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Application of Bacterial Cellulose in the Textile and Shoe Industry: Development of Biocomposites

Marta Fernandes ¹, António Pedro Souto ¹, Fernando Dourado ² and Miguel Gama ^{2,*}

¹ 2C2T-Centre for Textile Science and Technology, Campus de Azurém, University of Minho, 4800-058 Guimarães, Portugal; marta.fernandes@det.uminho.pt (M.F.); souto@det.uminho.pt (A.P.S.)

² CEB-Centre of Biological Engineering, Campus de Gualtar, University of Minho, 4710-057 Braga, Portugal; fdourado@deb.uminho.pt

* Correspondence: fmgama@deb.uminho.pt; Tel.: +351-253-604-418

Abstract: Several studies report the potential of bacterial cellulose (BC) in the fashion and leather industries. This work aimed at the development of BC-based composites containing emulsified acrylated epoxidized soybean oil (AESO) that are polymerized with the redox initiator system hydrogen peroxide (H₂O₂) and L-ascorbic acid and ferrous sulfate as a catalyst. BC was fermented under static culture. The polymerization of the emulsified organic droplets was tested before and after their incorporation into BC by exhaustion. The composites were then finished with an antimicrobial agent (benzalkonium chloride) and dyed. The obtained composites were characterized in terms of wettability, water vapor permeability (WVP), mechanical, thermal and antimicrobial properties. When AESO emulsion was polymerized prior to the exhaustion process, the obtained composites showed higher WVP, tensile strength and thermal stability. Meanwhile, post-exhaustion polymerized AESO conferred the composite higher hydrophobicity and elongation. The composites finished with the antimicrobial agent showed activity against *S. aureus*. Finally, intense colors were obtained more uniformly when they were incorporated simultaneously with the emulsified AESO with all the dyes tested.

Keywords: bacterial cellulose; acrylated epoxidized soybean oil; biocomposite; emulsion polymerization; leather; textile



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1. Introduction

An emerging trend within the fashion fabric industry concerns the eco-friendliness and sustainability of the production of fabrics in using bio-based materials or products derived from renewable resources with properties interesting enough to warrant commercial viability. The groundbreaking concept of self-grown fabrics from natural renewable resources such as bacterial cellulose, seaweed, algae, kelp, fungi and mycelium, has increased collaborative efforts between designers and scientists to explore the use of these natural green materials in textiles. A case in point is bacterial cellulose (BC), a highly pure biopolymer produced by fermentation of bacteria such as those of the genus *Komagataeibacter*. Under static conditions, BC is produced in the form of a gelatinous three-dimensional nano-fibrous network [1,2]. Compared to vegetable cellulose, BC presents unique properties including high crystallinity [3], high specific surface area [4], high water absorption [5] and high mechanical strength [6]. The unique structure and impressive physico-mechanical properties of BC have supported the development of several applications in different areas, such as food packaging [7,8], biomedical [9,10], cosmetics [11], filtration [12,13] and electronic devices [14,15]. BC is also emerging as a potential alternative to conventional woven/leather materials. The German start-up ScobyTec developed a vegan alternative to leather made of BC produced from kombucha, which was used to make various products such as gloves, children's shoes and business handbags. The material, called ScobyTec BNC, possesses high mechanical strength and is non-flammable [16]. In the project SOYA

C(O)U(L)TURE, settled by the Indonesian collective XXlab, BC is produced using the liquid waste from tofu production. The cellulose sheets are further pressed, dried, colored and coated [17]. The company Malai Design & Materials from India is also using coconut wastewater for the fermentation of BC. The obtained BC sheets are processed and can be reinforced with natural fibers, resins and gum to create a leather-like material [18]. The growing attention given to BC as an alternative to leather and cotton-based products is due to its leather-like appearance. Furthermore, the moldability of BC and the possibility of growing it in any shape are advantageous for the development of fashion products and an example includes the following: Fermenting BC under static culture which results in planar sheets or in pre-defined 3D forms. The formed BC could also be recultivated by resubmerging the sheets or 3D prototypes into fresh broth to produce complex structures and with textural characteristics. Alternatively, the formed planar BC could be dried in 3D molds (e.g., wooden mannequin) [19]. BC-based 3D art integrating SMD-LED (surface-mounted device-light-emitting diode) through conductive threads was developed by molding BC [20]. BC produced with a desired shape represents a peculiar approach to producing clothing with zero-waste. Each part of the garment was fermented to the required size and shape and then dyed and finished with animal oil or wax [21]. The moldability of BC was also studied by placing wet BC produced with a natural dye extract in a preform followed by drying [22].

In the following subsections, we review the scientific work carried out within the scope of the application of BC in the textile and fashion industry. Within this application scope, results from the development of novel bacterial cellulose (BC)-based composites containing emulsified AESO polymerized with a new redox initiator system are presented. This system, which is composed of hydrogen peroxide and L-ascorbic acid and ferrous sulfate as a catalyst, is biodegradable and can be used in the polymerization of AESO at amenable temperatures (30 °C). The composites were surface-treated with biocide to confer antimicrobial properties. Finally, these composites were also dyed.

