers; (2) the assembly and crystallization of cellulose fibrils. Cellulose-forming cells have from 50 to 80 pore-like sites through which thin (1.5 nm) filaments of a pre-cellulose polymer are penetrated. They then assemble and form the supramolecular

structure of bacterial cellulose. Other monomers do not participate in the assembly of the polymer carbohydrate chains that is why bacterial cellulose is a pure product [11,12].

The molecular structure of BC is identical to cellulose obtained from plant sources, but it has a higher degree of crystallinity (up to 89%) [13], a degree of polymerization (up to 14400) [14], adsorption capacity and mechanical strength in wet state [15–19]. In addition, it is worth noting that BC does not contain lignin and hemicellulose [20], while purification of the plant cellulose from these components is very expensive, and the yield of purified cellulose is essentially reduced [21]. Besides, the purification process itself has a harmful effect on the environment [22].

The final product of the synthesis is a film having a homogeneous, compact, three-dimensional structure formed by BC micro- and nanofibrils [23]. Due to this structure, hydrogels of BC became popular in various applications: from chocolate in food industry to sensitive diaphragms for microphones in radio-electronics [20,24–29]. A significant water absorption capacity, in practice, means that with a small addition of BC, the viscosity of liquid (aqueous) systems will increase significantly, i.e., BC can play a role a good thickener [30]. Since cellulose is a biologically inert material, medicine is the most interesting field of its application, in particular, for materials for wound dressing, artificial skin and blood vessels, etc.

As a rule, cellulose dispersions from plant-derived microcrystalline (MCC) and nanocrystalline cellulose (NCC) are mainly produced. These dispersions are used in pharmaceutical, cosmetic, food and others sectors. The main products from NCC are gel-like wound dressings, tissues, vascular grafts and other implants [31]. In cosmetic and food industry, NCC as a thickener and a source of dietary fiber is used.

From fundamental point of view, many researchers concentrated attention on possibility MCC and NCC gels form liquid crystalline (LC) state. The driving force of these attempts is theoretical predictions of Flory [32] for transition of solutions of stiff chain polymers into LC state at overcoming so-called critical concentration. The main reason of such transition is reducing an entropy of a set of rod-like macromolecules, such as poly- γ -benzyl-L-glutamates, aromatic polyamides and others, located in a limited volume. For stiff particles, formation of ordered phase, is induced by applying deformation [33,34]; this feature causes an additional interest to study rheological properties of such dispersions [35,36]. The matter is that for LC polymer solutions converting a polydomain LC system into monodomain one reflects on a shape of flow curves [37]; this peculiarity of rheological properties leads to additional functional capability to prove the LC state formation. This approach was used in [38] for NCC suspensions and typical for LC polymer solution the maximum on concentration dependence of viscosity at formation of LC phase [39] is mentioned in [40]. For NCC dispersions, the critical concentration for LC phase occurrence at shear as 3% was estimated. Meanwhile, there are no publications concerning analogous specific rheological behavior of BC dispersions.

As an alternative to plant cellulose, its analogs of bacterial origin are considered. The interest to BC in recent years has increased significantly, that is reflected in the number of scientific publications, which include various ways of its production and use. The advantage of such cellulose over cellulose of plant origin is its chemical “purity”, but disadvantage is much slower preparing process. The main method of production of NCC is to extract it from cellulosic biomass by acidic hydrolysis [41,42]. In the case of MCC, cellulose materials depolymerize in presence of mineral acids solutions at high temperature [43,44]. Both methods are accompanied by a significant amount of waste. Synthesis of BC occurs during the life of bacteria in the mother liquor. In this case, the mother liquor containing not more than 0.1% of the produced cellulose and residues of bacteria does not pollute the environment.

For the qualitative characterization of BC as a thickener, it is necessary to know in detail the rheological properties of its aqueous dispersions with different water content. Together with above mentioned role of deformation in ordering analogous NCC and MCC dispersions, reflecting on rheological behavior, the main objective of this research is to study rheological properties of BC dispersions.

