

Article

Assessing the Use of Supercritical Carbon Dioxide as a Carrier for Alkoxysilanes to Consolidate Degraded PUR Ester Foams: An Alternative to Traditional Methods

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Abstract: Degradation of ester-based polyurethane (PUR) foams results in extensive fragmentation, stickiness, and brittleness both at surfaces and in the bulk. Current methods to conserve museum objects comprising PUR foams include consolidation with solvent-based polymeric solutions. Besides the limitations of spray and brush application for deep consolidant penetration and the impracticality of immersing large-scale objects in solutions, these methods often require large amounts of toxic solvents that are harmful for both the user and environment. Carbon dioxide can be employed as a green solvent as it can be recovered, recycled, and reused without contributing to the greenhouse effect. Supercritical carbon dioxide (scCO₂)-assisted consolidation premises are that it may carry the consolidant deeper and deposit it consistently throughout the foam, whilst ensuring minimal interaction with the surface and avoiding material losses in severely degraded objects and the use of toxic solvents. The suitability of scCO₂ as a carrier is studied, and the results compared with spray application, a commonly used traditional method. Previous studies have shown that a mixture of alkoxysilanes has great potential for reinforcing the foam's structure and hydrophobicity when applied by immersion and other impregnation techniques. In this study, scCO₂-assisted consolidation has proven to be an effective and green alternative to consolidation by spray, reducing hazardous solvent emissions. After treatment, no visual changes were detected, the samples became less sticky, and the foam flexibility improved significantly. Analytical techniques confirmed the presence of the consolidant in all tested samples, both on the top surface and in-depth layers, in contrast to foams treated by spray.

Keywords: supercritical CO₂; sustainable conservation; polyurethane foam; consolidation; alkoxysilanes

1. Introduction

Polyurethane (PUR) foams are amongst the most unstable plastics in museum collections. Consolidation treatments are aimed at both limiting the impact of deterioration and restoring some mechanical properties to PUR foams. Ideally, consolidation should

allow a deep and homogenous penetration of the consolidant whilst maintaining the foam's flexibility [1]. This is especially important for ester-based PUR foams because their chemical deterioration causes drastic losses in cohesion in the entire foam network (both top and bulk layers) [2]. Ester-based foams degrade primarily by hydrolysis (caused by exposure to moisture and enhanced by heat and light), inducing crumbling, fragmentation and disintegration into a friable sticky mass as chain scission proceeds [3–7]. By contrast, deterioration of ether-based PUR foams is usually limited to surfaces [2,8,9], and therefore consolidation treatments with shallow penetration may be sufficient. Traditional consolidation methods involve the application of a chosen consolidant via brushing, facing (brushing through a membrane such as tissue), spraying, nebulisation, and immersion [10,11]. For consolidating and protecting ether-based PUR foams, a mixture of PUR in isopropanol/water (Impranil® DLV, Covestro, Leverkusen, Germany) and a light stabiliser (5% Tinuvin® B75, Bodo Möller Chemie, Offenbach am Main, Germany) has proven effective. Although the same dispersion has previously been applied to ester-based foams, when dealing with severely damaged ester-based foams, the conventional approach has been to replace the compromised foam or lacunae with new PUR foam [1,12]. A suitable treatment for ester-based PUR foams was not developed until 2011, when Pellizzi initiated an investigation into aminoalkylalkoxysilane (AAAS)-based treatments to improve the mechanical resistance of these foams while preserving their visual appearance [2,10,13–15]. In a pioneering study by Pellizzi [2], two types of AAAS (3-aminopropyl(diethoxy)methylsilane (APDEMS) and N-(2-amino-ethyl)-3-aminopropylmethyltrimethoxysilane (DIAMINO)) were applied separately in different concentrations in hexamethyldisiloxane (HMDSO). Results showed that AAAS-based treatments improved the mechanical compression properties by preventing cell collapse and restoring elasticity to the foam structure [13,15,16]. However, the amine group on the side chain of the bi-functional silanes also increased the foams' hydrophilicity [2]. Daher et al. [14] furthered this study by mixing an AAAS with a tri-functional hydrophobic compound (which alone would increase the rigidity of the foams). As a result, mixtures of the bi-functional APDEMS with the tri-functional n-octyltrimethoxysilane (OTMS) were studied [10,14]. According to Pellizzi and Daher et al. [2,14], the amine function of the bi-functional silane plays a crucial role in the affinity of the treatment to the degraded foam through the creation of chemical interactions between reactive species from PUR ester foam degradation products and the amine function in APDEMS. In addition, OTMS consists of a hydrophobic long-chain unbranched aliphatic moiety that compensates for the hydrophilic character of the amine group on the APDEMS side chain. Their random copolymerisation leads to the formation of a flexible copolymer network, with flexible linear poly-APDEMS segments inside the OTMS-based polymer network [14]. This binary mixture results in the reinforcement of the foam (by mechanically consolidating the foam structure) and the introduction of a hydrophobic character to the system whilst preserving the foam alveolar structure without obstructing the cell windows [14]. Nevertheless, consolidation by immersion has been the method of choice; however, it is not adequate for large-scale objects as it requires large quantities of HMDSO [10], which is a highly toxic solvent for aquatic life with long-lasting effects and highly flammable liquid and vapour [17]. Therefore, in alignment with the UN's Sustainable Development Goals [18], there is an urgent need for the study and development of a new consolidation methodology for ester-based PUR foams. These goals highlight the role of technological innovation to propel greener and more sustainable approaches, being cultural heritage conservation with no exception.

In recent years, sustainable methodologies (cost-effective and safe for the user and the environment) have gained increasing importance in the field of conservation of modern and contemporary art [19,20]. One approach to reduce hazardous solvent emissions is the use of supercritical fluids (SCF), substances for which both temperature (T) and pressure (p) are kept above their critical values. This phase is characterised by simultaneously combining the relatively high density of a liquid (enabling the dissolution of compatible solids and liquids) with the low viscosity of a gas (allowing the substance to diffuse deeper and

faster into a wide range of materials). Minor changes in temperature and pressure within the critical region may easily modify properties such as density, viscosity, and solvent behaviour [19,21–24].