1.1. BC Coated on Fibers, Yarns, Fabrics

An approach to the use of BC in the textile industry, consists of coating fibers, yarns, or fabrics with BC nanofibers, increasing the surface area and the mechanical properties of the obtained composites. The interfacial adhesion of natural fibers, such as hemp and sisal fibers, with biopolymers significantly increased by adding those fibers to the BC culture medium before fermentation [23]. In order to develop wearable electronics, cotton yarns were first soaked in BC nanofiber suspension under sonication to increase the surface area before the deposition of pyrrole [24]. Hybrid fabrics (wool/BC, silk/BC, cotton/BC, cellulose acetate/BC, nylon/BC, polyester/BC, Kevlar[®]/BC, viscose rayon/BC and Bemlise[®]/BC) were developed by producing BC with different fabrics added to the culture medium. In order to obtain double-sided coating, the fabrics were inverted during the experiments. Although BC was produced at the surface of all fabrics, it showed no affinity for the non-cellulosic material and easily peeled off during the NaOH washing step [25]. A similar procedure was used to develop cotton, polyester and rayon hybrid fabrics where the BC coating increased the thickness and bursting strength and decreased the penetration of water through the composite fabrics and the water vapor permeability [26]. A method to produce BC/ENM (regenerated cellulose electrospun nanofibrous membrane) hybrid fabrics with targeted dimensions was developed through in situ self-assembly, by adding a polypropylene mesh template to the fermentation medium. The growth of BC nanofibers into the empty voids of the mesh improved the fabric performance by decreasing the surface hydrophobicity and water uptake, while increasing the tensile strength of the composite [27].

1.2. Regenerated BC Fibers

Regenerated cellulose fibers have been used in the textile industry since the early twentieth century and currently possess a market share of about 6.4% of the total fiber

production. These fibers are traditionally produced from wood pulp or cotton linters, requiring a large plantation area. BC is a sustainable alternative to traditional cellulose sources which can be produced anywhere without the use of forest or land resources [28]. Despite some attempts to harvest cellulosic filament during the cultivation stage [29–31], dissolution seems to be the most promising method for the development of BC continuous filaments. Solutions of BC dissolved in dimethylacetamide/lithium chloride (DMAc/LiCl) and 1-allyl-3-methyl-imidazolium chloride (AMIMCl) were used to prepare BC/multi-walled carbon nanotubes composite fibers by wet-spinning [32] and by electrospinning [33], respectively. Regenerated fibers were also prepared by wet-spinning BC dissolved in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO·H₂O) [34] and in zinc chloride aqueous solution (ZnCl₂·3H₂O) [35]. Other authors prepared regenerated BC blend fibers by wet-spinning, such as BC/alginate using lithium hydroxide/urea/thiourea (LiOH/urea/thiourea) aqueous solvent system [36] or BC/hydroxypropyl chitosan using the solvent NMMO·H₂O [37]. More recently, regenerated BC fibers were produced by dry-jet wet-spinning using NMMO·H₂O as solvent [38].

1.3. Development of BC Macrofibers

The production of macrofibers from oriented BC nanofibers, with promising potential applications such as smart textiles and for structural reinforcement, can also be developed. Macrofibers obtained in a continuous process based on aligned BC nanofibers by wet-spinning were developed in a process where the cellulose suspensions were first prepared by TEMPO oxidation. Then, the suspensions were spun into an acetone coagulation bath and dried. Subsequently, the filaments with a controlled humidity were stretched to align the BC nanofibers. These macrofiber filaments were subjected to cross-linking by multivalent ions, to prevent the decrease of the mechanical properties due to the weakening of the interfacial linkage between the nanofibers in a high moisture environment [39]. BC macrofibers with improved mechanical properties were also prepared by wet-drawn stripes of BC membranes by using a tensile testing machine, to improve the filament alignment. Then the wet-drawn samples were twisted into macrofibers with nine turns per inch and then dried at 90 °C under tension to reduce the voids and to induce a strong interfilament hydrogen bonding. These macrofibers can be shaped and dyed, possessing interesting potential for application in the textile industry [40]. In another work, the alignment of BC nanofibers was achieved via a simple one-step solvent-assisted drawing process. Films of BC were first soaked in *N*-methyl-2-pyrrolidinone solvent, then wet-drawn and followed by hot-press drying at 60 °C. To obtain ultrathin films with high tensile strength and high toughness, layers of the BC film were removed using tape (mechanical exfoliation). These films were then soaked in water and twisted, resulting in strong fibers. The production of multifunctional fibers, namely dyed fibers, CNT (carbon nanotubes)/BC fibers and CoFe₂O₄/BC magnetic fibers, was also demonstrated by soaking aligned BC ultrathin films in the respective solutions followed by sonicating and then twisting and drying [41]. Hierarchical helical nanocomposite macrofibers were developed using a wet-spinning method by extruding mixtures of BC nanofibers dispersions and alginate through a capillary needle into a CaCl₂ coagulation bath, forming filaments with aligned BC nanofibers. Then, two single BC/alginate gel filaments were twisted together into a hierarchical helical BC/Alginate macrofiber, with certain twist levels according to a multilevel wet-twisting process. The alignment of BC contributed to the ultimate mechanical properties of the composite, whereas the alginate matrix contributed to the stress transfer between BC nanofibers, resulting in a simultaneous improvement of the tensile strength, elongation and toughness [42].

1.4. BC Purification, Bleaching and Dyeing

The possibility of coloring materials is a fundamental feature in the textile and footwear sectors. Several studies have been conducted for the color modification of BC, including bleaching, dyeing with natural and artificial dyes and in situ and ex situ dyeing

processes. After cultivation, BC presents a yellowish-brown color derived from the culture medium. Washing of BC with 3% NaOH solution results in the effective removal of bacteria and the remnants of the culture medium that does not affect the BC nanoscale 3D network structure. In order to ensure the subsequent uniform dyeing and bright colors, bleaching with 5% H₂O₂ solution for 60 min at 90 °C removed the brown-yellow color of BC (white index of 73.15), without deforming the cellulose structure [43,44].

