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Use of bacterial cellulose in degraded paper restoration. Part II: application on real samples

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Abstract Preservation of documentary heritage is one of the biggest challenges facing paper conservators today. The singular properties of bacterial cellulose (BC) lead us to propose to reinforce paper with BC sheets. In the first part of this study, the reinforcing capability of BC was tested on model papers of well-known fiber composition. The aim of the present study was to verify the suitability of rebuilding degraded old papers with BC. The degraded papers were characterized before and after the reinforcement. In addition, lined samples were characterized before and after an aging process in order to study the stability in time. The same methodology was used with Japanese paper (JP), a material commonly used by paper conservators, in order to compare both materials as reinforcement. Mechanical properties of paper lined with BC are as good as those obtained with JP. Papers lined with BC have more marked modifications on their optical properties than those restored with JP. Nevertheless, letters in books lined with BC are more legible. Moreover, only the papers restored with BC show high changes in porosity. The aging process leads to a slight decrement in burst index. Changes on tear index and optical properties with the aging process depend on the paper to be restored. This study suggests that BC improves deteriorated paper quality, without altering the information contained therein, and that this improvement is maintained over time. Hence, BC is a promising alternative material for the restoration of paper.

Introduction

Restoration of degraded paper is especially important for papers produced between 1860 and 1960, because in those years most of them were produced using mechanical wood pulp and/or sized with rosin resins. The main characteristic of the papers made from mechanical wood pulp is the presence of lignin [1], which is degraded by the action of the environment producing radicals and generating acid

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groups. Paper sizing with rosin has to be made at acid pH [2]. In both cases, an acid hydrolysis is produced causing a loss of paper strength with time. This loss of mechanical properties is significantly lower in papers made with pure cellulose and with no acid sizing.

Since the early 1970s, the search for solutions to the problem of acidic paper has been approached from a predominantly working line: neutralize the acids in the paper by treatment with alkaline agents. This process is called deacidification, in which two fundamental processes are involved: neutralizing acids and creating a pool of basic substances (alkaline reserve) in order to conserve the paper from future acid attacks [3].

Paper deacidification is able to extend the lifespan of treated papers from four to five times [4], thus slowing the degradation process. However, paper deacidification does not recover the physical–mechanical properties of paper lost by aging [5]; therefore, it is imperative to find out better solutions for the consolidation of the deteriorated supports. The British Library developed a patent in the 1990s based on polymerization of styrene, methyl methacrylate, and ethyl acrylate. However, the process never was sufficiently optimized, and consequently, this line of research was discarded.

Nowadays, one of the most common methods used to restore damaged papers is named "lining" [6]. This method consists in applying a reinforcing paper to the damaged document. Japanese papers (JPs), known as "washi papers," are commonly used to restore documents by lining old papers with them. These papers are made with very long fibers from kozo, gampi, or mitsumata, three typical Japanese plants that provide high resistance with very low basis weight.

On the other hand, the ability of bacteria *Gluconacetobacter sucrofermentans* to produce high-quality cellulose is well known [7]. It produces extracellular cellulose microfibrils to provide a firm matrix that floats and, therefore, allows the embedded bacteria to stay in close contact with the atmosphere. The macrostructure of this bacterial cellulose (BC) is fully dependent on the culture conditions; in static conditions is generated a film at the air/liquid culture medium.

The physical and mechanical properties of BC arise from their unique structure: high crystallinity, high tensile strength, elasticity, large surface area, etc [8]. Yamanaka et al. [9] concluded that a sheet prepared from a gel-like pellicle of BC has been found to have the highest Young's modulus ever known in two-dimensional organic materials (>15 GPa). Retegui et al. [10] found that BC has an excellent biological affinity.

BC has been widely studied, and numerous applications have been developed, for example, its use as potential biological substrate [11, 12], paper [13, 14], matrix protein immobilization or chromatographic packings [13, 15] and in the biomedical field [16, 17]. BC has been also widely used as reinforcement agent for composite applications. For instance, as reinforcement agent in glycerol-plasticized cassava starch bionanocomposites, BC increased the elastic modulus 17 times in comparison to that of the starch matrix [18]. The very good mechanical properties obtained for some nanocomposites reinforced with BC suggest a good interfacial adhesion between BC and the renewable polymers. Being a kind of degradable biopolymer with remarkable mechanical properties [19], BC was selected to restore historic silk textiles. Although all these applications suggest that BC is a potential candidate to be used as a reinforcing material, its use in paper restoration has not been explored sufficiently.

