Article

Evaluating the Impacts of Alcohol-Based Solutions on Silk: Chemical, Mechanical and Wettability Changes before and after Artificial Ageing

Rosa Costantini, Eleonora Balliana *, Davide Dalla Torre, Fabio Aricò and Elisabetta Zendri *

Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Scientific Campus Via Torino 155/b, 30173 Venice, Italy
* Correspondence: eleonora.balliana@unive.it (E.B.); elizen@unive.it (E.Z.); Tel.: +39-041-234-6730 (E.Z.)

Abstract: Due to the COVID-19 pandemic, since 2020, alcohol-based sanitisers have been frequently used in museums and historic sites. Although they provide a safer environment for visitors, the impact of the (components in) sanitisers on the cultural heritage on open display is still uncertain. The current study investigated the effects of ethanol and isopropanol solutions on silk artefacts specifically in relation to possible mechanical changes and to their long-term impact based on artificial ageing. Thus, samples from three modern silk fabrics were treated through spraying and immersion with six solutions, two of which contained benzalkonium chloride (BZK), a surfactant suggested by Italian national guidelines in the formulation of sanitisers for museums. The impact of the treatment was studied from a chemical perspective, i.e., through spectroscopic techniques, and considering changes in the mechanical strength through uniaxial tensile testing. In addition, water wettability was measured. To study whether the contact with the solutions can affect the degradation path of silk, after the treatment, samples were exposed to light ageing and were stored at medium and high RH, i.e., 55% and 80%. Furthermore, treated and untreated silk textiles were placed in the Museum of Palazzo Mocenigo (Venice) to define the behaviour in an actual museum environment. The results show that, even when silk is immersed in the solutions for 180 min, no relevant chemical and physical changes can be observed on silk fibres. Variations noted at the end of the light ageing occurred regardless of the treatments with the solutions, so they are not affected by the contact with sanitisers. Nevertheless, when treating the samples (also through spraying) with solutions containing BZK, the surfactant is adsorbed by the textile. Once adsorbed, BZK significantly increases the water wettability of silk, causing a persistent modification of the property as also observed at the end of the ageing and in situ tests.

Keywords: silk; alcohol-based solutions; sanitisers; textile conservation

1. Introduction

Since 2020, the SARS-CoV-2 pandemic has drastically impacted and limited the public access to cultural heritage. Actions and preventive measures have been taken worldwide by museums and historic sites in order to contain the spread of the virus. Common actions, still ongoing, include social distancing, limiting the number of visitors, requiring the use of personal protective equipment and hand sanitisation and ensuring the disinfection of potentially contaminated surfaces [1,2]. Issues and responses related to the social and economic impact of the pandemic on museums have been addressed by a number of studies [3–8], contrary to the effects of sanitisers on artworks.

In consideration of the inestimable value of cultural heritage, the solution to employ for sanitising hands and surfaces should be carefully evaluated so to avoid damaging effects on these valuable materials. This necessity has been highlighted by reports [1] and national guidelines, such as those published by the Italian Ministry of Culture (MIC, formerly MIBACT) [9,10]. In particular, the MIC suggests sanitisers containing 75% ethanol,

20% water, and 5% benzalkonium chloride (BZK), avoiding in any case the use of hydrogen peroxide, UV, and O_3 exposure [9,10].

In general, sanitisers for the inactivation of SARS-CoV-2 often include alcohols at concentrations above 70%, i.e., ethanol and isopropanol, since they are able to modify the virus lipid membrane and stop its metabolism [11–13]. Among the above-cited alcohols, it is thought that isopropanol has greater virucidal properties than ethanol, since SARS-CoV-2 has a very lipophilic membrane [12]. On the other hand, the efficacy of BZK in contrasting the virus's spread has been questioned. Although BZK as a surfactant could ease the spread of the sanitiser on surfaces, it is still unclear whether this quaternary ammonium compound (QACs) is also effective against SARS-CoV-2 or its action is limited only to nonenveloped viruses [11,14,15]. In addition, it is worth mentioning that BZK is known for being environmentally toxic [16].

Despite the MIC and other institutions, such as Historic England, briefly mentioned that using certain solutions in proximity to specific materials can be risky (e.g., alcohol-based products near lacquered wood) [9,10,17], so far investigations inherent to the effects of sanitisers on artworks are rather limited [1,2,18]. An exception is the work presented by the Library of Congress (Washington, DC, USA), which examined the consequences of hand sanitisers (alcohol-based and/or containing QACs) on collections of cellulosic items [18]. Another recent example was a study focusing on silk artefacts conducted at Ca' Foscari University of Venice which set the basis of the current study.

Aiming to define whether sanitisers can pose a threat to artworks, silk can be considered a pivotal case study, as this material is widespread in historical houses, churches, and museums; and it can be often found on open display as part of costumes, banners, tapestries, and especially upholsteries [19]. Artworks made of this proteinaceous fibre are of remarkable cultural and historical value; therefore, they require careful preventive conservation strategies. Moreover, among natural fibres, silk is known for being particularly sensible to specific environmental factors common in museums and historic sites. Namely, its sensitivity to light, both visible [20] and UV [21,22], has been heavily studied: photo-oxidation processes, triggered by the presence of aromatic amino acids in the fibres such as tyrosine and tryptophan, can lead to yellowing and embrittlement [23]. On the other hand, the roles of other environmental factors such as relative humidity (RH) and temperature (T), possibly responsible for thermo-oxidation and hydrolysis processes, are less researched and more debated [24–27]. Silk is indeed a hygroscopic material and therefore prone to modify its moisture content (and so shrink and swell) according to the humidity of the surrounding environment [28]. In consideration of the uncertain impact of humidity, also regarding fatigue [24,25], common guidelines indicate that textile artefacts should be displayed within quite narrow RH thresholds, usually around $50 \pm 5\%$ [29]. However, such strict thresholds are often unfeasible for many museums and historic houses [30].

As reported in the previously published work, the silk samples did not show significant chemical variations after being treated directly (immersion) or indirectly (vapour exposure) with the sanitiser solutions [2]. Nevertheless, when the MIC solution was used, FTIR, Raman spectroscopy and elemental analysis conducted through SEM-EDS demonstrated that residues of the salt remained on the textiles surface [2].

In consideration of the abovementioned preliminary reported data, the current work aims at further assessing risks faced by silk artefacts when directly and indirectly in contact with alcohol-based solutions, such as the one suggested by the MIC. Wettability and mechanical properties were investigated here for the first time, alongside chemical features analysed through non-destructive spectroscopic analysis (FTIR-ATR, Raman, and FORS). Importantly, to test whether photo-oxidation and humidity-related degradation could be promoted by the treatment with alcohol-based solutions, artificial ageing tests were carried out. Furthermore, a case study was set up in order to assess the impact of an actual museum environment on silk fabrics treated with the MIC solution. Thus, silk samples were displayed at the Museum of Palazzo Mocenigo (Study Centre for History of Textiles, Costumes and Perfume) in Venice. Ultimately, the present study aimed to define

whether it would be possible to improve the MIC formulation, so to ensure the use of a safe product for both visitors and textile artworks.

Since the current work looks at the interaction between silk fabrics and sanitising products, it should be noted that alcohols are sometimes employed also in textiles conservation. More specifically, the use of industrial denatured alcohol, commercially known as IMS or IDA, has been reported for wet cleaning [23], and for the application/removal of adhesives [31,32]. Furthermore, both alcohols and QACs are mentioned for the disinfection, i.e., for the elimination of microfungi and bacteria, of historic textiles [23,33]. It is relevant to underline that chemical in sanitisers may take part in conservation treatments, as this can expand the area of interest and applicability of the present study.

More broadly, nowadays silk fibroin is used for several types of application, ranging from tissue engineering to the optoelectronic industry [34]. Additionally, in such cases, the interaction between alcohol and silk fibroin has been investigated, since it can lead to (sometimes helpful) modifications in the chemical, optical and mechanical properties of the final material. Nevertheless, within these fields, the biopolymeric material is studied in form of films and mixed with alcohol as solution [35–37]. For this reason, results may not be always directly comparable to conservation studies where silk is tested as fabric.

2. Materials and Methods

2.1. Silk Fabrics

The three different silk fabrics employed in this study were newly woven and provided by Serica 1970® (Follina, Italy), a company specialised in the production of silk textiles. Since historic silk may already be the result of a complex and characteristic mix of degradation processes that are difficult to define, the use of modern fabrics allows a more impartial investigation of the impact of sanitising agents.