2. Materials and Methods

2.1. Materials

For synthesis of bacterial cellulose, the strain of *Gluconacetobacter hansenii* GH-1/2008 was used, which was isolated by the authors in 2008 (VKPM B-10547) [45]. The cultivation of the producer *G. hansenii* GH-1/2008 was carried out in a static culture for 10 days in a modified medium [17] of the following composition: sucrose—20, peptone—5, yeast extract—5, Na_2HPO_4 —2.7, citric acid monohydrate—1.15. By growing *G. hansenii* in the indicated medium at 30 °C using a rotary shaker for 3 days the sowing material was prepared.

After completion of the cultivation process, BC films were repeatedly washed with distilled water to remove the nutrient medium components and then the BC was released from the producer of cells components. The process of purification of BC films was carried out in several stages: first, they were washed with RIPA buffer (RIPA Buffer, Thermo Fisher Scientific, St. Peters, MO, USA) for 2 days with a buffer replacing every 24 h, then with RIPA buffer with sequential addition of enzyme Deoxyribonuclease I (RG1, Promega, Madison, WI, USA). Upon completion of purification steps, they were washed with distilled water for 3 days with an exchange of water every 24 h to remove the components of the RIPA buffer and the enzyme.

In addition, for comparison of rheological behavior, dispersions of nanocrystalline cellulose prepared via acidic hydrolysis method were studied.

2.2. Preparation of Aqueous Dispersions

Films of BC were finely ground, distilled water was added under 1 to 1 ratio and agitated until a homogeneous dispersion was obtained using SAI-2 (Shanghai Sower Mechanical & Electrical Equipment, Shanghai, China) series homogenizer at 10,000 rpm. It is important to note that with insufficient water content in the BC, it is not possible to achieve satisfactory results. The resulting aqueous dispersion containing 1.23% of BC, was sterilized by autoclaving at temperature of +121 °C and pressure of 1.5 atm. The objects containing different content of BC were prepared and studied.

NCC powder was combined with water for preparing dispersions containing 1.0%, 3.0% and 5.0% of polymer fraction. Each formulation was sonicated by ultrasonic disperser MEF93.T (LLC MELFIZ, Moscow, Russia) at 22 kHz for homogenization of composition. Interesting to note that the similar treatment of BC dispersion did not lead to homogenization, but the reverse effect was reached, i.e., the macro-phase separation (Figure 1). For this reason, only mechanical stirring to BC dispersions was applied.



Figure 1. Appearance of the neat dispersion containing 0.5% of bacterial cellulose BC (a) and the same dispersion after sonication (b).

2.3. Characterization Methods

2.3.1. Morphology

In order to examine the morphology of the BC, a MultiMode IIIa atomic force microscope (AFM) (Bruker Corporation, Santa Barbara, CA, USA) and polarizing microscopy Boetius (VEB Kombinat Nadema GmbH, Ruhla, former DDR) at ambient conditions were used. The AFM measurements were performed in a contact mode using silicon nitride cantilevers with 8 nm tip radius of NP series (Bruker Corporation, Santa Barbara, CA, USA) with the force constant of 0.12 N/m. To obtain AFM images of the bacterial cellulose, films were prepared from neat gels by drying under room conditions to an equilibrium moisture content. The dried film was stick to metal disc. Image processing using FemtoScan001 SPM image software (Center for Advanced Technologies, Moscow, Russia, 2012) was performed.

For microscopic observations, the thin layer of the neat BC gel between optical slide and cover glasses was prepared. The polarizing microscope Biomed 6 PO (Biomed, Moscow, Russia) was equipped with camera ToupTek E3ISPM5000 (ToupTek Photonics Co., Hangzhou, China) allowing to resolute up to 6 dots per micron.

2.3.2. Rheology

The rheological properties of the aqueous BC dispersions were measured on a rotational rheometer Physica MCR 301 (Anton Paar, Graz, Austria). The cone-plate and plate-plate operating units with a diameter of 25 mm was used. Tests in steady-state conditions at controlled shear rate in a range of 10^{-2} – 10^0 s⁻¹ were performed. Measurements in oscillatory mode were performed in the domain of linear viscoelasticity in a frequency range of 0.01–100 Hz. Measurements were carried out at 25, 40 and 60 °C.