The main goal of this study is to test the feasibility of BC to be used as a reinforcing material in paper restoration. For producing the BC layers, *G. sucrofermentans* has been cultivated on an optimized medium previously described [20]. A purification step to eliminate the bacteria and the culture medium has been included before their application to the document [21]. Afterward, an aging process is applied to evaluate the BC behavior in time, and consequently, the characterizations are made before and after this treatment. The reinforcing capability of BC over papers with different fiber compositions was previously tested on model papers in the first part of this extensive study (Part 1). The conclusions were promising (see Part I of this work), so the present study is focused on real samples. For this purpose, three books from 1940 to 1960 were selected and characterized, before and after reinforcement.

Characterizations of the treated samples have been made in terms of their mechanical properties (tear and burst strength), optical properties (opacity, brightness, yellowness, and gloss), surface properties (wettability and roughness), and air permeance. Mechanical, optical, and surface properties as well as air permeance are parameters of interest in papermaking and, therefore, they would determine the use and durability of BC in paper restoration.

Materials and methods

Microorganism

Gluconacetobacter sucrofermentans CECT 7291 was obtained from the Spanish Type Culture Collection (CECT). For maintenance, it was subcultured periodically in HS medium [22]. *G. sucrofermentans* was grown in HS solid medium placed in Petri dishes for 6 days, in order to obtain the suspension of bacterial cells to be used in the further experiments. 500 mL Erlenmeyer flasks containing 100 mL of liquid HS medium were inoculated with these plates and cultivated in static conditions for 4 days. Subsequently, the pellicles formed were cut in small pieces (about 1 cm × 1 cm) in sterile conditions and shaken with the liquid medium at 700 rpm for 30 min. The suspension obtained was filtered through gauze, centrifuged at 4000 rpm for 10 min and, after removing the supernatant, the pellet was washed with Ringer's solution (NaCl, 2.5 g L^{-1}; KCl, 0.105 g L^{-1}; $CaCl_2 \cdot 2H_2O$, 0.120 g L^{-1}; and $NaHCO_3$, 0.05 g L^{-1}). This solution was centrifuged again under the same conditions, and the pellets were resuspended in a small volume of Ringer's. The optical density of the solution was adjusted to be in the range of 0.59–0.64 (McFarland standards 3–4) with a wavelength of 600 nm upon diluting with Ringer's solution. 250 µL of this final solution were used to inoculate 100 mL of medium.

Cellulose layers' production and purification

Culture medium used for BC production was a modified HS medium (fructose, 20 g L^{-1}; yeast extract, 5 g L^{-1}; corn steep liquor, 5 g L^{-1}; Na_2HPO_4, 2.7 g L^{-1}; and citric acid, 1.15 g L^{-1}) with 1 % ethanol addition. In all cases, 100 mL of liquid medium was added to 150-mm Petri dishes, inoculated with the suspension described above and cultivated at 30 °C under static conditions. Cellulose layers were collected after 7 days of cultivation. The cellulose pellicles were washed with distilled water. To purify the BC, the pellicles were incubated at 90 °C in 1 % NaOH for 60 min. After the treatment, the pellicles were exhaustively washed with continuous distilled water and dried by filtering through a medium-porosity filter paper in a Buchner funnel. Subsequently, the cellulose layers were air dried.

Damaged books

Three books from 1940 to 1960 were selected according to their fibrous composition: book 1 (B_1) was made with chemical pulp from cereal straw; book 2 (B_2) was made mainly with chemical and semi-chemical pulp from softwood; and book 3 (B_3) was made mainly with softwood mechanical pulp. All of them have a surface pH in the range of 4–5.