The interest in SCF has increased significantly. Supercritical carbon dioxide (scCO₂) has proven to be a valuable alternative to water and many other solvents in industrial processes such as polymer synthesis and processing, particle formation, pharmaceutical formulation, cleaning, and food storage [22–25]. Carbon dioxide is low-priced, non-toxic, non-flammable, and chemically inert compared with other gases, with the critical point occurring at $T = 31.1\text{ }^{\circ}\text{C}$ and $p = 7.38\text{ MPa}$. Abundant in nature and being a major exhaust component of many industries, CO₂ is easily accessible and does not contribute to the greenhouse effect as it may be recovered, recycled, and reused [22–24]. In addition, CO₂-based methods are thought to be more energy-efficient than water and conventional solvent-based processes [21]. In this way, the replacement of previously used toxic solvents, in the aforementioned conservation treatments, with CO₂ also directly aligns with the 2030 agenda for the Sustainable Development Goals [18].

Supercritical CO₂ is an effective solvent for many non-polar and some polar low molecular weight compounds. Solubility in scCO₂ tends to decrease with increasing molecular weight; it is therefore considered a poor solvent for high molecular weight compounds, such as polymers. Notwithstanding, some polymers exhibit high solubility in CO₂. These usually feature a flexible backbone and high free volume (low glass transition temperature, T_g), weak interactions between the polymer segments and a weakly basic interaction site, such as a carbonyl group. Some examples are amorphous fluoropolymers, silicones, and selected hydrocarbon polymers, such as poly(methyl acrylate), poly(vinyl acetate), and poly(alkyl siloxanes) [22,23,26]. In the presence of scCO₂, alterations in the physical properties of polymers, such as density, diffusivity, and swell volume, have been observed. Moreover, a significant decrease in viscosity has been documented [22]. These characteristics increased our interest in studying the application of this technology to cultural heritage.

By matching the ideal T and p conditions with the material and treatment, scCO₂ may be advantageous in various conservation processes including cleaning, decontamination, deacidification, stabilisation, consolidation, and drying [25,27,28]. Recent publications have studied the application of scCO₂ to paper [27,29,30], wood [28,31,32], textiles [33–35], water-logged artefacts [36–39], archaeological heritage [40,41], and poly(methyl methacrylate) of historical value [42]. In the “PlasCO₂: Green CO₂ Technologies for the Cleaning of Plastics in Museums and Heritage Collections” project, conducted by the authors, scCO₂ technology was used for the first time to design a conservation treatment for a pair of heavily degraded goalkeeper gloves from Museum Benfica—Cosme Damião. This research studied the feasibility of scCO₂-assisted impregnation for synthetic latex-based foam (namely, composed of polyisoprene, polybutadiene, and polystyrene) and found it suitable because the samples’ surface cohesion was enhanced under certain experimental conditions [43]. However, to our knowledge, the consolidation of PUR foams via scCO₂ has not been explored.

With the main goal of finding a more sustainable and effective consolidation treatment for ester-based PUR foams, the current study investigates the suitability of scCO₂ as a solvent and carrier. To this end, a comparative study is presented between a traditional consolidation application (spray) and the scCO₂-assisted consolidation methodology, contrasting the use of HMDSO as the solvent for the spray consolidation with this alternative approach of using CO₂ as a green and non-toxic solvent. Based on the recent promising results of PlasCO₂ and the solubility of alkoxysilanes in scCO₂ described in the literature [23,26,44], a mixture of APDEMS and OTMS was selected as the consolidant.

2. Materials and Methods

2.1. Ester-Based PUR Foams and Artificial Ageing

Colourless ester-based PUR slabstock foam was obtained from Flexipol Espumas Sintéticas S.A. (São João da Madeira, Portugal). The foams were formulated with 2,6- and

2,4-toluenediisocyanates (TDI-65) and polyester-based polyols, had a density of 56.5 kg/m^3 , compression load deflection at 40% of 7.8 kPa hardness, and $68 \text{ L/m}^2/\text{s}$ air permeability. Individual samples measuring approximately $15 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$ were cut using scissors and a scalpel. Prior to use, the PUR slabstock samples were stored in the dark under laboratory conditions.

Samples were artificially aged to achieve a degree of degradation like those found in the case studies (with crumbling and sticky surfaces). They were light-aged by irradiating in a CO.FO.ME.GRA artificial ageing chamber (SolarBox 3000e, Milano, Italy) equipped with a Xenon-arc light source and a cut-off filter at 300 nm (simulating indoor exposure, $\lambda \geq 300 \text{ nm}$), with constant irradiation of 800 W/m^2 and a black standard temperature of 50°C for approximately 340 h (total irradiance = 946 MJ/m^2). This was followed by ageing in a FITOCLIMA 300 EDTU climate chamber (Aralab, Rio de Mouro, Portugal) for 960 h, at 80°C and 60% RH (relative humidity).

2.2. Consolidation Materials

Two different alkoxysilanes were used in this study: 3-aminopropyl(diethoxy)methylsilane (APDEMS, 97%, $M_w = 191.34$) obtained from Sigma-Aldrich (St. Louis, MO, USA) and n-octyltrimethoxysilane (OTMS, >97%, $M_w = 234.41$) from Alfa Aesar (Ward Hill, MA, USA). The alkoxysilanes were handled using a syringe and personal protective equipment. For the traditional consolidation treatment, a spray bottle from Derwent (ACCO Europe Ltd., Cumberland Pencils, Workington, United Kingdom) was used, and the solvent acquired for the binary mixture was hexamethyldisiloxane (HMDSO, $\geq 98\%$, $M_w = 162.38$) from Sigma-Aldrich.

To analyse the consolidants, three different films were prepared on glass slides with APDEMS, OTMS, and the mixture of both in equal proportions (50% *v/v* each) and undiluted. The glass slides were covered with aluminium foil and left in a continuous extraction hood for one month at 21°C and 59% RH. The OTMS remained liquid and APDEMS, by contrast, solidified. According to Daher et al. [14], this change may be related to the reactivity of the amine group in the APDEMS side chain to ambient water vapour, which induces the polymerisation of APDEMS through hydrolysis and condensation reactions. Furthermore, characterisation may only be carried out after one month when the polycondensation reaction of the two alkoxysilanes, leading to the formation of the polymeric network, may be considered complete.