Even though degummed silk is more common in artworks, it was decided to consider also un-degummed (raw) silk, which is also sometimes present in historic textiles [2]. Raw silk may behave differently with alcohol-based solutions, and exploring this could be an advantage for conservation purposes too.

The silk fabrics selected were named S1, S2 and S3 (Figure 1). As indicated by the manufacturer, S1 and S3 are both raw, and S2 is degummed. As is evident in Figure 1, the textiles differ in the weaving density and colour; in particular, S3 has a pinkish shade suggesting the use of dye(s), although no more specific information on dyeing process and colourant was provided by Serica 1970®. Regarding the weaving density, the thread count of the three fabrics were: S1 50 threads/cm in each direction; S2 50 threads/cm for the weft and 60 threads/cm for the warp; S3 60 threads/cm for the weft and 50 threads/cm for the warp. The numbers of warp and weft threads per unit length of each silk fabric were determined by counting the threads per length of 1 cm in the warp and weft direction. Although the two raw silk fabrics showed similar threat counts, the thicknesses of the threads differed, especially in the warp direction: warp threads in S1 were 0.20 mm thick, and in S3 0.05 mm. Including fabrics with different thread counts, thread thickness and processing, i.e., degumming and dyeing, was done to offer a wider variability of case studies.

For removing possible residues related to the fabrication, the textiles were washed with distilled water for 8 h. The deionised water was replaced every 2 h, and the neutrality of the solution was also monitored during the wash. After the wash, the textiles were left to dry in the laboratory (20–22 °C; 60–65% RH). No evidence of dye bleeding within the solution was recorded during this operation. More details on the size of the samples are provided in the Section 2.4.4.
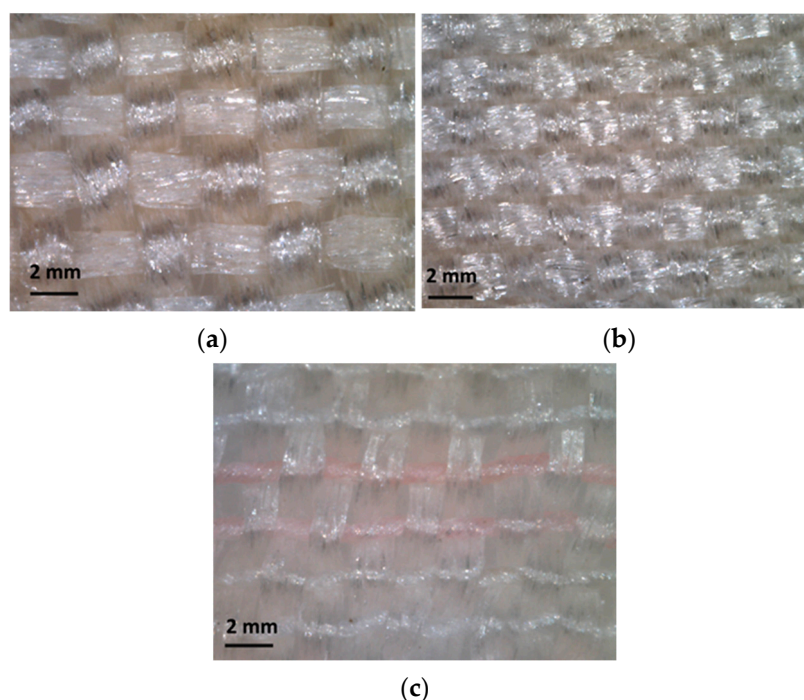
Figure 1. Modern silk fabrics employed to test the effects of alcohol-based solutions (215× magnification): (**a**) S1; (**b**) S2; (**c**) S3.

2.2. Treatments and Solutions

Samples cut from the three silk fabrics were treated, in two different ways, with six alcohol-based solutions (Table 1). One treatment consisted in spraying on the fabrics, at a fixed distance of 30 cm, with 2 mL of solution. The spraying was repeated for a total of 24 times (leaving 24 h between applications), and the samples were monitored after 8, 16 and 24 applications. For the second treatment, samples were immersed five times in the different solutions. Each of the five immersions per solution lasted 30 min, and between consecutive immersions the samples were left to dry for 180 min. Spraying was considered, as the treatment might be used for ordinary cleaning and disinfection of spaces, also through specific devices. On the other hand, direct contact through immersion in solutions was chosen to exacerbate possible interaction with the textiles. Specifically, immersion and drying cycles were employed to simulate the effects of possible dimensional changes of silk samples and whether alcohol-based products may play a role.

Table 1. Codes of the silk samples treated with the six alcohol-based solutions.

Treatment	Sol. 1	Sol. 2	Sol. 3	Sol. 4	Sol. 5	Sol. 6
Immersion	S1/i_Sol1	S1/i_Sol2	S1/i_Sol3	S1/i_Sol4	S1/i_Sol5	S1/i_Sol6
Spraying	S1/s_Sol1	S1/s_Sol2	S1/s_Sol3	S1/s_Sol4	S1/s_Sol5	S1/s_Sol6

The solutions (*v/v*) used for treating the samples were: 100% ethanol (sol. 1); 75% ethanol/25% distilled water (sol. 2); 100% isopropanol (sol. 3); 75% isopropanol/25% distilled water (sol. 4); 75% ethanol/20% distilled water/5% BZK (sol. 5); 75% isopropanol/20% distilled water/5% BZK (sol. 6). Pure solvents were purchased from Sigma-Aldrich®.

2.3. Artificial Ageing

The artificial ageing was carried out exclusively on the samples treated through immersion, as these were expected to show more evidently the effects of sanitisers on the degradation paths. Three different ageing procedures were employed to separately evaluate the influences of three variables [27]:

-   Light. The ageing was carried out by placing the samples in a ventilated chamber (22 ± 5% RH; 20 ± 3 °C) fitted with OSRAM Ultra-Vitalux® solar lamps (300 W, 230 V) providing an illuminance of 12,000 lux (checked with a luxometer Fervi® L014). The lamps emitted in the range between 280 and 2000 nm (13.6 W in the range 315–400 nm, 3.0 W in the range 280–315 nm). The ageing lasted 4 weeks, and samples were monitored every seven days through spectroscopic analyses; colorimetric and wettability measurements; and every fourteen days by tensile testing.
-   Medium relative humidity (55% ± 5 RH), through placing the samples in a desiccator with a saturated solution of $Mg(NO_3)_2$ [38].
-   High relative humidity (80% ± 3 RH), through placing the samples in a desiccator with a saturated solution of KCl [38].

Both desiccators for the ageing at fixed humidity, which lasted in total 8 weeks, were placed in a dark environment at 17 ± 2 °C. The RH level and temperature were monitored through a data logger, OM-EL-USB-2-LCD, by OMEGA®, placed in the desiccator and set to collect the environmental data every 30 min. The samples were monitored at the end of the two-month period at fixed RH.

When preparing artificial or accelerated ageing, it is always difficult to find a compromise among publications and standards; countries and those developed for industrial applications differ. For heritage materials, the selection of parameters (i.e., time and degradation factors) is even more complicated and open to discussion [27]. In this study, the ageing tests aimed to assess whether the treatment with the solutions may influence the degradation paths, photo-oxidation and hydrolysis, induced by light and humidity. The light ageing was selected, since it was often described in literature as the most impactful on silk [19–21,26,39]. Furthermore, the ageing at 55% and 80% RH was conducted in order to investigate whether the increased water wettability in silk samples treated with BZK may have some effects on the fabric response to humidity. In agreement with previous publications looking at the debated effect of humidity on textiles [25–27], the two ranges were selected considering the exposure at 80% RH as extreme and 55% RH as ideal for textile conservation in museums.

2.4. Analytical Methods

2.4.1. Colorimetric Measurements

Colorimetric coordinates, in the CIE 1976 L*a*b* space, of samples before and after treatment and ageing, were acquired using a Konica Minolta CM-700d spectrophotometer (illuminant D65, observer 8 degree viewing angle geometry) and elaborated with Spectra Magic NX 6 software. For each sample, the measurement was repeated in three different random points of the modern fabrics and using a 3 mm diameter target area. The mean Specular Component Included (SCI) values obtained from the analysis of untreated/treated and unaged/aged samples allowed us to measure possible colour differences. Colour variations before and after treatment/ageing, ΔE, were calculated according to the equation:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

According to the literature, when ΔE is greater than three, the colour difference can be defined as visible; and when it is higher than five, the chromatic change is, for artworks, unacceptable [40,41].