Dyeing of BC was carried out by producing BC in the presence of a direct acid or basic dye in the culture media. Optical microscopy observation showed that the direct and basic dyestuffs stained the BC, but the acid one did not. Analysis of wide angle X-ray diffraction (WAXD) data indicated that direct dyestuffs inhibited the crystallization of BC above 0.05 wt% dyestuff concentration in the culture medium, but basic dyestuff had almost no influence on the BC's crystallization [45]. In another work, in order to produce colored BC nonwovens, different natural and artificial dyes were added to the culture medium. Colors were successfully incorporated into the BC when natural dyes and the blue artificial dye were used, while other artificial dyes inhibited BC growth [46]. The dyeability of BC produced under static culture using in situ and ex situ methods was also studied using direct acid and reactive dyestuffs. Although only the lower half of the BC was colored during the cultivation (in situ method), after drying it showed uniform color on both sides and presented clearer colors when compared with the dried BC colored by the ex situ method [47]. An environmentally friendly process was developed for the bio-coloration of BC via phenolic oxidation by laccase immobilized onto BC. Specifically, flavonoids were successfully polymerized by the immobilized laccase, which gave rise to yellow, orange and dark brown oligomers that colored the BC. Best results were obtained with the flavonoids catechol and catechin [48]. BC films were also dyed by immersion of BC into plant-based natural dye (*Clitoria ternatea* L. and *Hibiscus rosa-sinensis*) solutions, while retaining the crystallinity, thermal and mechanical properties of BC [49].

1.5. Improvement of BC Flexibility, Hydrophobicity and Mechanical Properties

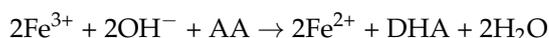
Despite its excellent properties, the hydrophilic nature of BC and the loss of flexibility and porosity upon drying (due to the collapsing of the 3D network) have limited its application in the textile and footwear industry. In order to improve the mechanical properties of BC and to reduce the water regain, PLA and PU-based biopolymers were embedded into BC by dip-coating and electrospinning. Although some improvement was observed in the tensile strength when BC was coated with PU-based biopolymer by electrospinning, further work is needed to, namely, reduce the moisture regain [50,51]. The hydrophobicity and flexibility of BC from kombucha were improved by immersing dried BC sheets in a textile softener solution followed by immersion in a hydrophobic finishing agent solution. BC was then dried at 120 °C for 1 min. From about 60° (native BC) the obtained hydrophobic composite had a water contact angle of 114° [52]. Laccase-assisted reactions allowed the functionalization of BC with poly(fluorophenol) and lauryl gallate oligomers, improving its hydrophobicity and durability (in terms of its dimensional stability and tensile strength). For the functionalization with poly(fluorophenol), laccase was first entrapped onto the surface of the BC fibers and then used to in situ polymerize the fluorophenol. For the lauryl gallate oligomers functionalization, wet BC was submerged in lauryl gallate oligomers that were previously synthesized by laccase. The resulting materials also presented hydrophobic surfaces and durability [53,54]. The flexibility and mechanical properties of BC were also improved by immersion in glycerol and coating the BC fibers with stearic acid [55]. In a recent work, the durability of BC was improved by physically entrapping plant-based proteins (from soy and mushroom) and glycerol to improve their processability. The reinforced BC also presented higher contact angle, tensile strength, improved flexibility, crease recovery and dimensional stability [56]. Two recently published reviews analyzed the methods of producing BC and their application in the fashion sector [57,58].

In our previous works, BC was used as a structuring material for the development of a new leather analogue from alternative biological products, specifically modified vegetable oils and other hydrophobic polymers. BC was submitted to an exhaustion process, allowing the bulk impregnation of hydrophobic polymers such as commercial nano/microparticles, Persoftal MS Con.01 (polydimethylsiloxane (PDMS)-based) and Baygard EFN (perfluorocarbon (PFC)-based) and acrylated epoxidized soybean oil (AESO) [59–61]. In our first approach, BC-based nanocomposites were developed by impregnating BC membranes with PDMS-based or PFC-based products, either separately or combined in a sequential process. The obtained composites were hydrophobic (maximum contact angle (CA) of 135°), breathable (maximum water vapor permeability of 373 g·m⁻²·24 h⁻¹) and possess satisfactory performance regarding the mechanical properties (maximum tensile strength of 48.4 MPa) [61]. Then, aiming at increasing the bio-based content of the composite, BC membranes were impregnated with acrylated epoxidized soybean oil (AESO) in a mixture also containing the PDMS-based polymer and polyethylene glycol (PEG) 400 as a plasticizer, yielding a product with greater elasticity and improved BC-polymers interfacial adhesion. The hydrophobic BC composites owned distinct performances, which were manipulated by varying the percentage of the polymer [59]. Using another approach, AESO resin was emulsified prior to the exhaustion process to allow its better diffusion into the bulk of the BC 3D network, being used in mixtures containing PEG 400, PDMS-based and PFC-based products. The resulting composites were hydrophobic (maximum CA of 138°) and thermally stable (up to 200 °C) and, overall, endowed with suitable mechanical properties for the proposed application (maximum tensile strength of 36 MPa) [60].

Despite the successful preparation of these composites based on BC and emulsified AESO [60], the catalysts used were highly toxic to the environment. In this work, we demonstrate the AESO polymerization with a less aggressive redox initiator system: hydrogen peroxide (H₂O₂) (oxidant), L-ascorbic acid (AA) (reductant) and ferrous sulfate (FeSO₄) as the catalyst; and under lower temperature (30 °C). The mechanism of redox reaction involves the transfer of a one-electron from the ferrous ion (Fe²⁺) to hydrogen peroxide, dissociating peroxide's oxygen–oxygen bond and generating one hydroxyl radical and one hydroxyl ion described as follows.