2.3. Consolidation Methodology

To validate whether the scCO₂ consolidation methodology was an effective alternative able to minimise potential damage from traditional consolidation techniques (material loss and foam disintegration), a comparative study was conducted. Spraying was chosen among traditional techniques due to its minimal contact with the sample. Nebulisation and immersion were discarded as these methods require larger quantities of a toxic solvent (HMDSO). Initial tests with scCO₂ were performed on unaged and aged ester-based PUR foams to assess the suitability and define potential conditions to further explore consolidation treatments. As no changes to the treated foams were detected, experiments on the solubility of the alkoxysilanes in scCO₂ were also conducted, confirming its high solubility. Therefore, the study proceeded to test the ability of scCO₂ to be a solvent and carrier in the consolidation of degraded ester-based PUR foams with the binary mixture of alkoxysilanes.

Characterisation of the PUR was performed on untreated samples and again after one month of the consolidation trials. Changes in the samples' visual appearance were evaluated by full-scale images and high-resolution images of the PUR cell structure, and weight changes were monitored. The mechanical assessment was evaluated qualitatively by touching the samples and observing their flexibility and stickiness. Chemical changes were also monitored—at the top surface and inner layers down to half the thickness of the foam—by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS).

2.3.1. Spray Consolidation (Traditional Method)

A solution of the consolidant (mixture of APDEMS and OTMS) in HMDSO solvent was prepared in a concentration of 10% *v/v*, following the instructions mentioned in Chaumat et al. [8]. The proportion of consolidant used was 50% *v/v* of each alkoxysilane to optimise both mechanical consolidation and hydrophobic properties. For each sample, 5 mL of the mixture was prepared and applied at a distance of approximately 10 cm between the spray nozzle and the sample surface: at 90° with the sample positioned on top of support to cover the four lateral surfaces; and at 45° creating diagonals, from the upper left corner to the lower right corner and from the upper right corner to the lower left corner, with sample rotation to evenly cover the upper surface of the sample. The methodology was repeated until the spray bottle with the prepared 5 mL mixture was empty.

Straight after treatment, the samples were covered with aluminium foil and left in a continuous extraction hood at 21 °C and 59% RH for one month before post-treatment characterisation. The samples were later placed in an aluminium foil inside a polypropylene box covered with black cardboard.

2.3.2. Supercritical CO₂-Assisted Consolidation

Supercritical CO₂ trials were performed in a high-pressure laboratory scale apparatus. The experiments were performed in a stainless-steel cell with a 33 mL capacity. Two samples were placed inside the cell above a stainless-steel net and closed with two sapphire windows enabling visual access to the samples during the procedure. The cell was immersed horizontally in a see-through thermostatic water bath pre-heated to 40 °C and the system was pressurised by a BlueShadow Pump 40P (Knauer, Berlin, Germany) with fresh CO₂ (99.998% purity from Air Liquide, Paris, France) until the desired pressure was reached in the cell.

Consolidation trials were performed at a temperature of 40 °C and pressure of 25 MPa in static mode for the experimental time of 60 min at constant *p* and *T* conditions. The consolidants were inserted into the cell with a syringe in equal amounts (2.5 mL of APDEMS and OTMS) without any other solvent. Air was removed from the cell with a CO₂ flow. At the end of each experiment, the cell was manually depressurised for approximately 30 s.

Treated samples were stored at 21 °C and 59% RH for one month before post-treatment characterisation.

2.4. Characterisation

Full-scale images were acquired using a 12 MP ultra-wide camera with Phase Detection Auto Focus (PDAF), aperture size of F/2.2, 13 mm of focal length, sensor size of 1/2.55" and 1.4 µm pixel size.

Weight measurements (g) were obtained using a Sartorius CP225D Semi-Micro Balance (Goettingen, Germany), with internal calibration, capacity of 220 g, readability of 0.00001 g, and linearity of 0.0002 g. Three independent measurements were performed per sample, and average and standard deviations were calculated.

ATR-FTIR spectroscopy was performed using an Agilent Handheld 4300 (Agilent, Santa Clara, CA, USA) equipped with a ZnSe beam splitter, a Michelson interferometer, and a thermoelectrically cooled DTGS detector coupled to a diamond ATR sample interface. The spectra were acquired between 4000 and 650 cm^{−1}, with a resolution of 8 cm^{−1} and 32 scans, and OriginPro 8 software (OriginLab Corporation, Northampton, MA, USA) was used for spectral interpretation. All spectra are presented as acquired, without baseline corrections or other processing.

Samples for SEM-EDS were placed on an Al stub using double-sided carbon tape and sputter-coated with a thin Au/Pd film in a Quorum Technologies coater, model Q150T ES (Lewes, UK). They were then analysed in a ThermoScientific desktop scanning electron microscope (SEM), model Phenom ProX G6 (Paralab, Linda-a-Velha, Portugal), with a CsB6 filament and equipped with a light elements energy dispersive spectroscopy (EDS) detector. High-resolution images were acquired in electron optical imaging mode with a

magnification range of 160–350,000 $\times$ and a secondary electron detector enabled for live mixing with backscattered electrons and an acceleration voltage of 10 kV. SEM-EDS data were acquired in electron optical imaging mode with a magnification range of 160–350,000 $\times$ and a Silicon Drift Detector (SDD). An ultra-thin silicon nitride (Si_3N_4) window was selected allowing the detection of elements B to Cf with an energy resolution $\text{Mn K}\alpha \leq 132$ eV.

3. Results and Discussion

3.1. Ester-Based PUR Foam, and APDEMS and OTMS Mixture References: ATR-FTIR Characterisation

Figure 1 shows the ATR-FTIR spectrum of the reference sample (degraded foam) with a typical ester-based PUR foam spectral profile: C=O stretching vibration from the ester group at 1728 cm^{-1} ; C=O stretching from the urethane group at 1643 cm^{-1} with strong hydrogen-bonding interactions; and C–O–C stretching from the ester and urethane groups, at 1174 and 1066 cm^{-1} [4,7,45]. The N–H stretching from the PUR hard segment is attributed to the region between 3500 – 3200 cm^{-1} , therefore, the band at 3300 cm^{-1} was assigned to the hydrogen-bonded N–H groups [46,47]. Furthermore, the information provided by the manufacturer about the chemical nature of the foam declares it was formulated with aromatic isocyanates. Thus, the presence of the absorption bands at 1598 cm^{-1} , assigned to C=C stretching, and at 886 , 815 , and 756 cm^{-1} , attributed to C–H wagging, confirmed the presence of aromatic structures associated with the isocyanate [4,7].

