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A new bio-based organogel for the removal of wax coating from indoor bronze surfaces

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Abstract
In this research, we propose an advanced system for the cleaning of wax-based coatings applied on indoor bronzes. To this aim we developed a new kind of eco-friendly gel based on PHB (poly-3-hydroxybutyrate) used as thickening agent, biodiesel (BD) and dimethyl carbonate (DMC). BD is a mixture of methyl esters obtained from palm oil, which acts as cleaning agent while DMC was added as additional solvent to partially solubilize PHB and forming a gelly phase. For the first time a PHB-based gel obtained by mixing two solvents with different proprieties was proposed, expanding the range of possible formulations, that can be used according to the specific restoration purpose. After the preliminary characterization of chemical and physical properties of the gel, an ad hoc analytical protocol was implemented to evaluate both the cleaning efficiency and the release of residues on the treated surfaces. Standard samples were prepared following ancient recipes and submitted to spectroscopic and chromatographic analysis before and after the cleaning procedures. Finally, the performances of PHB-DMC/BD gel were assessed on a real case of study presenting a wax-based coating: the Pulpito della passione attributed to Donatello and dated back to 1460. In situ analysis demonstrated the high cleaning efficiency of the proposed systems also for the removal of aged coatings.

Keywords: Green organogel, Polyhydroxyalkanoates, Indoor bronzes, Wax-based coatings

Introduction

The surface of indoor metal objects is a complex system characterized by the presence of inorganic products and organic coatings. Traditionally, at the end of the casting process, the bronzes were cleaned and the rough surface usually treated to obtain the desired surface finish [1–3]. To obtain a specific shade, the bronze surface can be treated with different chemical solutions, such as chlorides, nitrates and sulphates. Wax, lacquer, or varnish were applied to saturate the surface color and protect the patina and the metal surface from corrosion [4–6]. Among these different materials, natural wax - such as beeswax - is one of the mostly used coating for indoor bronzes, thanks to its properties such as low water vapor permeability and low gloss [7]. Waxes could also be applied as a maintenance treatment. Consequently, today one of the most common goals in the restoration of bronze objects is the removal of degraded wax-based coatings from objects.

Waxes are mainly composed of long chain aliphatic molecules containing 20–50 carbon atoms [8]. Usually non-polar solvents, such as dodecane, can be used to solubilize the wax [9]. Some alkaline compounds could also be used to remove the waxes from the surfaces, subsequently treated with weakly acidic solutions to neutralize their action. This application has been limited due to its aggressiveness for the artwork [10]. Additionally, traditional cleaning methods were based on the application of neat solvents. This cleaning approach may induce drawbacks mainly owing to the unrestricted action of the solvent, which leads to its penetration into porous matrices, producing undesired phenomena [11–14].

In the last decade, chemical and physical gels used for the removal of aged varnishes or coatings from artwork

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surfaces have gained considerable popularity. The main reason is the gel's ability to retain solvents and provide a controlled and efficient superficial cleaning action [9, 15–18].

For the cleaning of metal objects, different type of thickeners and confining systems (such as micellar solutions or microemulsions) were reported [19]. Recently, a new poly(vinyl)alcohol-based film has been proposed for the removal of corrosion products from historical bronzes [19]. Conversely, limited attention has been devoted to the impact that such cleaning systems might have on environmental and human safety.

To introduce powerful and sustainable alternatives for cleaning artworks, we have recently proposed new biocompatible cleaning systems for paintings based on the use of fully green components [20, 21]. In particular, in the previous researches we have demonstrated the efficiency of poly-3-hydroxybutyrate (PHB)-based gels with γ-valerolactone (GVL) as solvent, for the removal of terpenic and synthetic varnishes from oil and water sensitive egg tempera paintings [20, 21].