2.4.2. Spectroscopic Analyses

Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR) mode was conducted using a portable ALPHA II spectrometer by Bruker Optics® equipped with an ATR modulus with a single-bounce diamond. Spectra acquired in the range between 4000 and 400 cm^{-1} were obtained by collecting 64 scans with 4 cm^{-1} resolution. In accordance with past studies, three FTIR-ATR measurements were acquired per sample and then averaged [21,42].

Raman analysis was conducted through a Bravo portable Raman spectrometer by Bruker Optics® equipped with two lasers (758 and 852 nm). Spectra were collected in the spectral range between 3200 and 300 cm^{-1} (resolution 10 cm^{-1}). Three Raman measurements were acquired per sample and then averaged.

Fibre optics reflectance spectroscopy (FORS) was carried out using an ASD FieldSpec® 4 Standard-Res Spectroradiometer. Spectral data were collected within the range 350 and 2500 nm (3 nm resolution at 350–1000 nm, 8 nm resolution at 1000–2500 nm). For the analysis, samples were placed on a contact probe scattering light at 45°.

FTIR-ATR, Raman and FORS spectra were elaborated with Omnic® 10.0 and KnowItAll® Academic Edition 2021 software.

In accordance with our previous published work [2], FTIR-ATR and Raman spectroscopies were included, since they are often described as useful for studying changes in secondary structure elements of silk [43]. On the other hand, fewer studies looked at the applicability of FORS for assessing the state of conservation of textile artefacts [44,45]. FORS can represent a powerful non-invasive diagnostic tool for textiles, especially because it allows one to acquire information in the near infrared (NIR) range, not investigated through FTIR-ATR and Raman spectroscopies. Therefore, including all the three spectroscopic techniques intended also to look at their different feasibility in assessing silk degradation.

2.4.3. Wettability

The wettability of the silk samples before and after treatment/ageing was measured through the water drop contact angle method, according to the standard UNI EN 15802:2010 [46]. For each sample, the analysis was repeated three times.

Defining the water wettability of the material before and after treatments is relevant, as the use of BZK can increase it, thus making silk more prone to the effect of relative humidity [33].

2.4.4. Tensile Testing

Uniaxial tensile testing was carried out using an MTS Insight® Electromechanical Testing System fitted with 100 N load cell. The measurements were conducted following the standard BS EN ISO 13934-1:2013 [47] at a rate of 0.10 mm/s. The tests were carried out at 20 ± 3 °C and 50 ± 5% RH. All fabrics and samples were cut in the warp direction. For each sample, the analysis was repeated on five specimens measuring: 50 mm × 10 mm for S1 and S2; 50 mm × 5 mm for S3. Even if the specimens cut from S3 were smaller in size than those from S1 and S2, the testing aimed at highlighting differences within the same fabric before and after treatment/ageing. The experimental approach still allowed them to properly assess potential variations, as each fabric was evaluated separately. Presenting the data as stress vs. strain would have also allowed a direct comparison between samples with different sizes; however, accurately measuring the cross-sectional area in textiles is not trivial. Therefore, the data were presented and elaborated as load vs. extension, as performed by other researchers within the field [48,49].

2.4.5. Case Study: Museum of Palazzo Mocenigo

Samples of the three silk fabrics, untreated and immersed in the MIC sanitiser (sol. 6), were displayed in three of the rooms of the Museum of Palazzo Mocenigo, namely, Rooms 1, 4 and 9. As shown in Figure 2, the samples were pinned on the walls of the rooms, which are covered with contemporary silk upholsteries manufactured by Rubelli® (Venice).
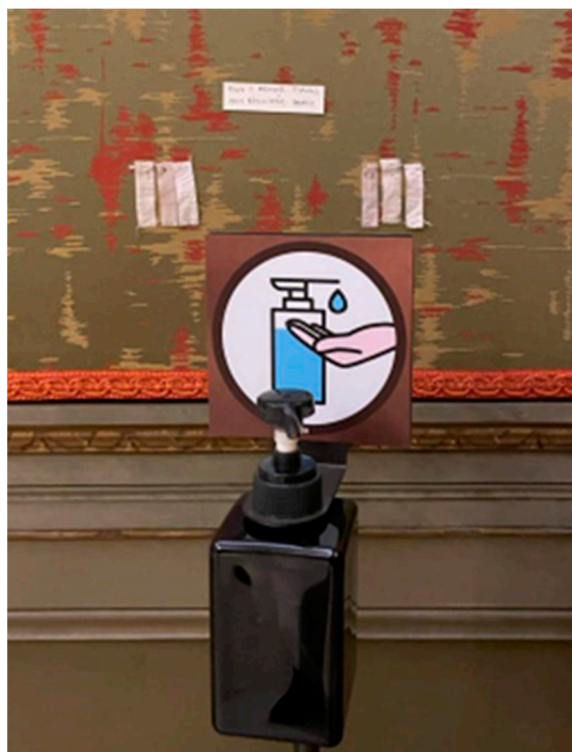
Figure 2. Silk samples displayed in the Museum of Palazzo Mocenigo.

A data logger was placed in one of the rooms of the Museum considered representative due to the stable conditions throughout the palace (Room 9) and set to register temperature and RH every 30 min, and the illuminance was recorded through a luxometer Fervi® L014. The samples were left in the museum for a total of twelve weeks, after which, potential spectral changes in the textiles were evaluated non-invasively through the techniques described in Section 2.4.2. Alongside spectroscopic changes, possible variations in colour and water wettability were also assessed.

3. Results and Discussion

3.1. Effects of Alcohol-Based Solutions on Silk Samples

As noted in our previous work on silk [2], all the solutions applied through either immersion cycles or spraying caused some changes in colour on the fabrics, some of which were visible ($\Delta E > 3$). In particular, visible changes occurred on S3 when using sol. 1–4, i.e., pure alcohols and the 75% aqueous blends. Since S3 was dyed, the notable chromatic variation was expected due to possible solubilisation of the colourants in ethanol and isopropanol [23].

Additionally, the data gained through the spectroscopic analyses, Raman and FTIR-ATR, are coherent with the ones reported in our preliminary study; we never observed substantial modifications in silk secondary structure due to the treatments [2]. Interestingly, a similar result was also noted for samples immersed five times in the solutions, indicating the lack of effects even after prolonged direct contact. Nevertheless, the presence of BZK on the samples treated with sol. 5 and 6 was detected through spectroscopic analyses, highlighting that both spraying and immersion led to the deposition of the QACs on the silk samples. While Raman and FTIR-ATR were already proved effective in revealing BZK through characteristic absorption at 2920, 2850 and 1000 cm^{-1} [2], the same was here noted for FORS analysis: a band related to the salt was identified at 2345 nm. Figure 3 depicts FTIR-ATR, Raman and FORS spectra of samples untreated and treated with the MIC solution, the latter being recognisable by the signals in the highlighted regions of interest. In general, the data acquired through the three spectroscopic techniques (Figure 3) show the characteristic signals of silk, such as those of amide I (at 1618 cm^{-1} for FTIR-ATR

and at around 1660 cm^{-1} for Raman), amide II (at 1515 cm^{-1} for FTIR-ATR and 2060 nm for FORS) and amide III (at around 1260 cm^{-1} for FTIR-ATR, 1230 cm^{-1} for Raman, and at 2205 nm for FORS) [43,45,50,51].