3. Results and Discussion

Aqueous dispersions of BC look like gels in a wide range of water content. They do not spread under action of gravity force. Visual observations during several months did not reveal any obvious changes in their appearance (Figure 2).

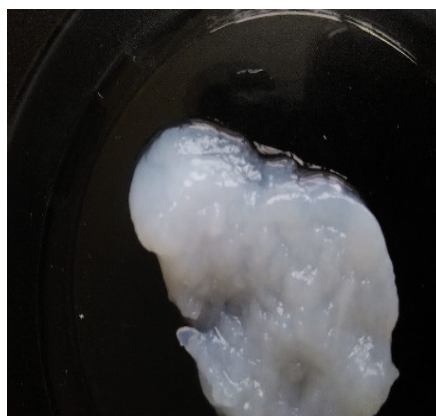


Figure 2. Appearance of dispersion containing 1.23% of BC.

The dispersion, when compressed, does not manifest syneresis, i.e., phase separation and elution of the liquid phase. Gels consist of a three-dimensional network formed by long entangled fibrils containing cells filled with liquid medium strongly interacted with BC fibrils by physical forces, presumably H-bonds (Figure 3).

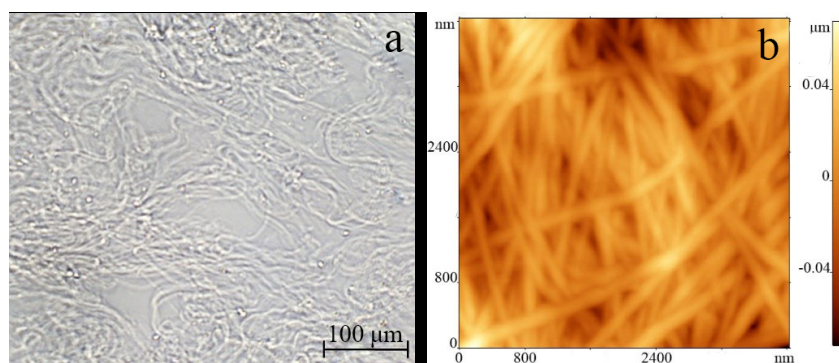


Figure 3. Micrograph of the BC aqueous dispersion (a) and AFM image of the film of BC (b).

The pictures of BC and NCC dispersions in polarized light are essentially different (Figure 4). In spite of less concentrated BC dispersion, the bright areas are evident, while for more concentrated NCC dispersion only birefringent spots. It says about existence in BC dispersion not only crystalline fibrils but also their domains with a various orientation. Do not excluded, that at steady shear such domains will transform to the real LC state. Nevertheless, already now it is possible to conclude that BC dispersion is more ordered compared with NCC dispersion.

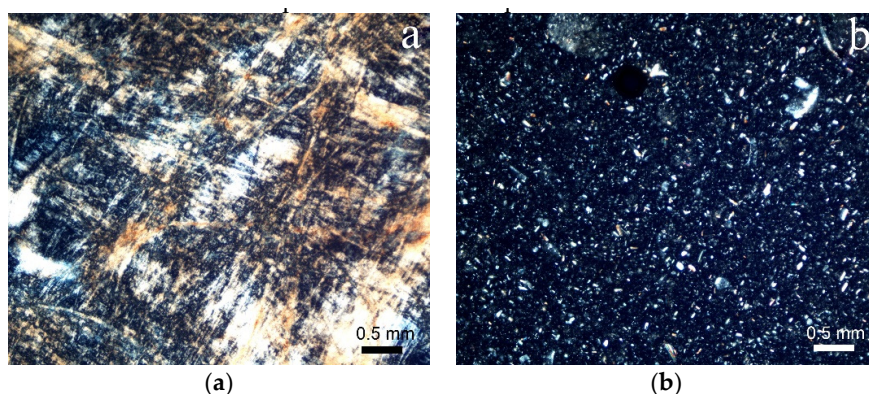


Figure 4. Micrographs in crossed Polaroids of 1.23% BC (a) and 5% NCC (b) dispersions.

Preservation of neat morphology of dispersions in time can be confirmed by constancy of the viscosity during at least two hours (Figure 5). Simultaneously, it should be noted that dispersions demonstrate strong non-Newtonian behavior that can be seen from significant difference of viscosities measured at low and high shear rates.