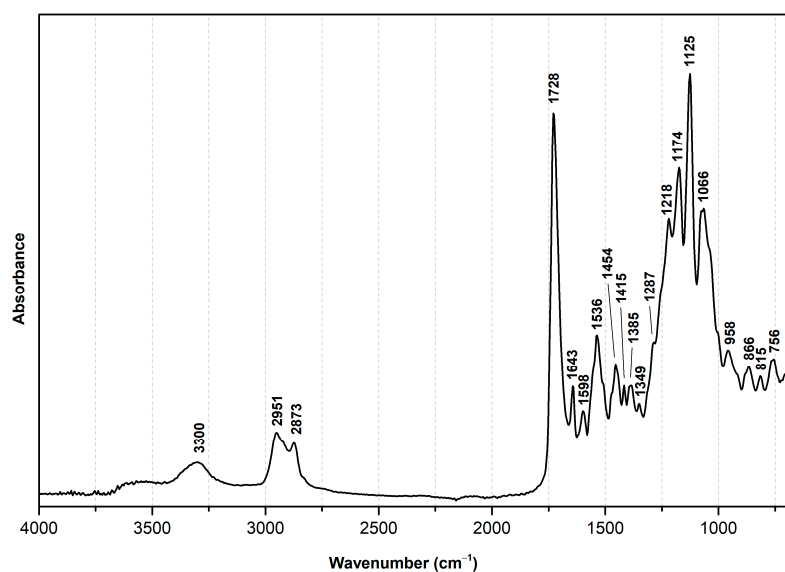


Figure 1. ATR-FTIR absorbance spectrum of the degraded ester-based PUR foam used as reference.

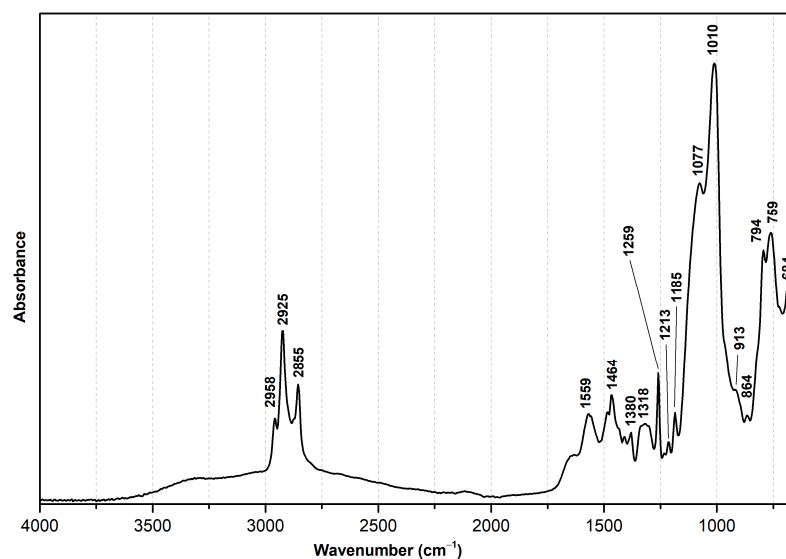
Table 1 summarises the infrared assignments of the reference sample for the main molecular vibrations and the remaining vibrations not mentioned in the text.

Figure 2 shows an ATR-FTIR spectrum of the alkoxysilane binary mixture (APDEMS and OTMS) with the characteristic bands identified: Si–O rocking (with methyl bonding interactions) at 2885 cm^{-1} ; Si–CH₃ stretching from APDEMS at 1259 cm^{-1} ; Si–R stretching from OTMS and APDEMS at 1213 and 1185 cm^{-1} , respectively; Si–O stretching at 1077 cm^{-1} is attributed to the bonding interactions with methyl and ethyl groups (alkoxysilyl groups); and siloxane single bond-stretching vibrations (Si–O–Si) at 1010 cm^{-1} assigned to the condensation of alkoxysilyl groups [14,48–50]. Table 2 summarises the molecular vibrations in the infrared that were identified for the alkoxysilanes mixture.

Table 1. ATR-FTIR assignment of the degraded ester-based PUR foam reference.

Wavenumber (cm ⁻¹)	Assignment [4,7,45–47] ¹
3300	ν (N-H), H-
2951	ν_{as} (C-H ₂)
2873	ν_s (C-H ₂)
1728	ν (C=O), ester
1643	ν (C=O), urethane (strong H-)
1598	ν (C=C), aromatic ring
1536	δ (N-H) and ν (C-N), urethane
1454, 1415, 1349	δ (C-H ₂)
1385	ω (C-H ₂)
1287	ν (C-N)
1218	ν (C-N) and δ (N-H)
1174	ν (C-O-C), ester
1125	ν (O-CH ₂)
1066	ν (C-O-C), urethane
958	δ (C-H ₂)
866, 815, 756	ω (C-H), aromatic ring

¹ ν = stretching, ν_{as} = asymmetric stretching, ν_s = symmetric stretching, δ = bending, ω = wagging.

**Figure 2.** ATR-FTIR absorbance spectrum of the alkoxysilane binary mixture (APDEMS and OTMS).**Table 2.** ATR-FTIR band assignments for the APDEMS and OTMS binary mixture.

Wavenumber (cm ⁻¹)	Assignment [14,48–50] ¹
2958, 2925	ν (C-H)
2855	ρ (Si-O), CH ₃ -
1559	δ (N-H)
1464	δ (C-H ₂)
1380	ω (C-H ₂)
1318	ν (C-N), masked
1259	ν (Si-CH ₃), APDEMS
1213	ν (Si-R), OTMS
1185	ν (Si-R), APDEMS; ρ (Si-O), CH ₃ -
1077	ν (Si-O), CH ₃ -CH ₂ -; ν (Si-O), CH ₃ -
1010	ν_{as} (Si-O-Si), polymer
913	ν (Si-OH)
910–665	ω (N-H ₂)
864	δ (Si-CH ₃)

¹ ν = stretching, ν_{as} = asymmetric stretching, δ = bending, ω = wagging, ρ = rocking.

3.2. Supercritical CO₂-Assisted Consolidation of Ester-Based PUR Foams with APDEMS and OTMS

In the following sections, the results obtained with this green alternative consolidation methodology will be presented, comparing the visual appearance of the samples, the tactile properties and weight changes, and the data obtained from the ATR-FTIR and SEM-EDS analyses.

3.2.1. Visual, Tactile Properties, and Weight Changes

Immediately after the high-pressure consolidation treatment, the samples appeared oily and shiny. This was an expected feature compared to observations by Daher et al. [14]. Alkoxysilanes have a thin oily consistency, which facilitates their penetration into the foam pores. Pellizzi et al. [16] and Daher et al. [14] mention the importance of the amine function for the interaction of the treatment with the degraded foam and the trifunctional alkoxysilane for the polymer network formation.