In the present research, bio-based components were selected to produce new organogels able to solubilize old wax coatings from indoor bronzes with a controlled action. To this aim, PHB was used as thickening agent and mixed with biodiesel (BD) and dimethyl carbonate (DMC). PHB can be obtained from bacteria through aerobic conversion of various carbon sources, and it is characterized by thermal and mechanical properties comparable to synthetically-produced degradable polyesters and similar to polypropylene (PP) [22]. PHB-based gels can be obtained by heating the polymer in an appropriate solvent and then cooled [20]. Therefore, the solvent used must be able to solubilize the polymer and at the same time must allow the formation of the crystalline phase which holds the structure of the gel together. However, PHB is a highly crystalline polymer, whose solubilization can be guaranteed by just a few green solvents, among which there are different polar molecules [20].

Biodiesel is a mixture of alkyl esters with long chain fatty acids, biodegradable and produced by renewable sources [23]. BD proved its ability in the removal of wax coating, making it a perfect candidate to produce a gel system active against non-polar coatings. However, PHB was completely insoluble in BD, and for this reason it was not possible to obtain a gel using these two components.

To overcome this drawback, new solvents mixtures were evaluated, with the aim of expanding the range of possible formulations that can be used, and possibly allowing the ability to tune the hydrophobic/hydrophilic character of the obtained gels for tailored applications.

To this aim, DMC was selected as additional solvent because it is soluble in BD and previous works have demonstrated that it is able to solubilize PHB at 70–90 °C and to form a gelly phase when cooled down to room temperature. Furthermore, DMC also has the advantage of being the same solvent used for the extraction and purification of the polymer from bacterial debris [24, 25]. DMC is characterized by a low toxicity, it is fully biodegradable and not classified as volatile organic compound (VOC) (EPA). In addition, DMC has a high vapor pressure (7.57 kPa at 25 °C), that guarantees a lower residual amount on the treated surface.

The ability of the triplet DMC, BD and PHB to provide gel was thus assessed and its performances were evaluated on standard samples and on the indoor bronze surfaces of the *Pulpito della passione* (1460 A.C.) attributed to Donatello to validate this innovative cleaning system.

Materials and methods

Dimethyl carbonate (DMC), poly-hydroxybutyrate (PHB) and cyclohexane were purchased from Sigma-Aldrich. Biodiesel (BD) from palm oil was purchased from Novaol, Ravenna (IT). All the chemical reagents were commercially available and directly used without treatment.

Gels synthesis and characterization

The green gel was synthesized by solubilizing polyhydroxybutyrate (PHB) into mixtures of dimethyl carbonate (DMC) and biodiesel (BD), in a closed vial, by stirring at 110 °C for 5 min, then cooled until room temperature in a Petri dish. Two formulations of gel were prepared with same procedure and further discussed in the present work (Table 1).

Oscillatory shear measurements were carried out on a Paar Physica UDS200 rheometer working at 25 °C (±0.1 °C Peltier temperature control system) using plate-plate geometry (25 mm diameter). Frequency sweep measurements were carried out at 5% strain. The storage and loss moduli (G' and G", respectively) and complex viscosity were measured over the frequency range 0.1 to 100 Hz. WAXS were carried out at room temperature with a PANalytical X'Pert PRO diffractometer equipped with an X'Celerator detector (for ultrafast data collection). A Cu anode was used as X-ray source (K radiation: $\lambda = 0.15418$ nm, 40 kV, 40 mA), and ¼° divergence slit was used to collect the data in 2θ range from 2° to 60°. Micrographs of dried gels were taken with a Scanning Electron Microscope (SEM) ZEISS EVO 50 EP in Environmental mode with ≈100 Pa pressure

Table 1 Composition of the gel formulations

Gel	PHB mg	DMC mL	Biodiesel mL
PHB-DMC/BD(3:1)	400	3	1
PHB-DMC/BD(1:1)	400	2	2

in the chamber. The capacity of the gel network to retain the solvent and thus reduce the evaporation rate, was evaluated by thermogravimetric analysis (TGA) using a TA Instruments STD-600 apparatus. Analyses on gels (about 25 mg) and neat solvents (sample weight about 25 mg) were performed under nitrogen flow. An isothermal run at 40 °C for 90 min was selected as the one most like the exposition condition of the restorer during cleaning practice. Rheological and thermogravimetric measurements were performed on a set of 3 replicates for each type of gel system studied and the trend show no significant differences.