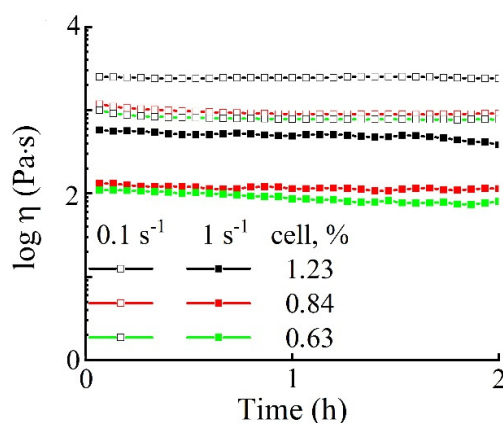


Figure 5. The time dependences of viscosity of dispersions with different BC content (indicated in figure) at shear rates of 0.1 and 1 s⁻¹.

The flow curves of aqueous dispersions of BC with different cellulose content are presented in Figure 6a. As is seen, all suspensions demonstrate strong non-Newtonian behavior. The constancy of the viscosity at low shear rates doesn't exist, that is why this kind of behavior can be characterized as close to viscoplastic one, though the yield stress does not appear distinctively in the applied range of the shear rates. In addition, all dispersions demonstrate thixotropic behavior, i.e., branches of the flow curves measured with increase of the shear rate do not coincide with corresponding branches measured in the opposite direction. Moreover, even at initial shear rate this difference remains, which means that destroyed at intense deformation structure does not recover during time of the experiment.

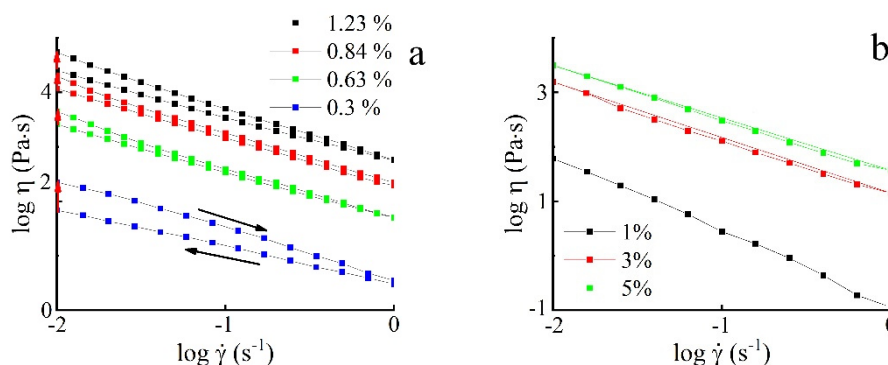


Figure 6. Flow curves of BC aqueous suspensions (a) and NCC suspensions (b). The polymer phase content indicated in figures.

The corresponding data for NCC dispersions are shown in Figure 5. Comparison with rheological behavior of BC dispersions says about very similar character of non-Newtonian behavior without realization of the initial Newtonian viscosity and two main distinctions. The first concerns much lower viscosity values for NCC dispersions. For almost equally concentrated dispersions: 1% in the case of NCC and 1.23% in the case of BC, the difference of viscosities at low shear rates reaches 2–2.5 orders in favor of BC. The second distinction consists in absence for NCC dispersions of thixotropic behavior, i.e., flow curves in modes of increase and decrease of shear rate coincides almost completely.

By the way very similar to obtained in this paper behavior was mentioned for NCC [38,40] and MCC dispersions [35]. The collected from different sources flow curves for suspensions of MCC and NCC, as well as cellulose whiskers with a length of 0.5–2.5 μm [40], NCC with a particle size of 35 nm [38] and even for MCC Avicel RC-591 with a particle size of 45–250 μm [36] are presented in Figure 7.