(**a**)

(**b**)

(**c**)
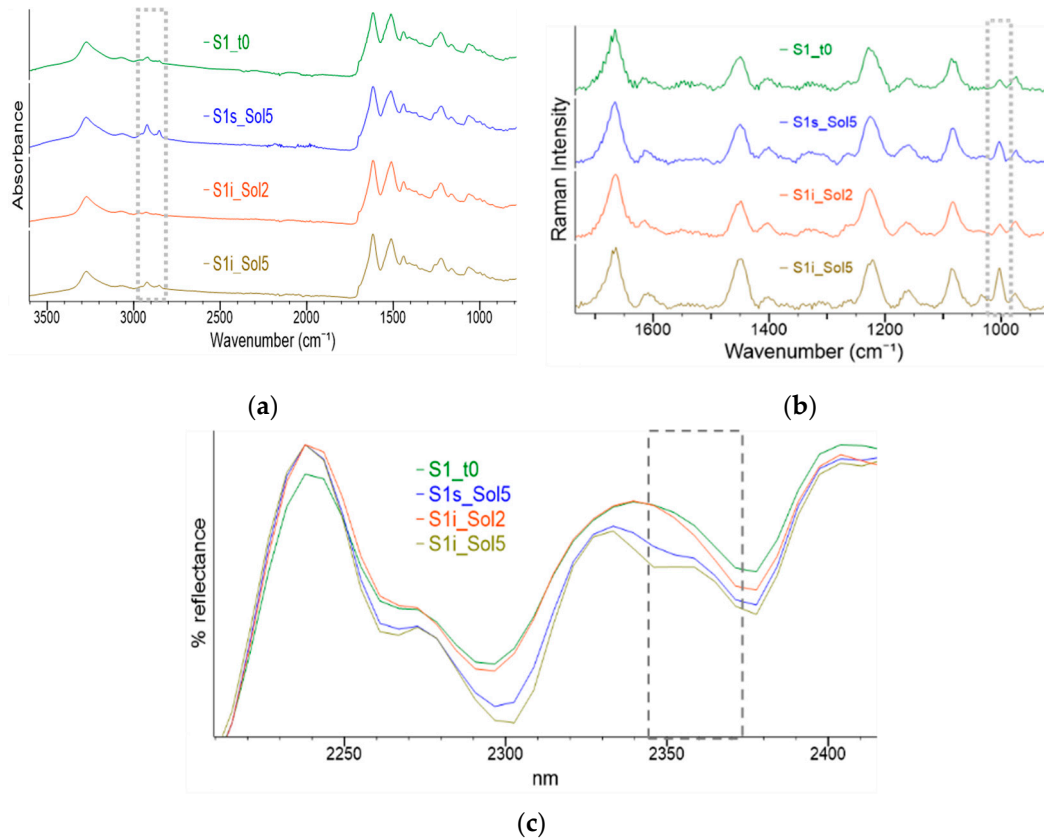
Figure 3. FTIR−ATR (**a**), Raman (**b**) and FORS SWIR (**c**) spectra of S1: at t0 (S1_t0); after spraying with sol. 5 (S1s_Sol5); after immersion with sol. 2 (S1i_Sol2); after immersion with sol. 5 (S1i_Sol5).

In the case of FORS analysis, the technique could provide complementary information to those given by FTIR-ATR and Raman spectroscopies, as it also allows one to investigate Vis and NIR wavelength intervals. While the investigation in the Vis range is useful for colour-related measurements, collecting data within the NIR and SWIR region was defined as possibly useful for the condition assessment of silk textiles [45,52]. Nevertheless, in this case, the non-invasive approach did not highlight any difference in the condition of the silk samples before and after treatment with the alcohol-based solutions, confirming Raman and FTIR data.

Similarly to what was assessed from the chemical perspective, the mechanical strength of the silk samples did not vary after the treatments with the solutions. This result, which integrates what was observed for the chemical properties [2], is evident from the data in Figure 4 indicating the load at break before and at the end of the five immersions. Considering the standard deviation from the five replicas per sample, the force at breaking point did not show noticeable variations. The same observations can be drawn from the outcomes of the mechanical testing after the milder spraying treatment. It should be underlined that differences in the load at break from fabric to fabric at t0, before the immersion/spraying of sanitisers, are influenced by intrinsic properties of the textiles, such as the weaving density, the geometry and pre-treatments of the fibres [53].
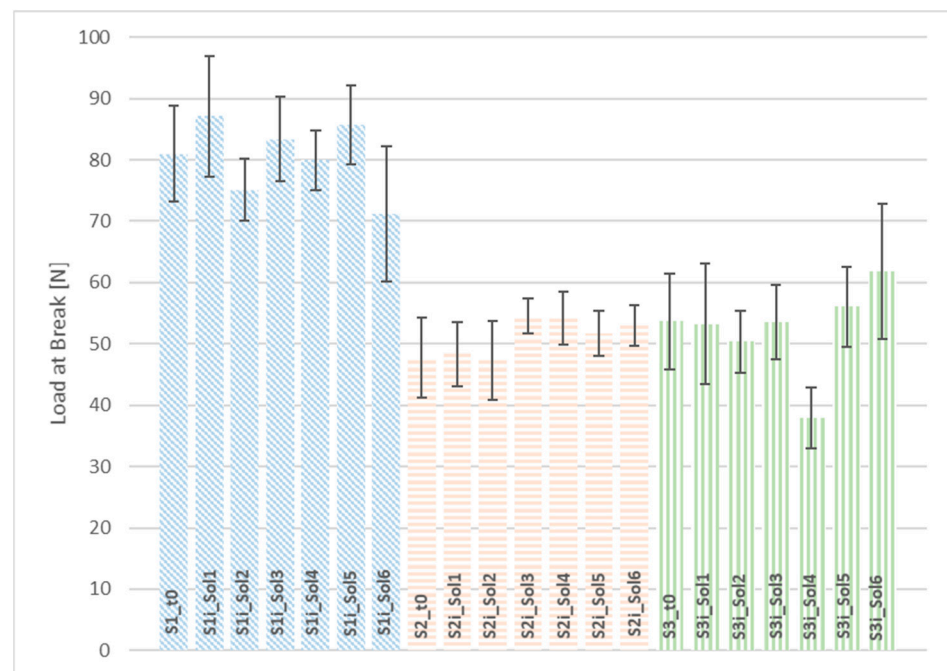
Figure 4. Load at break (N) of the three silk fabrics before and after the five immersion treatments with the six alcohol-based solutions. For each sample, the measurement was repeated on five specimens.

Importantly, the use of sol. 5 and 6, applied through immersion and as a spray, determined a drastic change in wettability in all the three silk fabrics; this value increased so much in comparison to t0 (contact angle $\approx 110°$) that it was impossible to carry out the measurements, as the water drops were immediately adsorbed by the textiles. The presence of BZK in sol. 5. and 6 was responsible for the increase in fabrics' water wettability, since a surfactant once adsorbed, reduces the interfacial tension [54]. As further discussed in the following section, even when water wettability cannot be determined via contact angle measurements, FORS analysis in the SWIR range can be useful in defining the moisture content of the fibre.

3.2. Effects of the Artificial Ageing on the Treated Samples

The silk samples immersed (five times, 30 min per immersion) in the six alcohol-based solutions (sol. 1–6) were artificially aged. In particular, the samples were exposed to simulated solar light for four weeks, and to fixed RH ranges, 55% and 80%, for eight weeks.
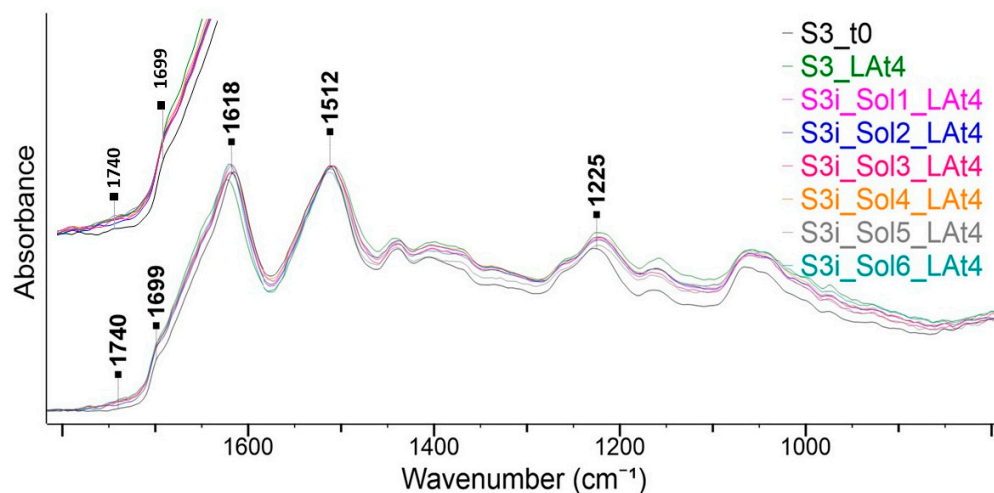
3.2.1. Light Ageing

Light caused visible chromatic variations in all the silk samples. The main changes occurred during the first week of exposure ($\Delta E > 5$), leading to evident yellowing of the fabrics (increase in b* values). The yellowing affected all the samples, treated and untreated.