Paper reinforcing

Lining is a general term for fusing together thin layers of different materials [6]. In archival contexts, lining refers specifically to the process of layering a sheet of archival paper with stronger materials, in order to strengthen the object. JP and BC were used in this study to evaluate their reinforcing capacity, using wheat starch as adhesive. The JP used as reinforcing material was Tengucho (Awagami Papers), which was selected because it is one of the most common JPs used in restoration (basis weight of 9 g m^{-2}, white, 100 % Kozo fibers, unsized).

Lining was performed following the traditional Japanese method. Previously, wheat starch was prepared in a proportion of 1:3 volumes of water, stirred, and cooked in microwave, stirring every 30 s until boiling for three times. After cooling it for 24 h, the starch paste is passed three times through a sieve of horsehair, then diluted in water three times, and batted with a brush and water to achieve the right consistence. The first step of the lining process was to spray with water the book sheet, and to apply the starch on the reinforcing material (BC or JP) with a brush. The reinforcing material was then applied on the book sheet using a palm fiber brush, also used to smooth the surface and to eliminate possible wrinkles. Afterward, the reinforced sheet was hit with an Uchibake brush to remove bubbles. Finally, it was air dried.

Ten sheets of each selected book were lined with BC (B_1-BC, B_2-BC, and B_3-BC) and ten with JP (B_1-JP, B_2-JP, and B_3-JP).

Aging process

Ten lined sheets from each selected book, five reinforced with JP and five with BC, were submitted to an accelerated aging process ($[B_1\text{-BC}]_A$, $[B_2\text{-BC}]_A$, $[B_3\text{-BC}]_A$, $[B_1\text{-JP}]_A$, $[B_2\text{-JP}]_A$, and $[B_3\text{-JP}]_A$) according to ISO 5630-3:1996 under 80 °C and 65 % relative humidity for 144 h.

Paper characterization

Paper characterization was performed before and after the reinforcement. Reinforced samples were also characterized after the aging process. In all cases, the samples were treated under conditions of standard atmosphere (23 °C and 50 % relative humidity) according to ISO 187:1990 prior to their testing.

The physical properties determined were burst strength (ISO 2758:2014) and tear strength (ISO 1974:2012). A reflectometer Elrepho 070 was used to obtain the optical properties: brightness (ISO 2470-1:2009), opacity (ISO 2471:2008), and yellowness (SCAN G5:1994). Specular gloss was determined using an angle of incidence of 75° (ISO 8254-1:1999). To measure the air permeance of the reinforced papers, a Gurley porosimeter was used (ISO 5636-5:2013). Each property has been tested at least in five replicates, and the standard deviation is always under 10 %.

Static contact angles (α) and dynamic contact angles (α_d) were measured for distilled water using a DataPhysics Instrument OCA 15 plus, running on SCA 20/21 software, and using the sessile drop method. For static angles, the images were captured by a CCD camera immediately after the drop rested on surface. The corresponding contact angle is calculated after fitting the drop contour line numerically, using the Young–Laplace method. In this study, 20 drop tests were conducted, using 2 µL of drop volume. Dynamic contact angles were assessed monitoring the change of the contact angle with water as a function of time. For each sample, eight videos recorded the evolution of the drop for 300 s, taking two frames per second, and applying droplets of 2 µL.

To evaluate the influence of the reinforcing materials on the legibility of the books, samples were observed by means of optical microscopy. A stereoscopic microscope, at 20 and 60 magnifications, and a binocular microscope using incident light at 100 magnifications, were used to observe the texts. Microphotographs were taken with a digital camera attached to the equipment.

The morphology of the reinforced sheets have been studied by means of Scanning Electron Microscopy (SEM) using a JEOL JSM 6335 F at 1 kV (at a maximum resolution of 5 nm) to avoid energetic degradation of the samples during SEM observation. Samples have been previously cryofractured after immersing them into liquid nitrogen, metalized with gold for 3 min and stored for 16–18 h at 50 °C in a vacuum stove (20 mmHg) to avoid the presence of water in the samples, before proceeding with SEM observations.