Standard samples and real case studies

Standard bronze samples have been prepared by the restorers of Opificio delle Pietre Dure (Florence), following ancient recipes. In more detail, the metal surface of a fresh cast bronze has been brushed with silver nitrate solution and heated with blue flame, until the surface turn to black. Then, a thin layer of beeswax was applied under soft flame.

Copper sheets were also used for the evaluation of the cleaning approach. Copper sheets were prepared by applying a thin layer of beeswax with soft brush after oxidation of the surface with flame.

Finally, the Pulpito della Passione (1460 A.C.) exhibited in the church of Basilica di Lorenzo and attributed to Donatello was submitted to the green gel cleaning procedure for the removal of an aged wax-based coating.

Cleaning procedures

The gel was sandwiched between two sheets of rice paper and left from 5 min to 15 min (according to the thickness of the layer to be removed) in contact with the sample surface. A light pressure guarantees a good adhesion of the gel to the surface to be treated. Rice paper is used to avoid the risk of PHB residues on the treated surfaces and to further control the release (and evaporation) of the solvents, without compromising the adhesion of the gel even on curved or vertical surfaces. Then the gel was removed, and the surface cleaned with neat DMC and dry cotton swabs. The neat solvent has been used for cleaning with cotton swabs. In more detail, the cotton is soaked in biodiesel and applied to the surface to be treated with a slight mechanical action for a minute. Then, a cotton swab soaked with dimethyl carbonate has been used to remove the residues of biodiesel for a few seconds.

Evaluation of the cleaning performances

An ad-hoc analytical protocol was set up for the evaluation of the gel cleaning performances in terms of: cleaning efficiency and presence of solvent residues after the treatment. Non-invasive and micro-destructive investigations were carried out on metal surfaces before and after the treatments.

To evaluate the presence of wax residues after the cleaning, an Infrared Microscope Thermo Scientific Nicolet iN10MX was used in total reflection mode to record spectra in the range between 675 and 4000 cm^{-1}, with a spectral resolution of 4 cm^{-1} and an optical aperture of 150×150 µm. To obtain representative data, spectroscopic analysis was performed on 3 different areas treated with the same cleaning procedure and 4 spectra were recorded before and after treatment.

Dino-Lite Premier2 digital microscope type AD4113T-I2 V with ×40 magnification was used to record the morphological changes of the treated surfaces.

The presence of solvent on treated surfaces was characterised by FTIR microscope in total reflection mode for qualitative characterization and by gas chromatography mass spectrometry (5977 Agilent GC–MS) for quantification. In this case, 1 cm^2 of copper sheets were treated with both gel and neat biodiesel and then extracted with cyclohexane (10 mL) under sonication for 20 min. The cyclohexane is commonly used for analysing and synthesising fatty acid methyl esters (main biodiesel constituents) by GC-MS. Thus, cyclohexane has been selected as a suitable solvent and its ability to solubilize biodiesel has been tested before the analysis. The GC-MS analyses of cyclohexane were performed using an Agilent HP 6850 gas chromatograph connected to an Agilent HP 5975 quadrupole mass spectrometer. The injection port temperature was 280 °C. Analytes were separated on a HP-5 fused-silica capillary column (stationary phase poly(5% diphenyl/95% dimethyl)siloxane, 30 m, 0.25-mm i.d., 0.25-µm film thickness), with helium as the carrier gas (at constant pressure, 33 cm s^{-1} linear velocity at 200 °C). Mass spectra were recorded under electron ionization (70 eV) at a frequency of 1 scan s^{-1} within the 12–600 m/z range. The temperature of the column was increased from 50 to 180 °C at 50 °C min^{-1} and then from 180 to 300 °C at 5 °C min^{-1}. Methyl nonadecanoate (0.05 mL of a solution 1000 ppm) was used as internal standard for the quantitation, assuming a unitary response factor for all the methyl esters. Chromatographic analysis has been carried out on 3 sample replicas for each cleaning procedure.