As confirmed by the spectroscopic techniques, BZK remained on the aged samples treated with sol. 5 and 6. This result was somewhat expected, since the salt was adsorbed within the textile and it would likely need re-solubilisation in order to be removed, even if applied as a spray solution. FTIR-ATR analysis pointed out how the extended exposure to light caused some modifications in the secondary structure of silk.

Figure 5 depicts the spectra of treated/untreated samples from the fabric S3 at t0 and the end of the light ageing, showing that the main modifications regard the broadening of the bands at 1699 and at 1230 cm^{-1}. While the change at 1699 cm^{-1} can be attributed to an increase in antiparallel ß-sheet (thus indicating a change in crystallinity), variations in the peak at 1230 cm^{-1} were ascribed to a distortion in random coil conformation in the amorphous region [21,55,56]. As shown by Figure 5, spectral differences before and after ageing were noted for both treated and untreated samples, suggesting that the photo-

oxidation processes were not influenced by the treatments. The mentioned spectroscopic changes were not observed for all the samples exposed to the simulated solar light, perhaps indicating that the modifications were not homogeneous and/or significant enough to be always tracked.
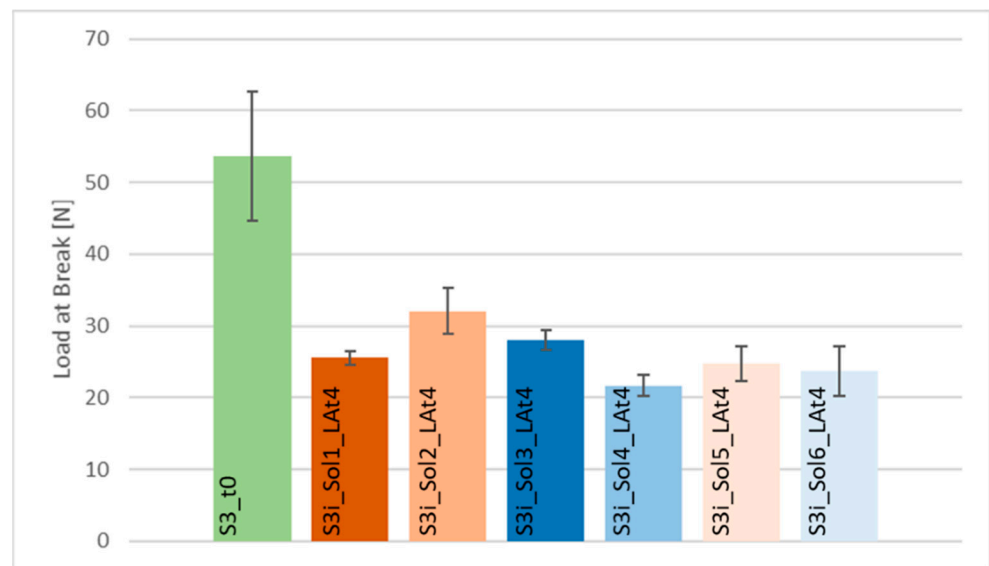

Figure 5. FTIR−ATR spectra of S3: untreated and unaged (S3_t0); untreated and light-aged for four weeks (S3_LAt4); treated and light-aged for four weeks (S3i_Sol1-6_LAt4).

The Raman spectra acquired after the ageing are comparable to those at t0, and are therefore unable to show effects of the photo-oxidation. Although previous works suggested considering the peaks related to tyrosine at 855, 830 and 645 cm^{-1} to track light-induced degradation through Raman spectroscopy [22,43,57], no significant changes were noted at these wavenumbers. In general, the Raman intensity of the tyrosine peaks was relatively low, and the signal noisy, possibly due to the relatively low abundance of tyrosine in *Bobyx mori* silk fabrics (up to 5% or less [20]). In comparison to the approach used, to accurately track tyrosine degradation, liquid and gas chromatography coupled with mass spectrometry can represent a better option [20,58]. It is underlined that no significant variations were noted in the FORS spectra of unaged and aged samples.

It can be concluded that the light exposure did not affect the wettability of the samples, and indeed those immersed in the MIC sanitisers remained highly water wettable. This means that the BZK likely remains on the textile in the long term (unless the material is cleaned, as the boiling point is greater than 100 °C), and therefore, it can cause a permanent modification of the wettability.

The data from the tensile tests after light ageing demonstrated the damaging effects of solar light on silk, responsible for drastic decreases (even up to 50%) in the tensile strength for all the samples. As illustrated in Figure 6 for the case of S3, the load at break was significantly reduced regardless of the treatment with sanitising solutions, which therefore did not play an evident role in the degradation process affecting the mechanical properties.

Figure 6. Load at break (N) of S3: untreated and unaged (S3_t0); treated through immersion with the six alcohol-based solutions and light-aged for four weeks (S3_Sol1-6_LAt4).

3.2.2. Ageing at Medium and High Relative Humidity

The two-month ageing at fixed RH, medium (55%) and high (80%), did not cause modifications in the secondary structure of the proteinaceous fibre trackable through spectroscopic analysis, as may be expected [21,26]. Differently from what was reported after the light ageing, FTIR-ATR spectra of silk samples stored at high and medium humidity were like those collected at t0. As an example, Figure 7 provides the spectra of S3 before and after the ageing at 80% RH. Although the spectra remained largely unvaried, peaks related to BZK were detected at the end of the ageing in all the samples treated with sol. 5 and 6. Again, this points out the persistence of the QACs on the textile.
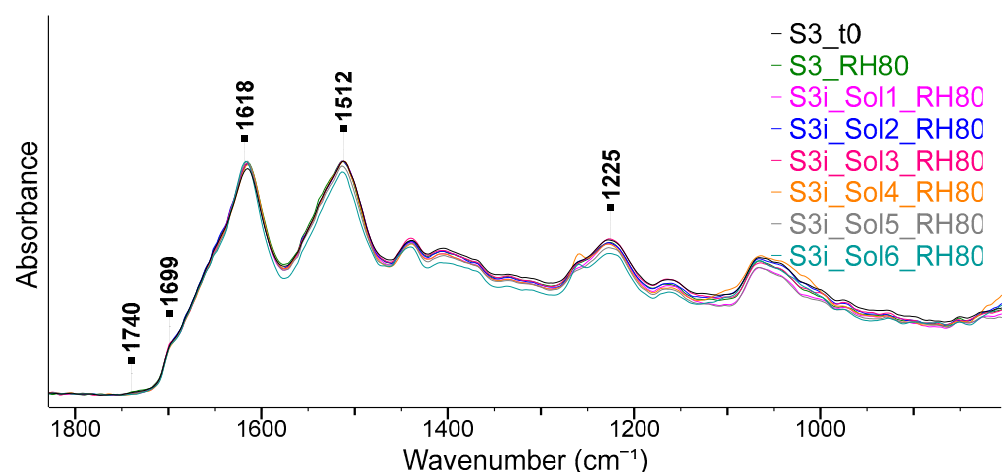
Figure 7. FTIR−ATR spectra of S3: untreated and unaged (S3_t0); untreated and aged at 80% RH for eight weeks (S3_RH80); treated and aged at 80% RH for eight weeks (S3i_Sol1-6_RH80).