Samples of 10 mm × 10 mm were coated with a layer of gold for LP analysis (Lehmann, Lehman Mess-Systeme AG, Baden-Dättwil, Germany). Ten LP topography images were acquired from each sample. The lateral and z-resolution of the LP system was 1 µm and 10 nm, respectively. The size of the local areas was 1 mm × 1 mm. The surfaces were horizontally leveled. The micro-roughness was assessed as a function of wavelength, between 5 and 320 mm. For details, see [23].

Results and discussion

Mechanical properties

Figure 1 shows the mechanical properties of the samples, before and after the aging process. As can be observed (Fig. 1a), the tear strength increases with the treatments. When samples undergo an aging process, the tear strength decreases but never falls below the original value. Both reinforcing materials, BC and JP, lead to an increment in the burst strength (Fig. 1b). After the aging process, there is a decrement of this property, but anyway, it remains higher than in the samples without reinforcement. Zou (1996) [24] found that cellulose degradation during aging leads to the loss of the mechanical properties of paper.

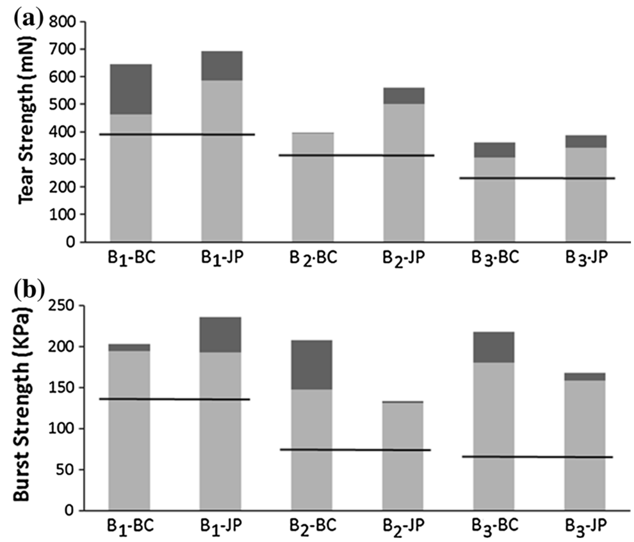

Fig. 1 Mechanical properties. Aged lined samples (*grey square*), non-aged lined samples (*black square*). **a** Tear strength, **b** burst strength. *Horizontal lines* show the original values of each book before lining

Regarding the abilities of BC and JP to reinforce damaged papers, it depends on the material to be restored. With the two reinforcing materials, B_1 shows a high increment in tear strength and a moderate one in burst strength, while the improvement in B_3 is mainly achieved in terms of burst strength. However, the main differences in mechanical properties along reinforcing materials are found in B_2, showing an important increment in tear strength only with JP, and a higher increment in burst strength with BC than with JP.

Optical properties

Values of optical properties of the original (non-lined) and treated samples with BC and JP before and after the aging process are shown in Table 1.

In all cases, opacity does not show significant variations, neither with the reinforcement treatment nor with the aging process. BC lining produces an increment in yellowness, while in papers lined with JP, this property remains at the original value. With both reinforcing materials, the aging process promotes an increment in yellowness, more noticeable in the case of BC. This could be explained because cellulose can become air-oxidized at elevated temperature, while in the presence of humidity, it can give rise to carbonyl species which absorb blue light [25].

Nevertheless, brightness fades when BC is used as the reinforcing material, but with JP this fading either does not take place or occurs moderately. Aging process always causes a loss in brightness, which is more pronounced with BC. These results are in accordance with [21], which

Table 1 Optical properties of the original and samples lined with BC and JP before and after the aging process

	Yellowness (%)	Opacity (%)	Brightness (%)	Gloss (%)
Book 1				
Non-lined	28.99	97.81	53.65	4.35
BC				
Non-aged	37.15	95.19	44.24	20.40
Aged	50.69	95.05	31.64	23.43
JP				
Non-aged	24.63	96.72	53.67	4.93
Aged	34.19	98.32	43.59	4.33
Book 2				
Non-lined	28.32	98.40	49.71	5.20
BC				
Non-aged	41.73	95.68	38.72	22.90
Aged	49.59	93.18	33.65	27.70
JP				
Non-aged	27.63	96.88	48.56	4.75
Aged	35.50	94.43	44.53	4.38
Book 3				
Non-lined	45.80	89.73	36.62	7.15
BC				
Non-aged	45.82	88.64	30.14	17.75
Aged	63.04	91.77	22.32	23.30
JP				
Non-aged	49.39	92.32	33.91	5.75
Aged	50.31	92.83	30.73	5.08

characterized BC layers and observed an increment in yellowness and a decrement in brightness after an aging process.