Samples were similar in appearance before and after scCO₂-assisted consolidation, as shown in Figure 3. The slight colour difference observed between the images resulted from minimal variations in ambient luminosity. There was no swelling or shrinkage and no change in colour and gloss. In the pre-treatment characterisation, it was observed that samples were yellow/orange, fragile, and very sticky due to the artificial ageing. Another characteristic identified when assessing the tactile properties was the low flexibility compared to unaged samples. After the scCO₂-assisted consolidation, samples became less sticky, and the foam flexibility increased significantly. Samples felt more cohesive and denser.

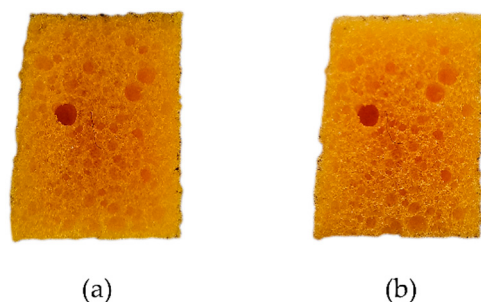


Figure 3. Ester-based PUR sample (a) before and (b) after scCO₂-assisted consolidation (measuring approximately 15 mm × 10 mm × 10 mm). No differences were detected after treatment.

Weight measurements were carried out and, on average, samples consolidated via scCO₂ increased their weight by 0.02 g (corresponding to an average uptake of 16%), which may indicate the presence of the consolidant.

3.2.2. ATR-FTIR Analysis

Analyses were performed both on the top and inner layers of the treated samples. Data processing revealed that all treated samples had similar chemical profiles, even when acquired at the top surface or inner layers. A representative spectrum of a sample consolidated via scCO₂ was selected and is shown in Figure 4 (black solid line).

Compared to the foam control sample (dashed grey line), the treated samples exhibit significant changes in their spectra. Examination of the representative spectrum of a consolidated sample (Figure 4, black solid line) shows similarities to spectra of the alkoxysilanes mixture prepared in the glass slides, suggesting that foams underwent consolidation successfully when treated. The region from 1300 to 900 cm^{−1} presents the most significant changes in the spectrum profile, which corresponds to the binary mixture's most characteristic bands. From the inset in Figure 4, it is possible to identify the presence of three characteristic bands of the alkoxysilanes mixture: Si-CH₃ and Si-R stretching vibrations from APDEMS at 1259 cm^{−1} and 1185 cm^{−1}, respectively; and Si-O-Si stretching at

1010 cm^{-1} , confirming that condensation between alkoxysilyl groups has occurred. The Si-R stretching vibration from OTMS may also be present at 1213 cm^{-1} , but it is likely to be masked by the C-N stretching vibration from the PUR foam at 1218 cm^{-1} .

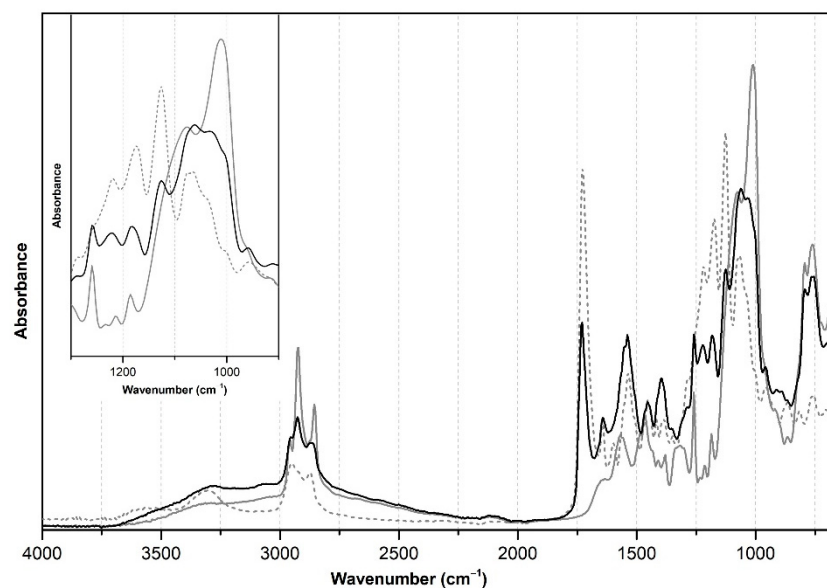


Figure 4. ATR-FTIR spectra of the degraded ester-based PUR foam surface (dashed grey line); APDEMS/OTMS reference film (grey solid line); and scCO_2 -assisted consolidated foam (black solid line). Inset: Detail of the region from 1300 to 900 cm^{-1} .

3.2.3. SEM Imaging and SEM-EDS Analysis

To confirm the foams' consolidation, SEM-EDS analyses were performed on the top surfaces and inner layers of each treated sample.

In Figure 5, two samples are displayed: a degraded reference sample (a) and a representative sample treated using scCO_2 -assisted consolidation (b). Comparing the cell surface of both samples, the non-consolidated sample exhibits a smooth and uniform surface with a collapsed and weakened structure, whilst the treated sample reveals a clearly distinct topography and a reinforced structure. A more textured surface is identified as well as a film deposited on the foam's surface and surrounding the cell struts while the cell window remains open.