FORS SWIR data (acquired immediately after ageing) showed differences in the moisture content of samples stored at 55 and 80% RH. As illustrated in Figure 8, there was variation in the intensity of the peak at 1930 nm (from the -OH combination) [59], which was higher for the samples aged at 80%. This difference is particularly evident when comparing the spectra of samples at high RH to those at the end of light ageing, which was responsible for the drying of the fibres.
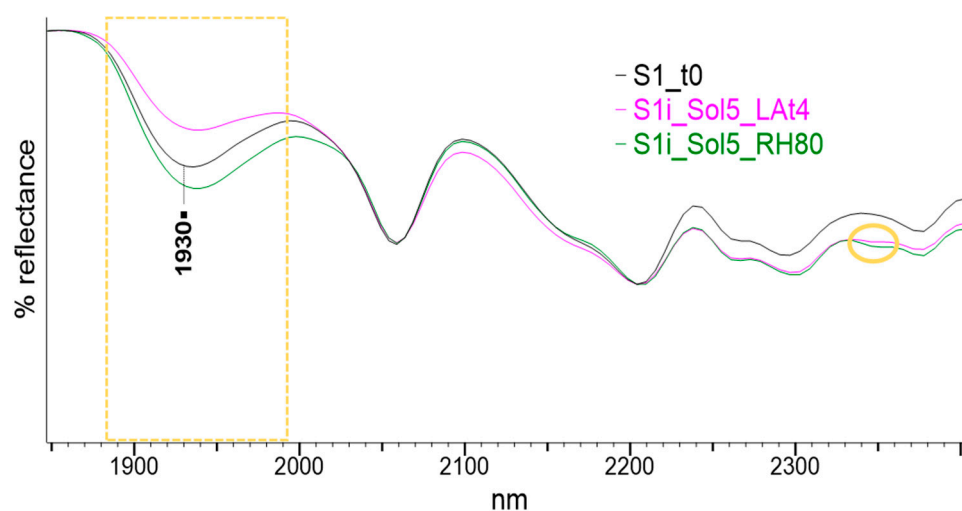
Figure 8. FORS SWIR spectra of S1 samples: unaged and untreated (S1_t0); treated through immersion cycles with sol. 5 and light aged for four weeks (S1_Sol5_LAt4); treated through immersion cycles with sol. 5 and aged at 80% RH for eight weeks (S1_Sol5_RH80).

As noted from the chemical perspective, the load at break did not vary as a consequence of the ageing at fixed humidity. This differs from what was observed at the end of the light ageing, as the effects of simulated sun light on the mechanical strength were relevant. These data are in line with our previous findings on the different impact of light and humidity on silk [21,26], although it should be underlined that the cited experiments, and those carried out in this study, lasted less than three months. It can be thought that longer time is needed to observe the impact humidity (both stable and fluctuating); indeed, Howell registered a decrease in the load at break after storing silk samples at 85% RH for six months [25].

3.3. Case Study: Effects of a Museum Environment on the Treated Samples

Samples from the three silk fabrics before and after the immersion cycles with the MIC solution (sol. 5) were displayed in different rooms of the Museum of Palazzo Mocenigo, located in Venice. After twelve weeks in the Museum, the textile samples were analysed to define whether any chromatic, spectroscopic, and/or wettability-related change occurred and if the treatment played a role.

The hygrothermal conditions in the museum were monitored throughout the three-month period of the study (January–March 2022). The collected data showed a stable environment, in line with conservation guidelines [60]: the registered RH was around $56 \pm 2\%$, and the average temperature was $21 \pm 2\,°C$. The illuminance was slightly different from room to room, although in all the cases the area was only artificially illuminated, as the solar light was completely prevented from entering from the windows by thick curtains. Namely, the illuminance in the spots where the samples were located (far from the centre of the rooms with a value of 140 lux where the main and only illumination system was present) ranged between 6 lux (Room 1), 19 lux (Room 4) and 8 lux (Room 9).

Regardless of the illuminance in the Museum, where windows are covered with thick curtains, some changes in colour were noted on some treated and untreated samples. As shown in Figure 9, the greatest chromatic variations (some of which visible) were observed in samples cut from S3, the only dyed textile, and they can be mainly linked to an increase in L*, indicating whitening. Similarly, the ΔE of some S1 samples was close to three because of the growth in L*. In both cases, samples displayed in Rooms 4 and 9 presented greater ΔE values than those in Room 1, likely as consequence of the higher illuminance of the space, still consistently below the CIE recommendations, i.e., 200 lux [61].
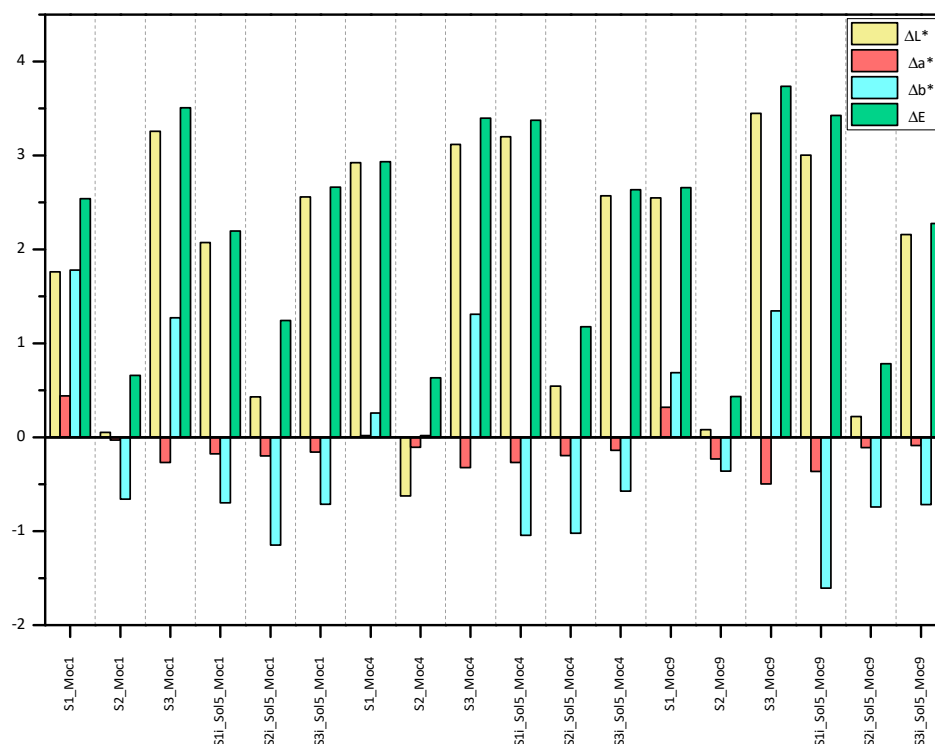
Figure 9. Variations in the chromatic coordinates L*, a*, b* and ΔE of untreated/treated silk samples after the three-month display at the Museum of Palazzo Mocenigo.

At the end of the twelve-week display at Palazzo Mocenigo, as expected, BZK was once again detected on samples treated with the MIC sanitiser; peaks related to the QACs were identified through the spectroscopic techniques, and the textiles were still highly water wettable. FTIR-ATR, Raman and FORS analysis did not highlight differences in the spectra acquired before and after the display in the museum. As a result, it can be suggested that the photo-oxidative degradation that possibly occurred, and was shown by the colorimetric measurements, was very limited.

4. Conclusions

This study looked at whether alcohol-based solutions, widespread in sanitisers, may have an impact on the degradation path of silk promoted by common environmental factors in historic sites, i.e., light and humidity. In total, six solutions were tested on three newly manufactured silk fabrics, considering as reference the sanitiser suggested by the Italian Ministry of Culture MIC (75% ethanol, 20% water, 5% benzalkonium chloride, BZK). Starting from our previous work focusing on the potential chemical changes caused by treatments with alcohol-based solutions [2], here mechanical and wettability variations were evaluated, alongside the ageing behaviour under different environmental conditions.

No chemical effects and mechanical (tensile strength) variations were observed after treatments, reinforcing previous results. On the other hand, the four-week exposure to simulated solar light caused some changes in the secondary structure of silk and in the physical strength of both untreated and immersed samples. Since the variations occurred in all the light aged samples, this indicates that the photo-oxidation process, also highlighted by the colorimetric data, was not influenced by the treatments with sanitisers. In general, the outcomes confirm the mechanical and chemical stability of silk (both unaged and light/humidity aged) when exposed to alcohol-based solutions.

From a technical perspective, FTIR-ATR was more successful than FORS and Raman spectroscopy in tracking changes in the secondary structure of silk due to the ageing. On the other hand, FORS analysis showed to be useful in providing complementary information in the SWIR range, e.g., related to the moisture content of the fibrous material. Regarding

the application of FTIR for textile applications, a few authors have pointed out that this technique may have reduced sensitivity for detecting possible degradation processes related to the use of specific products or to ageing processes—in particular, natural ageing. For this reason, although the instrumentation employed allows non-invasive analysis, which can be desirable in the case of cultural heritage, techniques such as limiting the viscosity number and chromatography coupled with mass spectrometry can provide relevant complementary information regarding proteinaceous macromolecules and amino-acid degradation. This could be critical to tracking variations, especially at the early stages and as a support in conservation and cleaning treatments.