Lining with JP keeps gloss in values close to the original ones. On the other hand, the use of BC to reinforce the samples leads to a modification in this property, although the values of gloss gain are moderate and do not affect readability to a significant degree.

These results suggest that, in terms of optical properties, the JP is more appropriate for reinforcing than BC, because it causes minor changes in the original material. However, these properties have been determined on the unprinted areas of the paper, while, on observing the printed areas, it was found that JP further modifies the readability of the text, as described below in the microscopical studies section.

Microscopical studies

As mentioned before, the modification of the optical properties is more noticeable when BC is used as reinforced material. However, the printed areas (Fig. 2) clearly demonstrate that the JP fibers reduce the legibility of the texts. As can be seen, letters covered with BC are totally readable. This effect is due to the crystalline structure of BC, as previously mentioned. Since the same behavior is observed in the three books, only B_1 is shown in Fig. 2.

The morphology of reinforced sheets was studied by SEM (Fig. 3). The study revealed that in all cases, the linkage between the reinforcing material and the original sheets is very close. The main difference between BC and JP, is that the first one is structured in smooth layers, while JP has a fibrous structure (Fig. 3). As described below, this structural difference causes considerable changes in several properties, such as porosity and wettability.

The topography of the samples was assessed by LP. The surface morphologies of the books and the aged ones were similar (data not shown). The main difference is caused by the reinforcement material (Fig. 4). Contrary to the apparently rough surface caused by the JP fibrous structure, samples lined with BC evidenced a smoother surface (Figs. 3, 4).

The LP results indicate that the BC application reduces the surface roughness significantly in all the tested books. In order to shed more light on how the material used for lining affects the surface morphology, the LP roughness was assessed at various wavelengths (Fig. 5). The results confirm the smoothening effect of BC on the surface

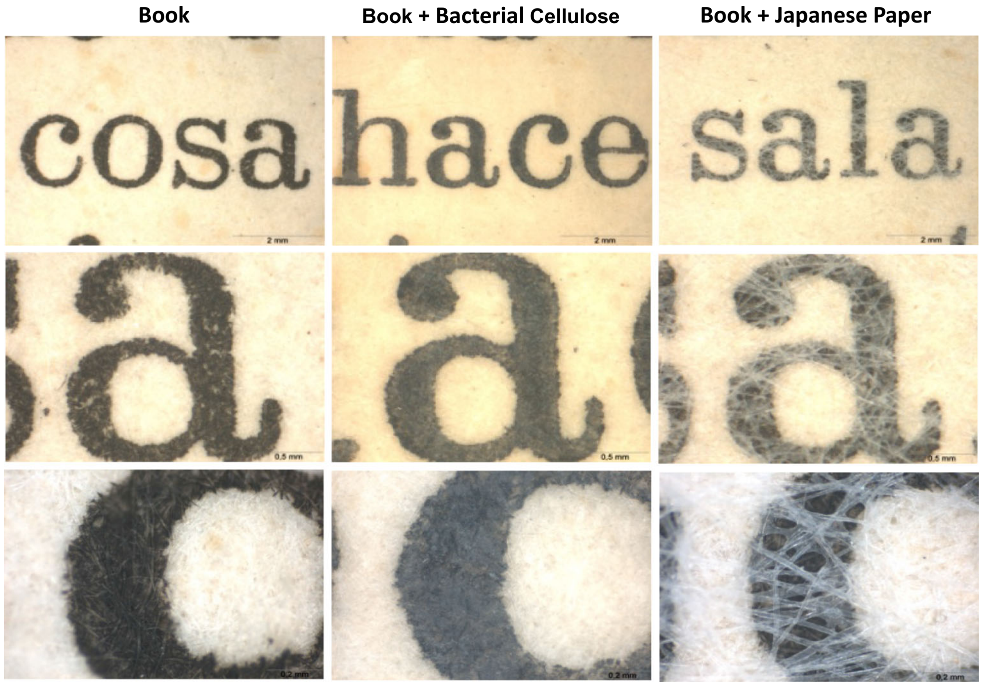

Fig. 2 Microphotographs taken observing Book 1 with a stereoscopic microscope (*first and second rows*), and with an optical microscope (*last row*)