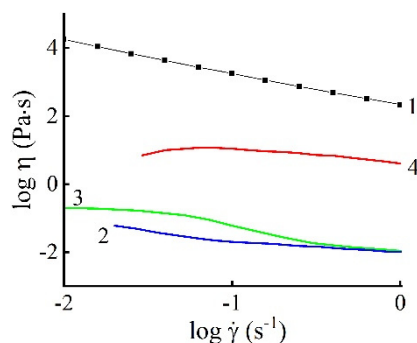


Figure 7. Flow curves of 1% wt. aqueous suspension of various particular celluloses: BC of this study—1, cellulose whiskers—2 [40], NCC—3 [38] and mixture of MCC and Na-carboxymethylcellulose—4 [36].

As is seen from the graph, the viscosity of aqueous dispersions of BC is more than 4 orders greater compared with the system based on nanocrystalline cellulose and ~ 3 orders higher than the

values obtained for microcrystalline cellulose. The character of the flow is strongly non-Newtonian. The exception concerns mixtures of the fibrillar MCC and almost spherical particles of Na-CMC. For them, very slight decrease in viscosity with increasing shear rate is observed. This feature indicates the decisive role in viscosity anomaly a presence of long anisometric particles. Without doubts, fibrils of BC are the most long and with highest aspect ratio. It is difficult to estimate these characteristics from microscope or AFM pictures (Figure 3), but according to [43] diameter of BC fibrils is about 100 nm and length up to 100 microns. The nature of such shape of fibrils belongs to bacteria, which construct very long and perfect macromolecules with polymerization degree overcoming 10^4 . Because of high enough rigidity of such macromolecules, it is difficult to suppose that they could form compact coils. Much easier for them is to contact each other preserving elongated shape. Combinations of extended BC chains creates long fibrils and the later—stacks of fibrils with high aspect ratio. This is the main reason of the mostly high structuring of BC gels accompanying with highest viscosity values and their strongest fall down under action of mechanical field, compared with gel-like systems prepared from plant cellulose. It is possible to expect that such kind of rheological behavior is stipulated by the excellent geometry of highly ordered ribbons of the dispersed phase, which, when deformed, split on individual fibrils and orient in the direction of the flow.

Above mentioned consideration gives a chance to realize a transition of BC gels to LC state at flow. We are planning to perform such experiments on original apparatus with transparent parts of the operating unit in near future.

The concentration dependence of BC dispersions in logarithmic scales is linear (Figure 8); this means that it obeys to power-law equation with the exponent value of 2.95. In principle, this behavior is close to analogical dispersions of anisotropic particles. In spite of some variations in the exponent value, it is possible to conclude that all of them can be described by power law dependences. Among all versions of cellulose dispersions, the BC dispersions have the maximal viscosity at much lower content of the cellulose phase.

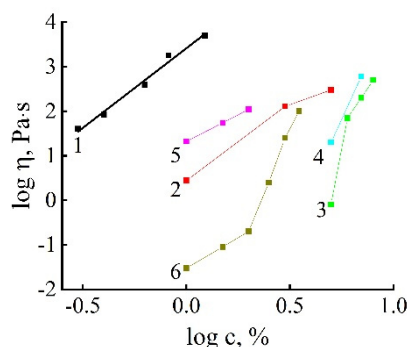


Figure 8. Concentration dependence of viscosity for different cellulose dispersions at 25 °C and $\gamma = 0.1 \text{ s}^{-1}$: BC—1, NCC (acidic hydrolysis)—2, NCC—3 [33], NCC—4 [38], MCC—5 [35], cellulose whiskers—6 [40].

In the oscillatory mode of deformation, one important task is a determination of the linear domain of viscoelasticity where the measured moduli are independent on the applied strain. Figure 9 represents evolution of the storage and loss moduli of the BC dispersion containing 1.23%, on the amplitude of deformation at a fixed frequency of 1 Hz.

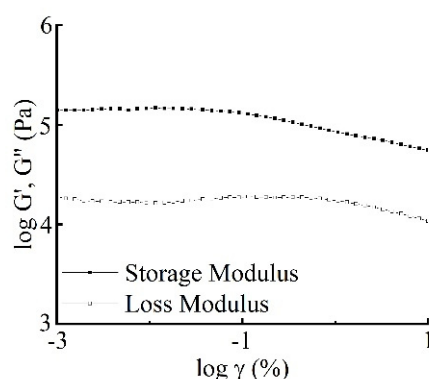


Figure 9. Storage (G') and loss modulus (G'') as a function of strain at 25 °C.