Importantly, at the end of all the ageing tests and the display at the Museum of Palazzo Mocenigo, BZK was detected (thanks to the spectroscopic techniques) on samples treated through immersion from the solutions containing the QACs. This points out that the surfactant remains on the textile, and it possibly modifies, in a permanent way, important properties of the material, such as the water wettability. Although further research is needed, perhaps including longer exposure time in museums environment, the presence of BZK, on a long term, could represent a risk for artworks made of hygroscopic materials such as silk, possibly promoting mechanical fatigue and dust cementation.

Considering the collected data, alcohol-based solutions appear to be a safe option for sanitising museum environments, at least in proximity to silk materials and from the fibres' perspective, though they may be risky for the dyeing in case of direct and prolonged contact. On the other hand, the addition of BZK in the product should be avoided, as this can deposit on the materials (even through nebulisation) and affect the behaviour toward relative humidity.

References

1. Skipper, P.; Fry, C.; Willett, C. Disinfection of Contaminated Heritage Surfaces from SARS-CoV-2 Virus. *J. Conserv. Mus. Stud.* **2021**, *19*, 3. [CrossRef]
2. Favaro, B.; Balliana, E.; Rigoni, F.; Zendri, E. A preliminary evaluation of chemical interaction between sanitizing products and silk. *J. Cult. Herit.* **2021**, *51*, 1–13. [CrossRef] [PubMed]
3. Khlystova, O.; Kalyuzhnova, Y.; Belitski, M. The impact of the COVID-19 pandemic on the creative industries: A literature review and future research agenda. *J. Bus. Res.* **2022**, *139*, 1192–1210. [CrossRef] [PubMed]
4. Choi, B.; Kim, J. Changes and Challenges in Museum Management after the COVID-19 Pandemic. *J. Open Innov. Technol. Mark. Complex.* **2021**, *7*, 148. [CrossRef]

5. Agostino, D.; Arnaboldi, M.; Lampis, A. Italian state museums during the COVID-19 crisis: From onsite closure to online openness. *Mus. Manag. Curatorship* **2020**, *35*, 362–372. [CrossRef]

6. King, E.; Smith, M.P.; Wilson, P.F.; Williams, M.A. Digital Responses of UK Museum Exhibitions to the COVID-19 Crisis, March–June 2020. *Curator: Mus. J.* **2021**, *64*, 487–504. [CrossRef]

7. Lerario, A. Languages and Context Issues of ICTs for a New Role of Museums in the COVID-19 Era. *Heritage* **2021**, *4*, 3065–3080. [CrossRef]

8. Spennemann, D.H.R. COVID-19 on the Ground: Managing the Heritage Sites of a Pandemic. *Heritage* **2021**, *4*, 2140–2162. [CrossRef]

9. MIBACT. Emergenza Epidemiologica da COVID-19—Linee Guida per la Sanificazione in Presenza di beni Culturali ai sensi del D-Lgs. 42/2004 e ss.mm.ii. 2020. Available online: https://www.lazio.beniculturali.it/wp-content/uploads/2020/05/Linee-Guida-ICR.pdf (accessed on 29 August 2022).

10. MIBACT; ICR. Allegato def ICR Indicazioni per la Sanificazione in Contesti Culturali. 2020. Available online: http://www.icr.beniculturali.it/documenti/allegati/Allegato%20def%20ICR%20Indicazioni%20per%20la%20sanificazione%20in%20contesti%20culturali%20(4).pdf (accessed on 29 August 2022).

11. Golin, A.P.; Choi, D.; Ghahary, A. Hand sanitizers: A review of ingredients, mechanisms of action, modes of delivery, and efficacy against coronaviruses. *Am. J. Infect. Control* **2020**, *48*, 1062–1067. [CrossRef]

12. Singh, D.; Joshi, K.; Samuel, A.; Patra, J.; Mahindroo, N. Alcohol-based hand sanitisers as first line of defence against SARS-CoV-2: A review of biology, chemistry and formulations. *Epidemiol. Infect.* **2020**, *148*, e229. [CrossRef]

13. Ghedini, E.; Pizzolato, M.; Longo, L.; Menegazzo, F.; Zanardo, D.; Signoretto, M. Which Are the Main Surface Disinfection Approaches at the Time of SARS-CoV-2? *Front. Chem. Eng.* **2021**, *2*, 1–16. [CrossRef]

14. Herdt, B.L.; Black, E.P.; Zhou, S.S.; Wilde, C.J. Inactivation of SARS-CoV-2 by 2 commercially available Benzalkonium chloride-based hand sanitizers in comparison with an 80% ethanol-based hand sanitizer. *Infect. Prev. Pract.* **2021**, *3*, 100191. [CrossRef]

15. Kampf, G.; Todt, D.; Pfaender, S.; Steinmann, E. Persistence of coronaviruses on inanimate surfaces and their inactivation with biocidal agents. *J. Hosp. Infect.* **2020**, *104*, 246–251. [CrossRef] [PubMed]

16. Daverey, A.; Dutta, K. COVID-19: Eco-friendly hand hygiene for human and environmental safety. *J. Environ. Chem. Eng.* **2021**, *9*, 104754. [CrossRef]

17. COVID-19: Cleaning and Disinfecting Historic Surfaces. Available online: https://historicengland.org.uk/coronavirus/historic-places/cleaning-disinfecting-historic-surfaces/ (accessed on 29 August 2022).

18. Villafana, T. Assessing the Impact of Sanitizing Products on Collection Items. Available online: https://blogs.loc.gov/preservation/2021/06/assessing-the-impact-of-sanitizing-products-on-collection-items/ (accessed on 29 August 2022).

19. Luxford, N. Silk durability and degradation. In *Understanding and Improving the Durability of Textiles*; Annis, P.A., Ed.; Woodhead Publishing: Oxford, UK; Philadelphia, PA, USA, 2012; pp. 205–232.

20. Vanden Berghe, I. Towards an early warning system for oxidative degradation of protein fibres in historical tapestries by means of calibrated amino acid analysis. *J. Archaeol. Sci.* **2012**, *39*, 1349–1359. [CrossRef]

21. Serrano, A.; Brokerhof, A.; Ankersmit, B.; van Bommel, M. From the bottom of the sea to the display case: A study into the long-term preservation of archaeological maritime silk textiles in controlled atmosphere. *J. Cult. Herit.* **2020**, *45*, 91–100. [CrossRef]

22. Shao, J.; Zheng, J.; Liu, J.; Carr, C.M. Fourier transform Raman and Fourier transform infrared spectroscopy studies of silk fibroin. *J. Appl. Polym. Sci.* **2005**, *96*, 1999–2004. [CrossRef]

23. Timar-Balazsy, A.G.; Eastop, D. *Chemical Principles of Textile Conservation*; Routledge: London, UK, 1998; p. 480. [CrossRef]

24. Bratasz, L.; Lukomski, M.; Klisinska-Kopacz, A.; Zawadzki, W.; Dzierzega, K.; Bartosik, M.; Sobczyk, J.; Lennard, F.J.; Kozlowski, R. Risk of Climate-Induced Damage in Historic Textiles. *Strain* **2015**, *51*, 78–88. [CrossRef]

25. Howell, D. Some Mechanical Effects of Inappropriate Humidity on Textiles. In Proceedings of the ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland, 1–6 September 1996; Preprints. Bridgland, J., Ed.; James & James: London, UK, 1996; Volume 2, pp. 692–697.

26. Vilaplana, F.; Nilsson, J.; Sommer, D.V.P.; Karlsson, S. Analytical markers for silk degradation: Comparing historic silk and silk artificially aged in different environments. *Anal. Bioanal. Chem.* **2015**, *407*, 1433–1449. [CrossRef]

27. Luxford, N.; Thickett, D. Designing accelerated ageing experiments to study silk deterioration in historic houses. *J. Inst. Conserv.* **2011**, *34*, 115–127. [CrossRef]

28. Ballard, M.W. Hanging Out Strength, Elongation and Relative Humidity: Some Physical Properties of Textile Fibers. In Proceedings of the ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland, 1–6 September 1996; Preprints. Bridgland, J., Ed.; James & James: London, UK, 1996; Volume 2, pp. 665–669.