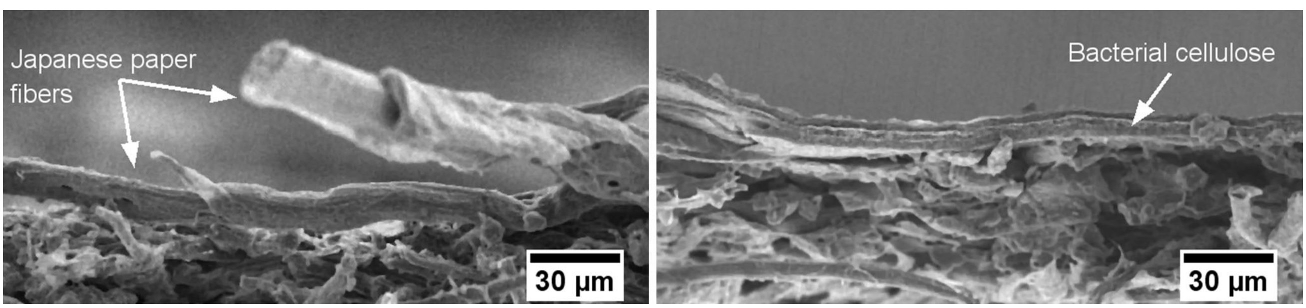

Fig. 3 SEM images of the transversal sections of reinforced sheets from Book 1. The JP fibers (*left image*) and layer with BC (*right image*) on the surface of a Book 1 sheet are exemplified

structure. The effect is clearly evidenced for wavelengths lower than 40–80 µm, indicating that the BC layer is filling cavities created between the fibers of the original papers. On the other hand, the rougher structure created by the JP layer was confirmed.

The surface topography is one of the factors affecting the glossy appearance of paper. In the Part I of this study, it was demonstrated that the facet orientation was relatively high for all the samples, which caused a low gloss level. In the present study, the smoother surface created by the BC layer increases the gloss levels significantly from 4 to 7 % (depending on the book paper) to 18–28% (Figs. 4, 5; Table 1). The rougher JP fibers increase the roughness and consequently caused a slight decrease in the gloss levels.

Surface wettability

Static contact angles (α) are shown in Table 2. All the original books have high α values, which means high hydrophobicity. The high sizing grade of the books could explain this behavior as sizing agents have low water affinity [26, 27].

α values of lined samples are influenced not only by the reinforcing materials but also by the starch used as adhesive. In the first part of this study (Part I), it was observed that α values for model papers lined with BC did not depend on the model paper selected to restore. This was due to the low porosity of BC, which caused that the starch remained on the surface. In contrast, JP presents very high