The reducing agent (AA) is transformed into dehydroascorbic acid (DHA) during the regeneration of Fe²⁺ to Fe³⁺, allowing the generation of new radicals, which is described as follows [62].



The biodegradability of vegetable oils, which is advantageous from an ecological and environmental point of view, implies their susceptibility to an enzymatic attack by microbial lipases. The scientific literature describes the enzymatic degradation of epoxidized, acryloylated and cross-linked vegetable oils [63]. Using biocides could be a simple strategy to delay this biodegradability during the useful life cycle of the materials. In order to minimize the chances of a rapid degradability of the composites, the surface functionalization of the BC composites with antimicrobial properties was studied.

The dyeing of cellulosic fibers is commonly achieved using reactive, direct or vat dyes. They are applied by different processes, according to the conditions required to achieve a good diffusion and fixation rate, uniformity and adequate fastness. Exhaustion processes are carried out in aqueous solutions of dyes in the presence of suitable auxiliaries capable of promoting affinity between the dye and the fiber at the appropriate temperature and time to complete the diffusion of the dye, its adsorption and fixation onto the surface of the fiber [64]. Although the general mechanisms involved in the BC-based composites dyeing can be generally drawn from the dyeing process of textile cellulosic fibers, adding polymeric mixtures in the production of the composites may change the dyeing process. Thus, in

this work, the dyeing of composites with different dyes was tested by applying the dye (i) simultaneously with the production of the composites and (ii) in the obtained composites.

2. Materials and Methods

2.1. Materials

BC membranes were offered by Satisfibre S.A. (Braga, Portugal). Soybean oil, epoxidized acrylate (Sigma-Aldrich, Steinheim, Germany), lauryl methacrylate (97%) (Acros Organics, Geel, Belgium), 1,6-hexanediol diacrylate (80%) (Sigma-Aldrich, Steinheim, Germany), tri(propylene glycol) diacrylate (Sigma-Aldrich, Steinheim, Germany), Triton X-100 (Sigma-Aldrich, Steinheim, Germany), isobutanol (Merck Millipore, Darmstadt, Germany), hydrogen peroxide (30%) (Sigma-Aldrich, Steinheim, Germany), L-ascorbic acid (Sigma-Aldrich, Steinheim, Germany), ferrous sulfate (Merck Millipore, Darmstadt, Germany) and polyethylene glycol 400 (Merck Millipore, Darmstadt, Germany) were used as received. Persoftal MS Conc.01 and Baygard EFN (Tanatex Chemicals, Ede, The Netherlands) were offered by the ADI Center (Santo Tirso, Portugal). The antimicrobial finishing chemicals and the dyes were kindly supplied by Smart Inovation (Barcelos, Portugal) and DyStar (Porto, Portugal), respectively.

2.2. Development of Composites with AESO Emulsion Polymerized before and after Exhaustion

2.2.1. Emulsion Polymerization and Development of the Composites

For the production of BC-based composites by the incorporation of a mixture of Persoftal MS Conc.01 (polydimethylsiloxane (PDMS)), polyethyleneglycol (PEG) 400 and acrylated epoxidized soybean oil (AESO), different mixtures were prepared as presented in Table 1.

Table 1. Proportions of each component in the mixtures used in the production of BC composites.

AESO Mixture (%)		AESO Emulsion (%)		Polymers Mixture (Exhaustion) (%)	
AESO	50	AESO mixture	20	AESO emulsion	75
Lauryl methacrylate	40	Triton-X-100/Butanol (2/1)	2	Persoftal MS Con.01	20
1,6-hexanediol diacrylate	5	Water	78	PEG 400	5
Tri(propylene glycol diacrylate	5				

First, a mixture was prepared by adding different reactive monomers to AESO to improve its processability and enhance crosslinking. This mixture was composed of AESO (50% m/m); lauryl methacrylate (40% m/m)-a fatty acid-based reactive diluent to reduce the viscosity of the mixture [65]; 1,6-hexanediol diacrylate (5% m/m) and tri(propylene glycol diacrylate (5% m/m) used as crosslinking enhancers [66]. Then, a mixture with a mass ratio of 20:2:78 (AESO mixture/surfactant (Triton-X-100/Butanol 2/1)/water) was emulsified using a homogenizer (Unidrive X 1000 D, CAT, Staufen, Germany) at a speed of 25,000 rpm for 12 min.

The polymerization of the AESO emulsion was first tested using a redox initiator system, hydrogen peroxide (H₂O₂) (oxidant), L-ascorbic acid (AA) (reductant) and with ferrous sulfate (FeSO₄) as the catalyst. A flask containing the AESO mixture emulsion was placed in an ultrasound bath to avoid agglomeration and, per 100 g of the emulsion, 0.003 g of FeSO₄ were added followed by 1.5 g of H₂O₂ (30%) (previously dissolved in water); after 20 min, 0.9 g of AA (previously dissolved in water) were added to the mixture in five portions and in intervals of 20 min each. The polymerization was carried out for 3 h more at 25 °C.

For the production of the composites, 8 BC membranes with about 3.5 cm in thickness, a size of 13.0 × 24.0 cm and weighting 900 g (wet mass) were first mechanically pressed to remove the excess of water to a final wet mass of 200 g, corresponding to 5.5% dry mass in BC and a thickness of around 0.5 cm. The compressed membranes were then treated by exhaustion with 1200 mL of a mixture containing 75% of the emulsified AESO mixture, 20%

Persoftal MS Con.01 and 5% PEG 400 (Table 1): four of which with the emulsified AESO mixture previously polymerized as described above (Composite A) and another four with the non-polymerized emulsified AESO mixture (Composite B).