Bruker Alpha portable FTIR spectrometer was applied to monitoring the cleaning procedure on the real case of study, with reflectance mode sampling and spectral range 400–7000 cm^{-1}. The instrument has a measurement spot of 6 mm in diameter and working distance of approximately 15 mm. 256 scans were acquired for each spectrum at a resolution of 4 cm^{-1}.

Results and discussion

Gel formulation and characterization

In order to assess the ability of a mixed solvent system such as DMC/BD to produce a gel in the presence of PHB, two gel formulations, obtained by varying the ratio between solvents (DMC: BD, Table 1), were produced. Preliminary tests showed that BD can dissolve wax, while DMC is used mainly as a tool to promote gel formation and does not seem to contribute to the cleaning. Both the gels were thickened at the end of the procedure, leading to a gel with a whitish, opaque aspect (Fig. 1). In both cases the polymer was able to swell up roughly 10 times its starting dry weight (400 mg PHB vs. 4 ml solvent mixture) demonstrating an interesting attitude in acting as solvent carrier to be used for conservation purposes. Both gels were characterized to select the most suitable as cleaning system. Indeed, materials suitable for the cleaning procedures should be easy to be handle and to be removed from the artwork surface, and they should guarantee an adequate stability over time. Hence, microstructure, rheological behaviour and thermal properties were characterized to evaluate the gel performance and stability.

The mechanical properties of the two gels were investigated via rheological measurements. Figure 2a shows the complex viscosity as a function of the applied shear rate. For both samples, a decrease in complex viscosity was observed with increasing frequency. However, the gel containing a higher amount of DMC (DMC/BD 3:1) display a viscosity which is higher by an order of magnitude if compared with the DMC/BD 1:1 gel. This means that the gel is more rigid than the previous formulation and that the simple modification of the solvent system hardly impacts the system properties. Both samples displayed also a high storage modulus (Fig. 2b), indicating good mechanical proprieties in terms of gel stiffness, allowing an easy handling and removal of the gel. The gels presented a gel-like behaviour and in all the cases storage modulus G’ was higher than that of the loss modulus G”. The storage modulus quantifies the elastic behaviour of the gels, while the loss modulus shows the dissipation ability of the polymer network. This feature proves the ability of DMC to form the gel, building a 3D network. The stiffness and rigidity are positively correlated with G’ and G”. The DMC/BD 3:1 gel has higher modulus than the DMC/BD 1:1, making the latter less stiff. Considering that PHB is insoluble in BD, the higher viscosity recorded for the gel with a higher DMC fraction might tentatively be attributed to a stronger ability to interact with the more akin solvent system, and such a stronger interaction would in turn hinder the polymer chain mobility. On the bases of this outcome, the DMC/BD 3:1- based gel seems the most suitable candidate for cleaning purposes, since stiffer formulations could be easier to peel off and leave a lower (up to none) extent of residues behind.

Organogels are stable as long as the solvent, or a fraction of it, does not evaporate. The DMC/BD 3:1-based gel showed a good stability over the time. Thus, the shelf