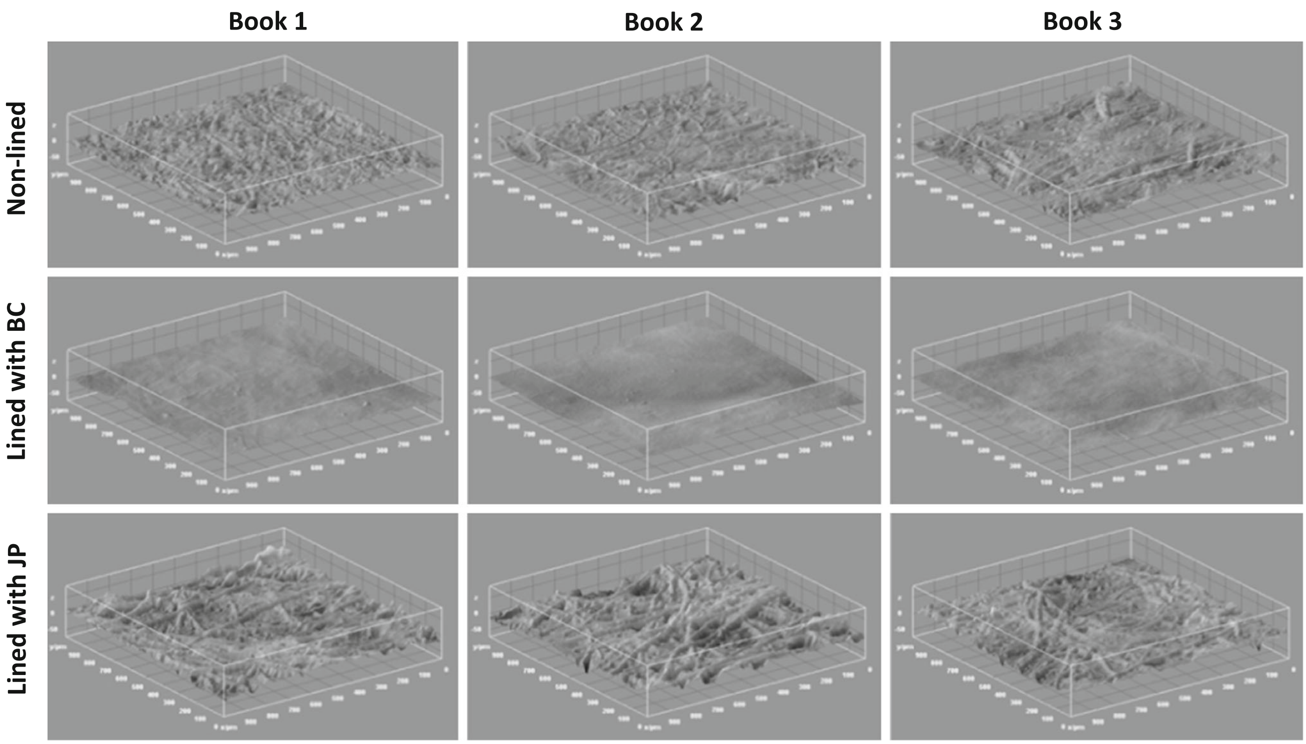

Fig. 4 LP images of the different non-aged samples, non-lined, and lined with BC and JP

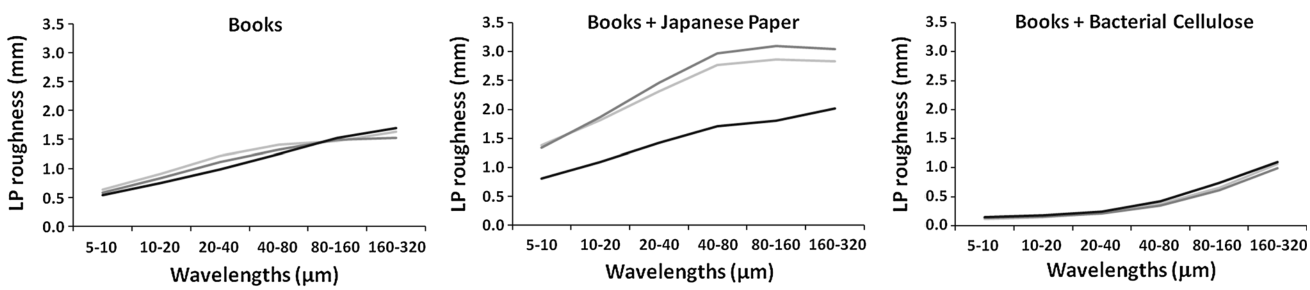

Fig. 5 LP Analysis. The surface roughness as a function of wavelength. Book 1 (*light grey square*), Book 2 (*grey square*), Book 3 (*black grey square*)

Table 2 Static contact angles of the samples (non-aged and aged), non-lined, and lined with BC and JP

	Non-lined	BC		JP	
		Non-aged	Aged	Non-aged	Aged
Book 1	122.6	89.1	80.9	99.3	106.5
Book 2	121.4	88.7	78.5	117.7	116.2
Book 3	118.6	91.5	82.6	101.1	102.9

porosity, so the starch migrates from the surface into the model paper's structure. In this case, the α values depended on the paper to restore.