29. Thickett, D.; Luxford, N.; Lankester, P. Environmental Management Challenges and Strategies in Historic Houses. In Proceedings of the Artifact, Its Context and Their Narrative: Multidisciplinary Conservation in Historic House Museums, Los Angeles, CA, USA, 6–9 November 2012.

30. Lucero-Gómez, P.; Balliana, E.; Izzo, F.C.; Zendri, E. A new methodology to characterize indoor variations of temperature and relative humidity in historical museum buildings for conservation purposes. *Build. Environ.* **2020**, *185*, 107147. [CrossRef]

31. Macken, A.; Smith, M.J. Solvent Vapour Use—The Unintended Consequences in Textile Conservation. *Stud. Conserv.* **2019**, *64*, 352–362. [CrossRef]

32. Krejčí, J.; Drábková, K.; Bureš Víchová, J.; Škrdlantová, M. Reversibility of adhesive techniques applied on historical textiles. *Eur. Phys. J. Plus* **2021**, *136*, 642. [CrossRef]
33. Drábková, K.; Krejčí, J.; Škrdlantová, M.; Ďurovič, M.; Bacílková, B. Influence of Disinfectants on Natural Textile Fibres. *Restaurator. Int. J. Preserv. Libr. Arch. Mater.* **2021**, *42*, 67–86. [CrossRef]
34. Wang, H.-Y.; Zhang, Y.-Q.; Wei, Z.-G. Dissolution and processing of silk fibroin for materials science. *Crit. Rev. Biotechnol.* **2021**, *41*, 406–424. [CrossRef] [PubMed]
35. Minoura, N.; Tsukada, M.; Nagura, M. Fine structure and oxygen permeability of silk fibroin membrane treated with methanol. *Polymer* **1990**, *31*, 265–269. [CrossRef]
36. Kaewpirom, S.; Boonsang, S. Influence of alcohol treatments on properties of silk-fibroin-based films for highly optically transparent coating applications. *RSC Adv.* **2020**, *10*, 15913–15923. [CrossRef] [PubMed]
37. Bucciarelli, A.; Motta, A. Use of Bombyx mori silk fibroin in tissue engineering: From cocoons to medical devices, challenges, and future perspectives. *Biomater. Adv.* **2022**, *139*, 1–29. [CrossRef]
38. *ISO 12571:2021*; Hygrothermal Performance of Building Materials and Products—Determination of Hygroscopic Sorption Properties. CEN-CENELEC Management Centre: Brussels, Belgium, 2021.
39. Luxford, N.; Thickett, D.; Wyeth, P. Applying preventive conservation recommendations for silk in historic houses. In Proceedings of the Joint Interim Conference. Multidisciplinary Conservation: A Holistic View for Historic Interiors, Rome, Italy, 23–26 March 2010.
40. Izzo, F.C.; Balliana, E.; Perra, E.; Zendri, E. Accelerated Ageing Procedures to Assess the Stability of an Unconventional Acrylic-Wax Polymeric Emulsion for Contemporary Art. *Polymers* **2020**, *12*, 1925. [CrossRef]
41. Zendri, E.; Falchi, L.; Izzo, F.C.; Morabito, Z.M.; Driussi, G. A review of common NDTs in the monitoring and preservation of historical architectural surfaces. *Int. J. Archit. Herit.* **2017**, *11*, 987–1004. [CrossRef]
42. Zhang, X.; Gong, D.; Gong, Y. Insight into the orientation behavior of thermal-aged and historic silk fabrics by polarized FTIR microspectroscopy. *J. Cult. Herit.* **2019**, *38*, 53–63. [CrossRef]
43. McGill, M.; Holland, G.P.; Kaplan, D.L. Experimental Methods for Characterizing the Secondary Structure and Thermal Properties of Silk Proteins. *Macromol. Rapid Commun.* **2019**, *40*, 1800390. [CrossRef]
44. Kissi, N.; Curran, K.; Vlachou-Mogire, C.; Fearn, T.; McCullough, L. Developing a non-invasive tool to assess the impact of oxidation on the structural integrity of historic wool in Tudor tapestries. *Herit. Sci.* **2017**, *5*, 49. [CrossRef]
45. Richardson, E.; Garside, P. The use of near infrared spectroscopy as a diagnostic tool for historic silk artefacts. *J. E-Preserv. Sci.* **2009**, *6*, 68–74.
46. *UNI EN 15802: 2010*; Conservation of Cultural Property—Test Methods—Determination of Static Contact Angle. CEN-CENELEC Management Centre: Brussels, Belgium, 2010.
47. *BS EN ISO 13934-1:2013*; Textiles—Tensile Properties of Fabrics—Part 1: Determination of Maximum Force and Elongation at Maximum Force Using the Strip Method. ISO/TC 38/SC 24 AFNOR: Paris, France, 2013.
48. Young, C.; Jardine, S. Fabrics for the twenty-first century: As artist canvas and for the structural reinforcement of easel paintings on canvas. *Stud. Conserv.* **2012**, *57*, 237–253. [CrossRef]
49. Smith, M.J.; Flowers, T.H.; Lennard, F.J. Mechanical properties of wool and cotton yarns used in twenty-first century tapestry: Preparing for the future by understanding the present. *Stud. Conserv.* **2015**, *60*, 375–383. [CrossRef]
50. Edwards, H.G.M.; Farwell, D.W. Raman spectroscopic studies of silk. *J. Raman Spectrosc.* **1995**, *26*, 901–909. [CrossRef]
51. Pereira, R.F.P.; Silva, M.M.; de Zea Bermudez, V. Bombyx mori Silk Fibers: An Outstanding Family of Materials. *Macromol. Mater. Eng.* **2015**, *300*, 1171–1198. [CrossRef]
52. Garside, P.; Wyeth, P.; Zhang, X. Use of near IR spectroscopy and chemo-metrics to assess the tensile strength of historic silk. *E-Preserv. Sci.* **2011**, *8*, 68–73.
53. Liu, D.; Christe, D.; Shakibajahromi, B.; Knittel, C.; Castaneda, N.; Breen, D.; Dion, G.; Kontsos, A. On the role of material architecture in the mechanical behavior of knitted textiles. *Int. J. Solids Struct.* **2017**, *109*, 101–111. [CrossRef]
54. Schramm, L.L.; Stasiuk, E.N.; Marangoni, D.G. 2 Surfactants and their applications. *Annu. Rep. Sect. C Phys. Chem.* **2003**, *99*, 3–48. [CrossRef]
55. Koperska, M.A.; Łojewski, T.; Łojewska, J. Evaluating degradation of silk's fibroin by attenuated total reflectance infrared spectroscopy: Case study of ancient banners from Polish collections. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2015**, *135*, 576–582. [CrossRef] [PubMed]
56. Koperska, M.A.; Pawcenis, D.; Milczarek, J.M.; Blachecki, A.; Łojewski, T.; Łojewska, J. Fibroin degradation—Critical evaluation of conventional analytical methods. *Polym. Degrad. Stab.* **2015**, *120*, 357–367. [CrossRef]
57. Uring, P.; Chabas, A.; Alfaro, S.C. Textile ageing due to atmospheric gases and particles in indoor cultural heritage. *Environ. Sci. Pollut. Res.* **2021**, *28*, 66340–66354. [CrossRef]
58. Sabatini, F.; Nacci, T.; Degano, I.; Colombini, M.P. Investigating the composition and degradation of wool through EGA/MS and Py-GC/MS. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 111–121. [CrossRef]
59. Zhang, X.; Wyeth, P. Moisture Sorption as a Potential Condition Marker for Historic Silks: Noninvasive Determination by Near-Infrared Spectroscopy. *Appl. Spectrosc.* **2007**, *61*, 218–222. [CrossRef]

60. Lucero-Gómez, P.; Balliana, E.; Farinelli, V.; Salvini, S.; Signorelli, L.; Zendri, E. Rethinking and evaluating the role of historical buildings in the preservation of fragile artworks: The case study of the Gallerie dell'Accademia in Venice. *Eur. Phys. J. Plus* **2022**, *137*, 150. [CrossRef]
61. Cuttle, C. Control of damage to museum objects by exposure to optical radiation. In Proceedings of the 24th Session of the CIE, Warsaw, Poland, 24–30 June 1999; Volume 1, pp. 324–328.