The exhaustion process was carried out in an Ibelus machine equipped with an infrared heating system using a container with a capacity of approximately 2200 cm³, with a rotation of 50 rpm for 40 cycles. Starting from room temperature, the desired temperature (30 °C) was achieved using a gradient of 2 °C·min⁻¹. The treatment lasted for 7 days at 30 °C, after which the samples were oven dried (WTC binder oven) at 40 °C until constant mass. For the Composite B (samples produced with the non-polymerized AESO emulsion), after exhaustion and before drying, the membranes were treated again by exhaustion with a new solution containing the redox initiators and the catalyst for 3 days at 30 °C to polymerize the impregnated emulsion.

2.2.2. Characterization of the Composites

The obtained composites were evaluated according to their wettability, water vapor permeability (WVP) and mechanical and thermal properties.

The wettability of the samples was characterized via static contact angle measurements using a Dataphysics instrument and OCA20 software (version 1.5, Dataphysics, Filderstadt, Germany) with a video system for the capture of images in static mode using the sessile drop method. At least five measurements at different places were taken for each sample by positioning a drop of 5 µL of distilled water on the composite's surface with a microliter syringe.

The samples' WVP was determined following the Standard BS 7209:1990 [67]. Briefly, a sample is sealed over the top of a test dish containing 46 mL of distilled water. The assembly is transferred to a rotating turntable for 1 h, under isothermal conditions, to equilibrate the water vapor pressure gradient across the sample. The assembly is then weighted and rotated for 24 h and then weighted once more.

The WVP is represented by the following Equation (1) and expressed in g·m⁻²·24 h⁻¹:

$$\text{WVP} = \frac{24W}{At} \quad (1)$$

where W is the mass (g) of water vapor lost in t hours, A is the area of the sample exposed to vapor (m²) and t is the time between the various weightings (h).

For the tensile strength measurements, the full width of the sample (25 mm) was fixed. A length that allows an initial distance between the clamps of the strength tester equipment (Hounsfield HSK100, Salfords, UK) of 100 mm was set out between grips; the samples were then submitted to tensile. Four samples of each material were tested at a constant speed of 100 mm·min⁻¹.

Thermogravimetric analysis (TGA) was done using a Hitachi STA7200 (Tokyo, Japan). For this, samples weighing 7–9 mg (the exact mass was recorded before each assay) were placed in platinum pans. The temperature range was from 25 to 600 °C, using a heating rate of 10 °C·min⁻¹, with nitrogen flushed at flow rate of 200 mL·min⁻¹.

The dynamic mechanical properties of the BC composites were measured on a Hitachi DMA7100 (Tokyo, Japan) equipment in tension mode. The storage modulus (E') was recorded from 25 to 250 °C, at a frequency of 1 Hz and heating rate of 2 °C·min⁻¹. The dimensions of the samples were 10 mm × 10 mm (tested area).

2.3. Finishing and Dyeing

2.3.1. Antimicrobial Finishing

The humidity and warm temperatures developed in footwear are favorable to the growth of bacteria, fungi and molds, some of which contain lipases that may accelerate the biodegradation of the materials and release undesirable malodors. In order to evaluate the antimicrobial action of the finishing treatments of BC composites with commercially available biocides, the Si BAC (Smart Innovation, Barcelos, Portugal) product was selected

for which the active ingredient is benzalkonium chloride. Solutions containing the biocide with different concentrations and the fixative (Smart Fix, Smart Innovation, Barcelos, Portugal) were prepared and applied to dried BC composites by exhausting at 40 °C in a bath ratio of 1:20 (*m/v*) (Table 2).

Table 2. Conditions used in the antimicrobial finishing of BC composites.

Sample	Si BAC (%) (<i>w/w</i>)	Smart Fix (%) (<i>w/w</i>)	Time (min)
Control	-	-	30
1 BAC	2	0.4	30
2 BAC	2	0.4	60
3 BAC	4	0.4	60

After drying until constant mass, the antimicrobial activity of the composites was evaluated using the agar diffusion plate test, ISO 20645:2006 [68]. This method allows the qualitative determination of a surface antibacterial activity by detecting the presence of a halo around the edges of the sample (zone of inhibition) and the bacterial growth underneath. Suspensions of Gram positive *Staphylococcus aureus* (*S. aureus*) and Gram negative *Escherichia coli* (*E. coli*) were prepared in trypticase soy broth and left to grow overnight at 37 °C and 120 rpm. Then, their concentration was adjusted to 1×10^7 CFUs/mL and added to tryptic soy agar. The agar was then poured into 55 mm diameter sterilized Petri dishes and, after solidification, squared-sized BC composites of 1×1 cm were placed above them, guaranteeing maximum contact and incubated for 24 h at 37 °C.

2.3.2. Dyeing of the Composites

Dyeing is an essential process in the development of textile and footwear products. In order to ascertain the dyeability of BC-based composites, different classes of dyes (direct, reactive, dispersed and acid) were used. Their application was tested at the beginning of the exhaustion process during the production of the composites and in the dried composites.