The linear viscoelastic domain exists until strain of $\sim 0.1\%$. At higher strains, the storage modulus starts to decrease while the loss modulus increased slightly. This is not traditional behavior because as a rule both moduli decrease in the non-linear domain of viscoelasticity. In other words, the complex modulus of viscoelasticity remains almost the same for BC dispersion. Nevertheless, it is reasonable to assume that observed changes of moduli reflect conversion of elastic response to dissipative one due to destroying the structure of BC gels.

Frequency dependences of dispersions with different content of the BC are presented in Figure 10.

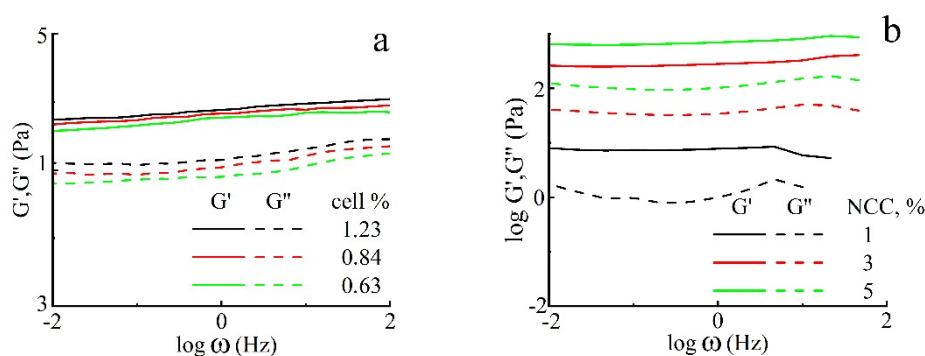


Figure 10. Dependences of elastic and loss moduli on oscillation frequency at strain of 0.01% for dispersions containing 0.63%, 0.84% and 1.23% of BC (a) and for dispersion with 1.0%, 3.0% and 5.0% of NCC (b) at 25 °C.

As can be seen from the figure, the storage modulus is higher than loss modulus and this means that the dispersion has prevailed elastic behavior. Both moduli change slightly with increasing of oscillation frequency. Such kind of behavior is typical for gel-like or even rubber-like systems.

Since such dispersions can be used at elevated temperatures, it is of interest to study changes in the mechanism of the flow with increasing of temperature. This important for such processes as sterilization at autoclaving, the introduction of additional components into the system during heating, etc. Flow curves of 1.23% aqueous dispersion of BC at different temperatures and dependence of viscosity on temperature in Arrhenius coordinates are shown in Figure 11.

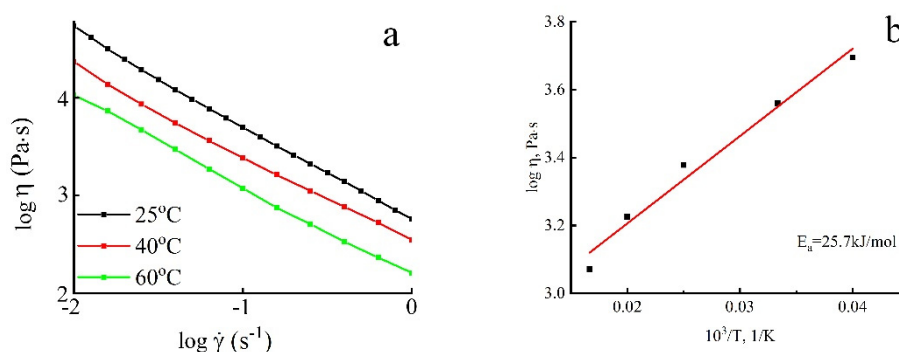


Figure 11. Flow curves of 1.23% BC aqueous dispersion at different temperatures (a) and dependence of viscosity measured at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ on reciprocal temperature (b).

With increasing temperature, the nature of the flow did not change: viscosity decreased with shear rate almost linearly. Based on the data presented in Figure 11a, the dependence of $\log \eta$ on $10^3/T$ was constructed. The character of obtained dependence was linear, which suggests that the temperature dependence of viscosity can be described by the Arrhenius equation. There was no significant changes of dispersion structure in the temperature range studied.