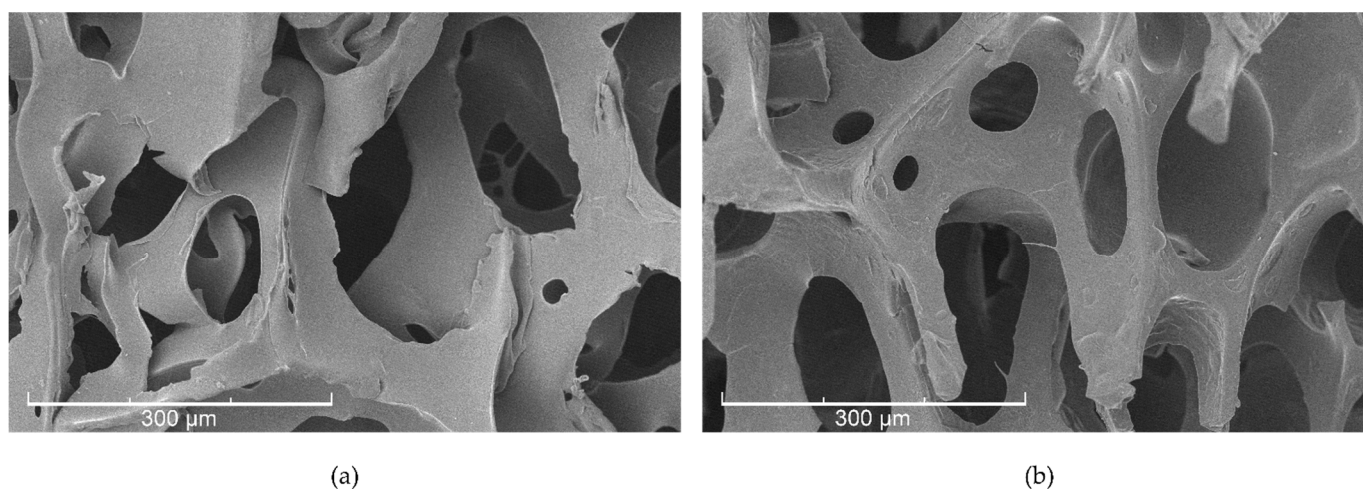


Figure 5. SEM images of (a) a weakened cell structure of a degraded ester-based PUR foam without consolidation and (b) a reinforced cell structure after scCO_2 -assisted consolidation at a magnification of 400 $\times$.

SEM-EDS analyses corroborate the previous ATR-FTIR results. An illustrative spectrum is shown in Figure 6a, with three intense peaks for carbon (C), oxygen (O), and silicon (Si). C and O are present as structural elements of ester-based PUR foams, whilst the prominent peak of Si identifies the presence of alkoxysilanes (Figure 6a,b). Although no mapping was performed, Si was detected in every sample, in multiple areas and at different depths (Figure 7), which suggests the consolidation of the foams as no silicon was detected on the untreated samples.

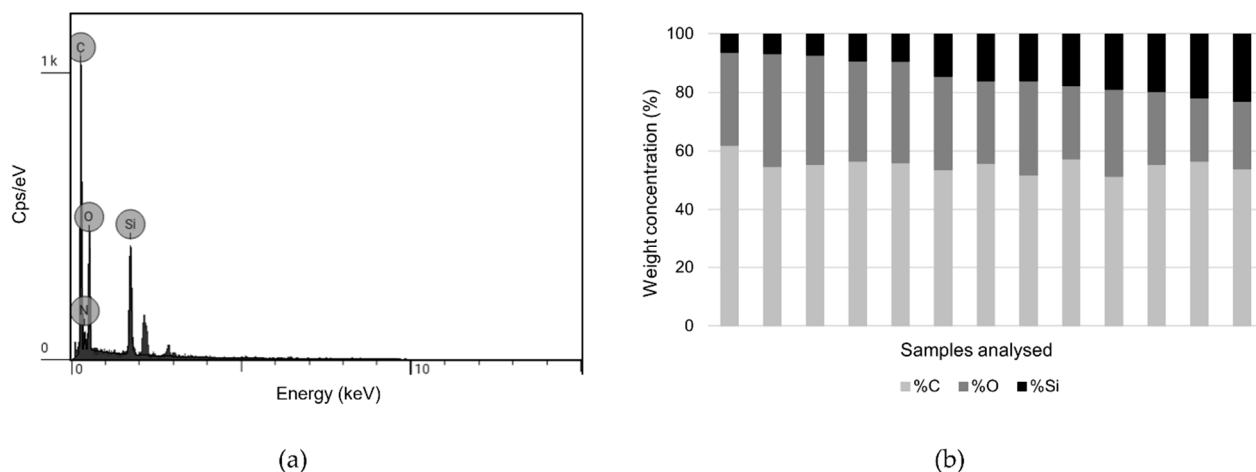


Figure 6. (a) SEM-EDS spectrum of the scCO₂-assisted consolidated foam. Concentration by weight: 55.9% of carbon (C), 28.1% of oxygen (O), and 16.0% of silicon (Si)—22,368 counts in 22 s (978 c/s). (b) Graph exhibiting the weight concentrations of the elements present in all samples analysed by SEM-EDS: light grey represents carbon (% C), dark grey represents oxygen (% O), and black represents silicon (% Si).

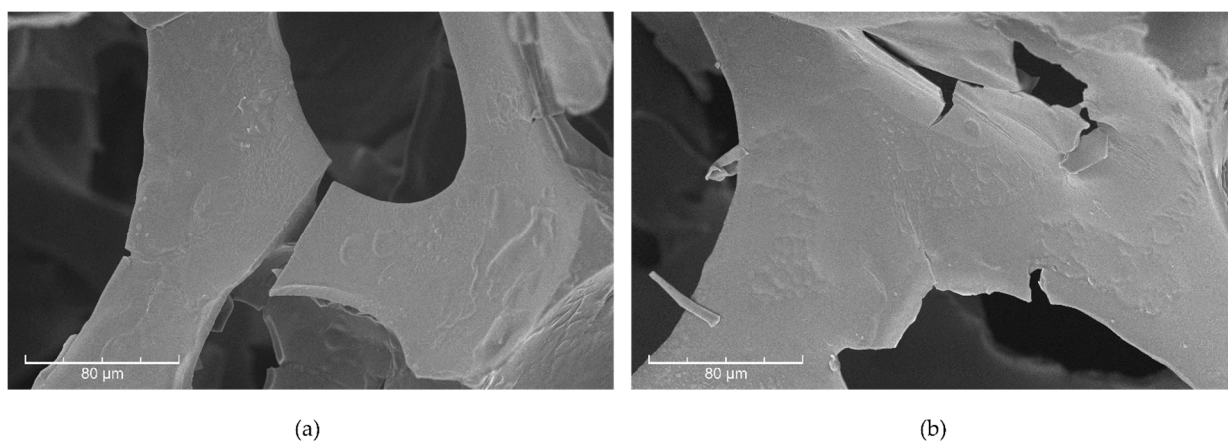


Figure 7. SEM images of (a) the top surface and (b) the inner layer of the scCO₂-assisted consolidated foam (both images at a magnification of 1650×).

To assess the consistency of the data, the dispersion of Si weight concentration (wt%) in the scCO₂-assisted consolidated samples was investigated (Figure 6b). It should be noted that this information represents relative data, as EDS does not detect all elements present in the foam-consolidant system. Comparing the samples' changes in weight with the Si wt%, it was noticed that the samples that changed the most correspond to the samples with the highest Si wt%.