Simultaneous dyeing and production of the BC-based composites were carried out as follows:

- (a) Sirius Scarlet K-CF direct dye (0.1 g/100 g) was added to the mixture containing the AESO emulsion, PDMS and PEG 400 polymers, followed by the polymerization of the emulsion. The BC composites were then produced by the exhaustion process;
- (b) Same process used in (a) but with Procion Red H-E3N reactive dye;
- (c) Same process used in (a) but with Dianix Scarlet CC disperse dye;
- (d) Procion Red H-E3N reactive dye (0.1 g/100 g) was added to the mixture containing the AESO emulsion previously polymerized and the other polymers. The BC composites were then produced by the exhaustion process;
- (e) Procion Red H-E3N reactive dye (0.1 g/100 g) was added to the mixture containing the AESO emulsion and the other polymers. Then, the membranes were exhausted and finally polymerized;
- (f) Same process used in (e) but with Dianix Scarlet CC disperse dye.

For the dyeing of dry composites, the following tests were performed:

- (g) Dyeing with the reactive dye Procion Red H-E3N (0.1 g/100 g) aqueous solution for 1.5 h at 30 °C;
- (h) Dyeing with the acid dye Solvaderm Black (0.1 g/100 g) aqueous solution for 1.5 h at 30 °C; and
- (i) Dyeing with the disperse dye Dianix Blue S-BG (0.1 g/100 g) aqueous dispersion for 1.5 h at different temperatures: 60, 80, 100 and 120 °C.

3. Results and Discussion

3.1. Properties of the Composites

The obtained composites were characterized with respect to their wettability, water vapor permeability (WVP), mechanical and thermal properties (Table 3, Figures 1 and 2).

Table 3. Properties of the BC and BC composites.

Sample	Thickness (mm)	WCA (°)	WVP ($\text{g}\cdot\text{m}^{-2}\cdot 24\text{ h}^{-1}$)	Tensile Strength (MPa)	Elongation (%)
BC	0.48 ± 0.01	63.1 ± 4.7	289.6	37.5 ± 0.8	3.6 ± 0.6
Composite A (pre-polymerization)	1.27 ± 0.01	93.1 ± 5.7	65.1 ± 1.3	12.1 ± 1.8	15.5 ± 0.9
Composite B (post-polymerization)	1.22 ± 0.01	103.6 ± 3.2	28.8 ± 2.7	8.3 ± 0.4	19.1 ± 4.5

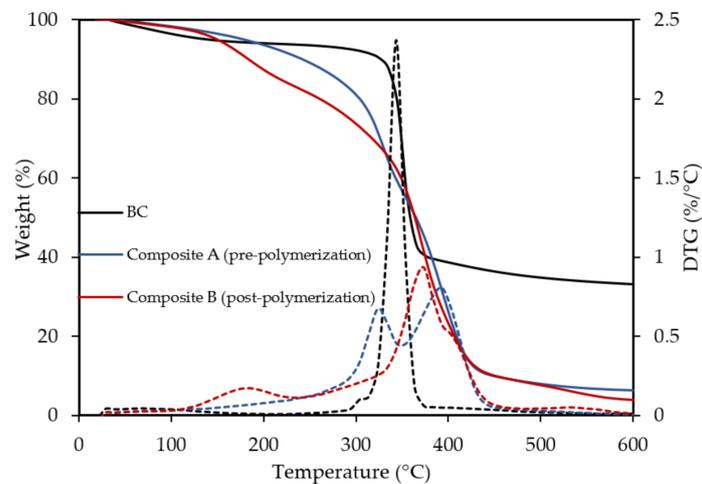


Figure 1. TGA curves (solid lines) and respective derivative (dashed lines) of BC and BC composites.

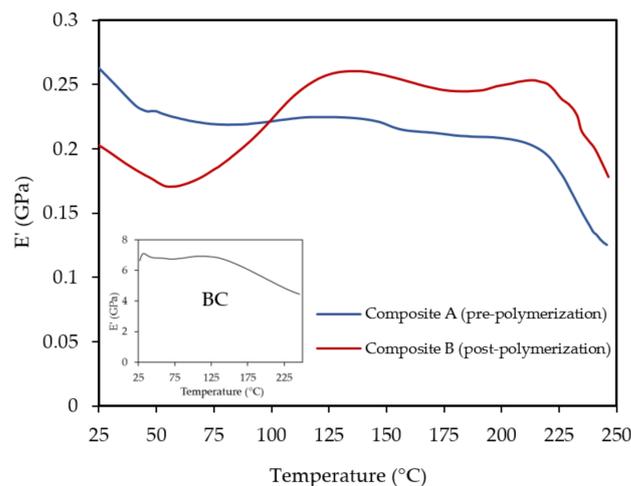


Figure 2. Evolution of the storage modulus (E') versus temperature at 1 Hz for BC (inserted graph) and BC composites as obtained by dynamic mechanical analysis.

As observed by the considerable increase in thickness (Table 3), the AESO emulsion mixture (Table 1) penetrated well into the BC membranes. The water contact angles values further confirmed the impregnation of the BC by changing its surface wettability ($\text{WCA} > 90^\circ$), which is slightly higher in the sample with the AESO polymerized after the

exhaustion process (Composite B). As observed in our previous work [60], the incorporation of PDMS-based polymer into BC significantly increased the WCA of the composites. The low surface tension of PDMS, which is $19.5\text{--}23.6\text{ mN}\cdot\text{m}^{-1}$ [69,70], contributes to the decrease in the free energy and the surface wettability of the composite. Furthermore, AESO resin contains hydrophobic long-chain non-polar fatty acid chains [71], which improve the hydrophobicity of the composites.

Regarding the water vapor permeability, although the BC porosity was not completely obstructed by the incorporation of the polymer's mixture, the WVP values were much lower than those of pristine BC which can also be explained by the higher thickness of the composites and their hydrophobic character. As shown in our previous work [60,61], the increased thickness and water resistance of the composites affected the adsorption process of the water vapor permeation mechanism.