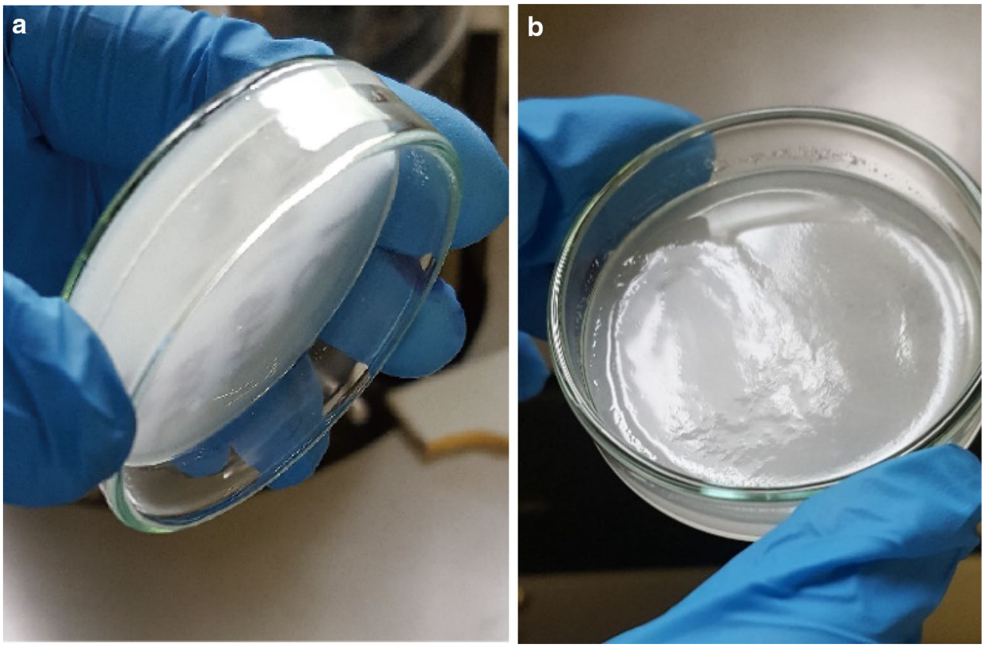

Fig. 1 The aspect of **a** PHB-BD/DMC (3:1) gel; **b** PHB-BD/DMC (1:1) gel

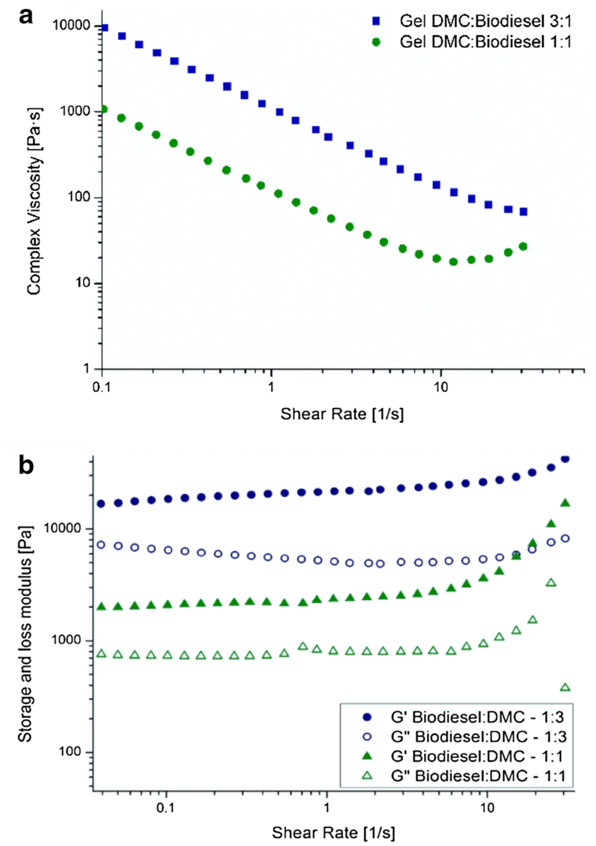

Fig. 2 Complex viscosity (**a**) and Storage and loss modulus (**b**) as a function of frequency for PHB-DMC/BD (3:1) gel (blue) and PHB-DMC/BD (1:1) gel (green)

life of the gels was estimated at a time interval of 2 weeks, keeping the gel closed between two Petri dishes in a laboratory environment. At that time the gel has unchanged mechanical properties and good cleaning efficiency. Furthermore, previous studies have demonstrated the possibility of recycling PHB after its use in gel formulations [20].