Since the data tend towards a linear distribution, it is assumed the representativeness of the statistical calculation of the average and standard deviation of Si wt% to be 16% and 6%, respectively. Although Si was systematically identified in all consolidated samples, the

standard deviation value highlights the inhomogeneous distribution of the consolidant in the samples. This phenomenon may be related to the silane's greater affinity to bond with degradation products such as carboxyl groups [14], suggesting that the consolidant distribution may depend on the foam's degradation profile.

In addition to being a more sustainable alternative, this methodology also allows for an effective in-depth consolidation of the foams without the need for sample manipulation during treatment.

3.3. Supercritical CO₂-Assisted Consolidation vs. Spray Consolidation

Spray-consolidated samples had an oily appearance immediately after the treatment, as did samples treated via scCO₂. Within one month, spray-consolidated samples also showed the same pre-treatment appearance, namely, no visible swelling/shrinkage and no colour or gloss alteration. In contrast to the previous set, the spray-consolidated samples maintained their fragile and sticky appearance. In addition, no improvement in the foams' flexibility could be detected by touch. Even so, there was a low weight increase, which may indicate the presence of the consolidant. On average, these samples increased their weight by 0.007 g (corresponding to an average uptake of 5%, contrasting to the 16% uptake of scCO₂-consolidated samples).

ATR-FTIR and SEM-EDS analyses were also performed on the top surfaces and inner layers of each spray-treated sample. Contrary to expectation, ATR-FTIR did not detect the alkoxy-silanes binary mixture in any of the analysed samples. Figure 8 shows the spectra of the degraded PUR foam without consolidation, the APDEMS/OTMS film and the spray-consolidated foam (black solid line). The spectrum of the treated sample resembles the untreated foam. In addition, the characteristic region of the alkoxy-silanes mixture (from 1300 to 900 cm⁻¹) does not show significant changes as identified in the scCO₂-assisted consolidation (Figure 4).

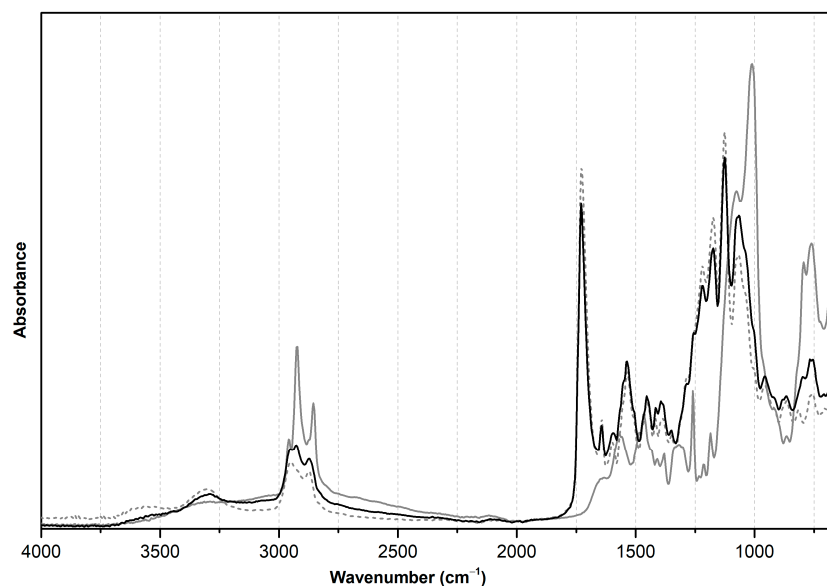


Figure 8. ATR-FTIR absorbance spectra of degraded, ester-based PUR foam (dashed grey line); APDEMS/OTMS reference film (grey solid line); and spray-consolidated foam (black solid line).

Unlike the foams treated via scCO₂, a film was not found on all samples consolidated by spraying (Figure 9a). On further examination, where visible, films appeared to be randomly deposited rather than continuous and cohesive. Also, they imparted rougher and more uneven appearances than those treated by scCO₂, as illustrated in Figure 9b.

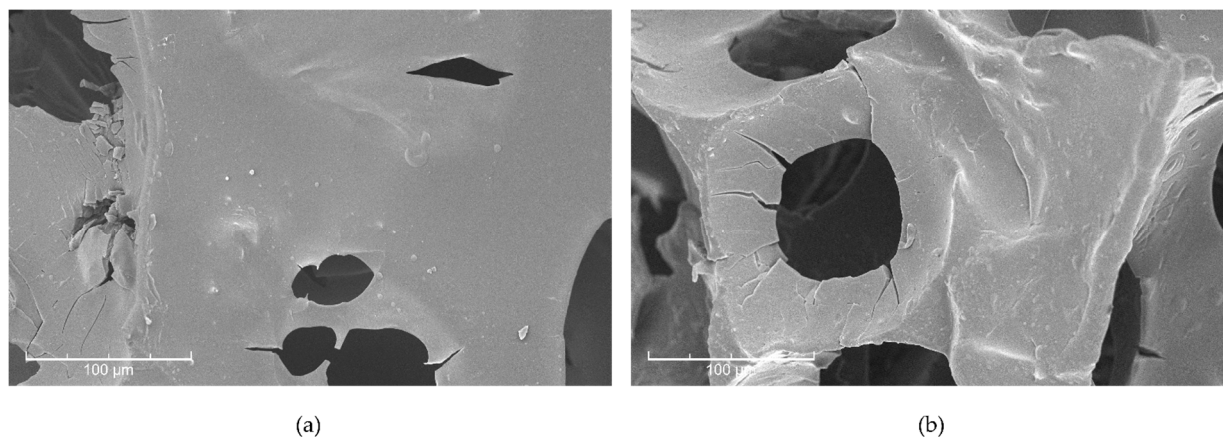


Figure 9. SEM images of (a) a spray-treated sample where no consolidant was detected and (b) where the consolidant has been detected (both images at a magnification of 1450 $\times$).

Only examination by SEM-EDS confirmed the presence of the consolidant in the areas where the film was visible.

As in the scCO_2 -consolidated set, the elemental composition identified in the Si-containing samples also had C and O. Figure 10a shows a spectrum of a spray-consolidated sample containing Si; however, the Si peak is not as intense as those of scCO_2 -assisted consolidation.