Although lining with JP leads to a slight decrease of these contact angles, not all of them decreased at the same rate. BC produces a higher decrement of α, but anyway moderate, reaching similar values in all the BC lined books (around 90°). After the aging process, static contact angles decrease by 10° in all samples treated with BC, whereas with JP, the behavior is irregular. It can be concluded that due to the BC's closed laminar structure (Fig. 3), it offers stable surface properties to the reinforced papers, regardless the nature of the degraded paper.

The wettability of the samples was studied using the dynamic contact angle. To compare the effects of treatments, the dynamic contact angle values were normalized in relation to the corresponding initial values at 0 s (Fig. 6). As can be observed, each book has a different wettability, that is qualitatively maintained when the papers are reinforced with JP. In the case of being lined

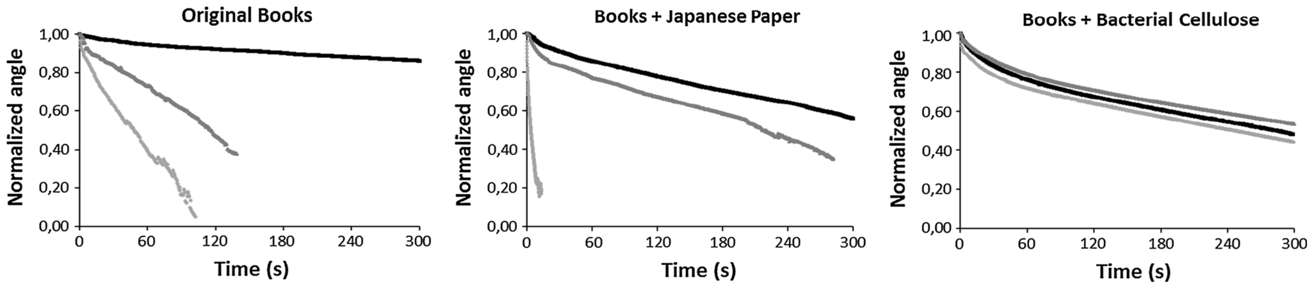

Fig. 6 The dynamic contact angle of lined and non-lined samples. Book 1 (*light grey square*), Book 2 (*grey square*), Book 3 (*black grey square*)

with BC, the three analyzed books showed similar behavior, which means that the resulting wettability seems to be independent of the paper to restore, which confirms the previous results.

The influence of the BC structure in the air permeability of the samples was assessed based on Gurley air permeance. All the original books have Gurley air permeance values in the range of 20–40 s. When they are reinforced with JP, these values are not significatively modified, not even after the aging process. On the contrary, if the papers were reinforced with BC, Gurley air permeance values are always higher than 900 s. This result indicates that the closed structure of the BC prevents the air flow therethrough, which is in concordance with Yousefi et al. [28], who found that paper made with BC has no air permeability. The reinforcement with BC could result in protection of book against atmospheric pollutants, which is a major cause of paper degradation [29].

Conclusions

When degraded books are lined with BC, their mechanical properties are improved; burst and tear indexes increase or, at least, remain similar to the original value, even after the aging process.

When focusing on optical properties, it is concluded that lining with BC modified them up to 18 points (for gloss), while changes with JP are minor, always being less than 5 points. However, the legibility of the texts is much better when books are reinforced with BC, which is very important when the documents to restore have a high historical value.

As the papers to restore must be conserved because of their value, it should be adequate to have a reinforcing material with a very close structure, in order to protect the documents from humidity and atmospheric pollutants, which are two of the most important agents in paper degradation. BC provides adequate protection to avoid the effects of these possible degradation agents, regardless of the paper to restore.

This study suggests that BC is a promising material for restoration of paper documents because its characteristics and its high stability over time indicate that it can contribute to the reinforcement of degraded paper.

In view of all these properties, it can be concluded that BC could be appropriate for lining. Although this characterization is specific to the selected BC and JP, it is expected that the results do not differ much while considering other types of BC and JP.

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