The activation energy value allows us to assess the minimum energy required to break the physical bonds between the BC-gel fragments for irreversible displacement each relatively others. The minimum values of the activation energy were observed for aqueous dispersions based on cellulose fibrils with small values of the aspect ratio. An increase in the length-to-width ratio led to an increase in the activation energy. The activation energy value for BC dispersion was equal to 25.7 kJ/mole. It is comparative with the corresponding value for aqueous dispersions of rayon short fibers with various aspect ratios, described in [46]. Objectively, for long BC fibrils the number of physical contacts is larger and, as a result, the activation energy is higher in comparison with rayon-based systems.

The heating of aqueous dispersions of BC up to 60 °C caused slight decreases in the viscosity values, and in turn, may be used to facilitate the technological process for such systems, for example, dosing and packaging at increased temperatures. It should be noted that the dispersions of BC with different ratios of water and cellulose after heat treatment in an autoclave did not show any visual signs of degradation and separation at least in one year. Thus, we can confirm the stability of the system over long periods of time even after heating.

In the course of work, an additional question arose—is it possible to use BC gels obtained as stabilizing systems? To answer this question, we prepared a water suspension of nanodiamonds and added to it BC gel to observe the stability over time (Figure 12).

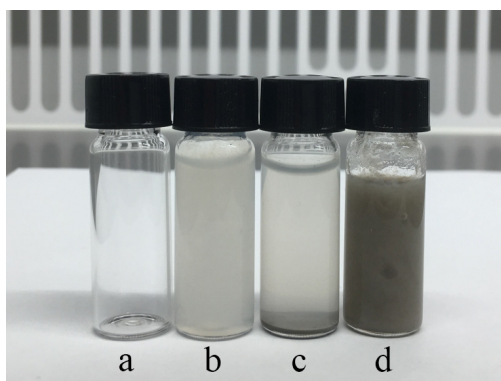


Figure 12. Photos (from left to right): an empty glass container (a), aqueous 0.5% BC dispersion (b), 0.5% aqueous dispersion of nanodiamonds (c) and mixed aqueous dispersion of 0.5% BC + 0.5% nanodiamonds (d).

Nanodiamonds were not pretreated for stabilization; the resulting 0.5% dispersion in water was not stable and after few hours a sedimentation of nanodiamonds takes place and its deposition in the bottom of a flask (Figure 12c). When an equivalent amount the BC was added to diamonds dispersion and mechanically mixed (Figure 12d), the system remained stable at least for two weeks. Thus, BC may play a role of not only a thickener, but also a stabilizer.

4. Conclusions

For the first time, aqueous dispersions of bacterial cellulose—synthesized by the strain of *Gluconacetobacter hansenii* GH-1/2008, with a polymer content of up to 1.23 wt %—were subjected to detail rheological characterization including steady state and oscillatory regimes of shear deformation. The most preferable method of BC dispersion preparation was mechanical stirring. Sonication led to syneresis and phase separation of dispersions. The time dependences of viscosity and repeated experiments over long periods of time revealed the stability of the values of viscosity. The obtained results were compared with the corresponding data for various aqueous dispersions of the plant cellulose. According to visual appearance and rheological response, the aqueous BC dispersions were gel-like systems with prevail elastic reaction, i.e., storage modulus was always higher than loss modulus. Because of high aspect ratio of BC fibrils and strong intermolecular interaction they exhibited strong viscosity anomaly and thixotropic lag time. Such kind of behavior inherent also to other cellulose gel-like dispersions based on plant cellulose, but the absolute value of viscosity of BC dispersions was several times higher compared to the values for similar systems based on nanocrystalline or microcrystalline cellulose. The temperature dependence of viscosity obeys to Arrhenius equation without any specific deviation on linearity. This supports the stability of dispersions in wide temperature range. According to the results of rheological studies, it could be argued that bacterial cellulose is the most acceptable material as a thickener and a stabilizer of different aqueous dispersions. This was shown on an example of the nanodiamond suspensions.

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Conflicts of Interest: The authors declare no conflict of interest.

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