Concerning the mechanical properties, as compared to BC, the tensile strength of the composites was lower but the elongation was much higher. These results can be explained by the extensive surface coating of the surface hydroxyl groups of the cellulose nanofibers which prevents their contribution to the mechanical strength through hydrogen bonding [72–74]. Hence, the mechanical strength and elongation of the composites become dependent on the intermolecular bonding of the matrix polymers. The added polymers also had a plasticizing effect, which increased the free volume and allowed greater mobility between the different layers of the BC membrane [75–77]. Composite B showed lower tensile strength value owing to the lower degree of polymerization of the crosslinked AESO, as will be discussed below.

Thermogravimetric analysis (TGA) was used to evaluate the thermal properties and kinetics of degradation of the composites. The TGA and the derivative thermograms (DTG) are shown in Figure 1.

The DTG curve of BC shows a single and narrow weight loss at $351.0\text{ }^{\circ}\text{C}$, indicating a fast degradation involving dehydration, depolymerization of the main polymer network and the decomposition of glucosyl units followed by the formation of a charred residue [78,79]. In the case of the composites, each of the samples presented two distinct peaks. Composite B (post-polymerization) shows one first event at $182.4\text{ }^{\circ}\text{C}$ before the main degradation. This degradation stage can be assigned to the evaporation and decomposition of unreacted monomers, catalysts or other low molecular weight components in the composites [80–83]. On the other hand, Composite A (pre-polymerization) had the first degradation peak only at $328.3\text{ }^{\circ}\text{C}$ and, hence, it can be inferred that the pre-polymerization using the redox initiator system hydrogen peroxide/L-ascorbic acid was more effective when compared to the post-polymerization approach. This can also explain the lower WVP and tensile strength, higher contact angle and the higher elongation values of Composite B. The lower polymerization of AESO may have resulted in the aggregation or coalescence of the emulsified AESO particles, reducing the porosity of the composite, but allowing higher mobility between the different layers of the BC membrane due to the plasticizing effect of the added polymers [60]. The main mass loss step of both composites corresponding to the highest percentage of mass loss occurred at higher temperatures as compared to BC, respectively, at $392.6\text{ }^{\circ}\text{C}$ and $373.1\text{ }^{\circ}\text{C}$ for Composites A and B. This can be attributed to the decomposition of PDMS-based polymer and crosslinked AESO. The temperature corresponding to the maximum rate of weight-loss of the polymers was around $420\text{ }^{\circ}\text{C}$ [84,85].

The storage modulus (E') obtained by dynamic mechanical analysis (DMA) of pure BC and the composites over a temperature range of $25\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ at a frequency of 1 Hz is presented in Figure 2.

The obtained data show that BC has high stiffness with a storage modulus at room temperature of 6.5 GPa due to the strong hydrogen bonds between the nanofibers. However, a considerably lower storage modulus was observed for the BC composites, which can be ascribed to the plasticizing effect of the impregnated polymers resulting in the segmental mobilization of the nanocellulose chains. Among the composites, Composite A showed a

higher storage modulus for temperatures up to approximately 100 °C. These results are in good agreement with the tensile strength measurements, which were plausibly associated with a higher crosslinking density. In addition, it was also possible to observe that the storage modulus of Composite B decreased when the temperature rose to 55 °C and then increased when it rose to 130 °C. This could be due to the loss of unreacted material, as was observed in the TGA results, which consequently gave rise to densification of the composite structure during heating, allowing an improved stress transfer behavior at higher temperatures.

Comparing the results of these composites, by using the redox initiator system hydrogen peroxide and L-ascorbic acid with the ones from our previous work [60] a substantial improvement in the elongation at break (pre-polymerization and post-polymerization) and in the tensile strength (pre-polymerization) was achieved. Overall, the polymerization of the AESO emulsion using biodegradable catalysts was validated and since the polymerization occurred before the exhaustion process, this method was more effective in the preparation of the composites.

3.2. Antimicrobial Activity

The antibacterial activity of the BC composites finished (surface-functionalized) with different concentrations and time of exhaustion of the biocide benzalkonium chloride (BAC) against *S. aureus* and *E. coli* was determined using the zone of inhibition method. *S. aureus* and *E. coli* are among the most prevalent species of Gram positive and Gram negative bacteria, respectively. As shown in Figure 3, all samples with the biocide compound produced a zone of inhibition (halo) against the *S. aureus* (Gram positive) and this area increased with concentration and with the time of treatment.