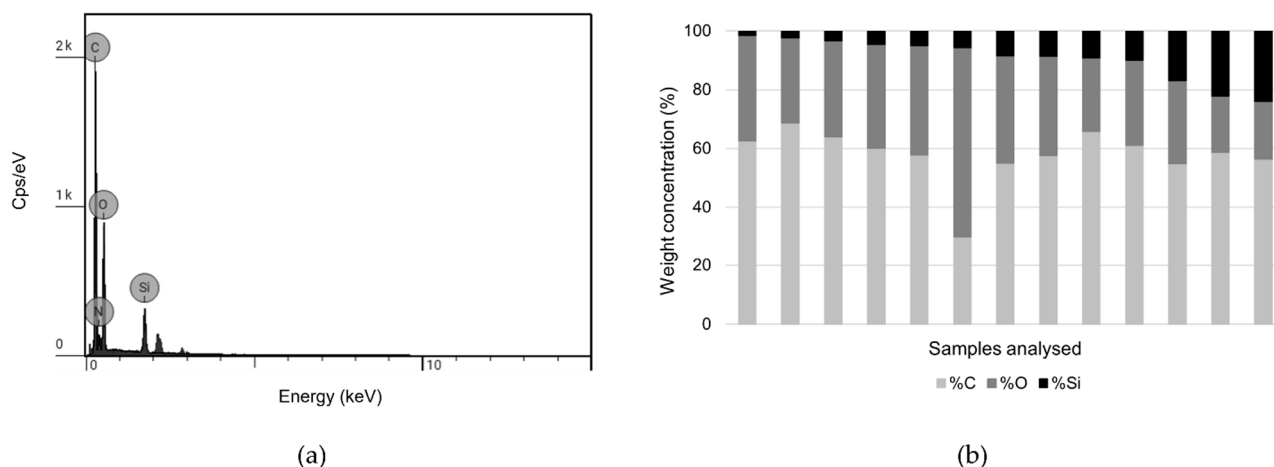


Figure 10. (a) SEM-EDS spectrum of the spray-consolidated sample. Concentration by weight: 55.0% of carbon (C), 36.6% of oxygen (O), and 8.4% of silicon (Si)—29,796 counts in 22 s (1305 c/s). (b) Graph exhibiting the weight concentrations of the elements present in some samples analysed by SEM-EDS: light grey represents carbon (% C), dark grey represents oxygen (% O), and black represents silicon (% Si).

As for the Si wt% in the spray-treated samples, it was not possible to calculate its “real dispersion” (considering that these values are relative data). The presence of Si in these samples was not consistent, thus only the partial distribution is presented (distribution of Si wt% in the samples where Si was detected). The Si wt% partial average and standard deviation of the spray-consolidated samples are 8% and 7%, respectively. From Figure 10b, it is seen that Si wt% is mainly lower than that recorded in the scCO_2 -treated samples. In addition, from the SEM images, it is noticeable that the deposition of the consolidant is not only inhomogeneous but also non-systematic, corroborating the absence of Si in several areas of the analysed samples. This inhomogeneity is also shown by the last three bars in Figure 10b, with greater Si wt%. These values are inconsistent with the expected partial distribution, which may be related to the spray methodology. Considering that the

spray consolidation process is manual, reproducing the treatment conditions in all samples presents a great challenge.

Comparing the two treatment applications, it is worth noting that scCO₂-assisted consolidation was significantly more effective than spray consolidation. Moreover, it has proven to be the safest methodology for both the user and the environment, not only during application but also in the preparation phase of the treatment. Assuming the long-term stability of the consolidant, the fact that scCO₂-assisted consolidation provides an in-depth treatment, reinforcing and protecting the degraded areas of the foam may also lead to a reduction in short-term consolidation treatments, making the conservation process more sustainable. With spray application, consolidation is inconsistent and mostly superficial, leaving degraded areas of the foam exposed. This not only fails to meet the needs of this type of foam but also requires treatment reapplication to ensure the preservation of the object, leading to the use of more reagents and prolonged exposure to these harmful products.

4. Conclusions

This study introduced the use of scCO₂ as a carrier and solvent of APDEMS/OTMS for the consolidation of ester-based PUR foams. The consolidation methodology investigated is safer for the user and the environment, and it has proven to also being safer for the foam as well as a more efficient alternative to spray application. scCO₂-assisted consolidation minimised the contact with the sample and restricted the use of harmful solvents, such as HMDSO, needed to solubilise the consolidant mixture for spray application or other traditional methods. Although neither spray nor scCO₂ methodologies resulted in visible changes in the treated samples, ATR-FTIR and SEM-EDS detected significant differences between the two methods. In samples treated via scCO₂, the effectiveness of the treatment was confirmed through ATR-FTIR by identifying characteristic bands of the APDEMS/OTMS mixture. SEM imaging and SEM-EDS analysis revealed reinforced and textured surfaces where Si was detected, confirming the presence of the consolidant in all samples, both at the top and inner layers of the foams. This indicates the successful solubilisation and diffusion of the consolidant in-depth by scCO₂, as intended. However, ATR-FTIR analysis was inconclusive in detecting the consolidant on the spray-treated samples. Additionally, SEM-EDS did not consistently detect the consolidant in the samples and, when identified, the Si weight concentration was lower than for samples treated using scCO₂. With scCO₂ consolidation treatments, an increase in weight was observed and significant improvement in the flexibility of the foam was achieved, suggesting interaction of the consolidant with the degraded foams.

To conclude, we should emphasize that our results confirmed that this green methodology is a promising and effective alternative to treating degraded ester-based PUR foams. As previously explained, the scCO₂-based-assisted consolidation uses a solvent that is readily available in nature and as an industrial by-product that can be recovered, recycled, and reused, being less harmful to the environment and users. Furthermore, not only has it successfully improved the condition of degraded foams, it also has the potential to make the whole process a more sustainable conservation treatment. Spray application, a common consolidation method, tends to be superficial with periodic reapplications being required, leading to greater consumption and longer exposure times to harmful products. Given that the scCO₂ technology allowed for a more consistent and deeper consolidant application, this positions the treatment as a more sustainable choice once it better protects the foam, working also as a preventive conservation measure and minimising the need for future re-consolidation.

Further work is being carried out within the doctoral project “PURscCO₂: scCO₂-assisted consolidation of PUR foams with an alkoxysilane mixture” to optimise the methodology, further understand the mechanisms involved, and assess its long-term sustainability (safety and efficacy) so that it may be applied to a real museum object.

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