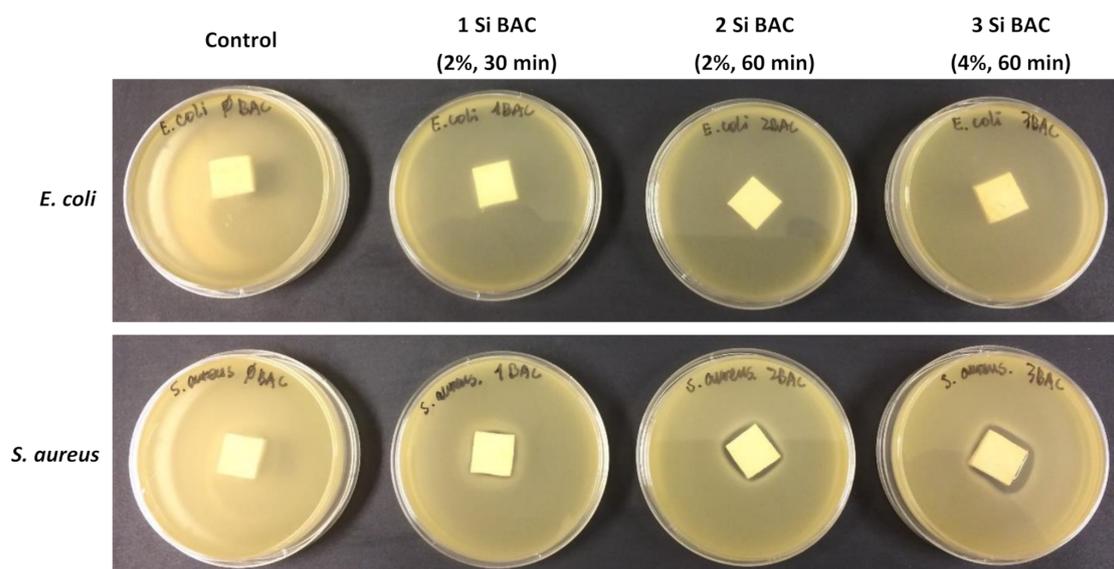


Figure 3. Antibacterial activity of the BC composites surface functionalized with benzalkonium chloride-based product against *Escherichia coli* and *Staphylococcus aureus*.

No inhibition was observed against *E. coli*, possibly due to the poor antimicrobial capacity of the benzalkonium chloride (cationic) against Gram negative bacteria [86].

3.3. Dyeing

Figure 4 shows sample photos of the dyed composites. All samples showed intense colors and were very flexible and hydrophobic (inserted photo in Figure 4e as an example). For samples dyed during the exhaustion with the AESO mixture as shown in Figure 4a–f, the dye diffused well into the bulk of BC and resulted in more uniform colors. However, in samples dyed after the production of the composites as shown in Figure 4g,h, the dye only

remained in the outer layers (inserted photo in Figure 3g) and the color was less uniform. It was also possible to observe that by increasing the temperature during dyeing with the dispersed dye as shown in Figure 4i, more intense colors were obtained and, despite the greater shrinkage, this change contributed to obtaining a material with a texture more similar to that of leather.

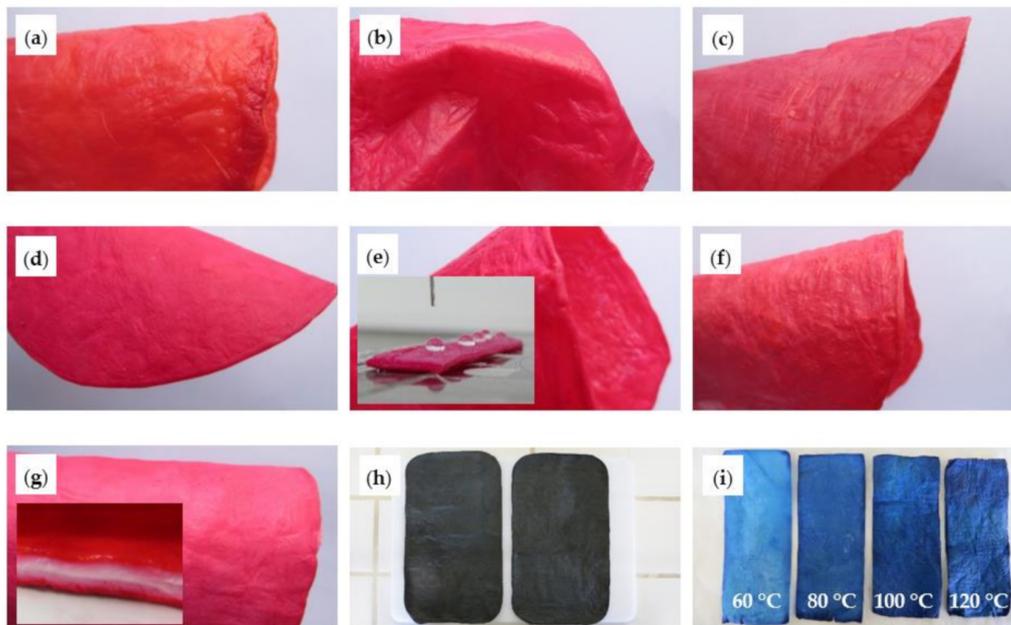


Figure 4. Photos of the dyed BC composites. Letters (a–i) correspond to the experimental conditions described in Section 2.3.2. Simultaneous dyeing and production of the BC-based composites (a–f) and dyeing of dry composites (g–i).

From the above, incorporating the dye simultaneously with the AESO mixture is a more efficient approach towards dyeing BC composites. These results also permitted a simple and potentially low-cost strategy for this process, albeit it will be necessary to carry out color washing and rubbing fastness tests, as well as to optimize the process conditions by considering the variables of pH, bath ratio, temperature, dye concentration, auxiliary products and the duration of the process.

4. Conclusions

Coupled with the increase in the population growth rate and resource consumption, environmental awareness and social concern regarding the environmental impact of the textile industry is emerging, which highlights the increasing need for the development of green and sustainable approaches throughout this industry's supply chain. Self-grown fabrics from renewable resources has streamlined the textile and fashion industries, with BC as an exemplary model of a product that could match the growing needs for sustainability. Several approaches have been taken, from semi-empirical to more systematic ones, towards improving the properties of BC for use in the textile and leather industries, which were reviewed here.

The possibility of producing BC, AESO, PDMS and PEG 400 composites through the exhaustion process using biodegradable catalysts was validated here. The polymerization of the AESO emulsion before the exhaustion process proved to be more effective in terms of WVP, tensile strength and thermal stability. However, more work is required to optimize the process. Composites finished with biocides showed antimicrobial activity against *S. aureus* and incorporating the dye simultaneously with the AESO mixture was the most efficient approach towards composites with intense colors.

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