While the capacity of both mixtures of solvents for producing a gel-like structure was proved, the effect on the polymeric component was assessed in terms of ability to crystallize. Wide-angle X-ray scattering technique was used to evaluate the crystallinity of the gels under investigation. As shown in Fig. 3, black diffractogram is referred to the pristine PHB polymer, prior gelation, while spectra in Fig. 3a refer to the diffraction pattern of freshly prepared DMC/BD gels. Wet gel samples DMC/BD 3:1 and DMC/BD 1:1 diffractograms showed both the presence of narrow reflections typical of a crystalline phase besides the obvious amorphous halo expected for a wet sample, where the solvent is still most of the analysed volume. The comparison of such reflections with the pristine PHB powder spectrum revealed a good agreement of the 2θ positions, confirming once again, that the presence of a gel-like phase is strongly connected to the ability of the solvent system to allow polymer crystallization, without contemporary forcing its complete precipitation in a solid phase precipitate. Moreover, DMC/BD 3:1 wet gel (diffractogram b) seemed to be characterized by a broader amorphous halo. When gels are dried of the solvent system, the analysis of the PHB recovered still displayed reflections positioned accordingly with those of pure PHB. However, WAXS diffractograms recorded after the complete drying of the gels (Fig. 3b) showed a broad amorphous halo, suggesting that the polymer is not prone to re-crystallize again with a similar morphology like the pristine polymer, as observed in the presence of GVL, and previously recorded [20]. Such a hindering effect towards crystallization ability might be due to the sequential volatilization of the solvent that promotes a preliminary evaporation of the DMC, thus leaving the polymer in the presence of a non-solvent which not allow mobility and reorganization of the polymeric chains in a crystalline fashion. Additionally, the different solvent systems can affect the ability to recrystallize after liquid phase removal, and the presence of a smaller fraction of BD worsen the quality of the PHB crystals, as observed by the comparison of the shape and intensity of the diffractogram peaks.

SEM analysis, performed to characterise the microstructure of the gels, was carried out on dried samples. SEM images of PHB-DMC/BD gels with different DMC and BD ratio of 3:1 and 1:1 are shown in Fig. 4, after fracture. Both the systems display a compact irregular surface, with some morphology typical of plastic deformation. The gel DMC/BD 3:1 shows a finer structure with micro-indentations typical of a more homogeneous material. This behaviour well compares with the WAXS study previously discussed, that shows a more amorphous system for the dried DMC/BD 3:1 gel.

Once the structure and morphology of the proposed gels has been established, their ability to slow down solvent evaporation was evaluated. The solvent evaporation from gels was studied with TGA, in comparison to the pure solvent behavior, i.e. in conditions that rule out any possible thermal degradation contribution to the recorded material weight loss. This investigation should indeed provide proof of the ability of the gelled solvent to be retained within the polymer 3D network. In the applied conditions (90 isotherm at 40 °C) the weight loss can only be attributed to some solvent evaporation, which is mainly ascribed to DMC, since the biodiesel has a low volatility and high boiling point. The relative weight loss was calculated for each sample, referring to the sole liquid components. This is due to the reason that the polymer (PHB) will never volatilize in the applied conditions, and results are resumed in Table 2. Results are resumed in Table 2.

Results clearly show that the solvent is kept more effectively in the gels under the same measuring conditions (Fig. 5). The bars in green show the difference between the weight of DMC present in the pristine gel (discarding the PHB fraction) and the actual weight loss recorded during the thermogravimetric measurement, considering only the solvent fraction. The blue bars represent the difference between the weight of DMC in the sole solvent mixture and the total weight loss recorded during the application of the isotherm in TGA. The solvent retention within the gels is higher for every ratio of dimethyl carbonate and biodiesel. The higher is the biodiesel fraction, the more efficient is the retention of DMC in the gel system. This is a useful feature that can be used to modify the evaporation properties of highly volatile materials (such as DMC), which are generally more complicated to use, while also ensuring greater gel stability.

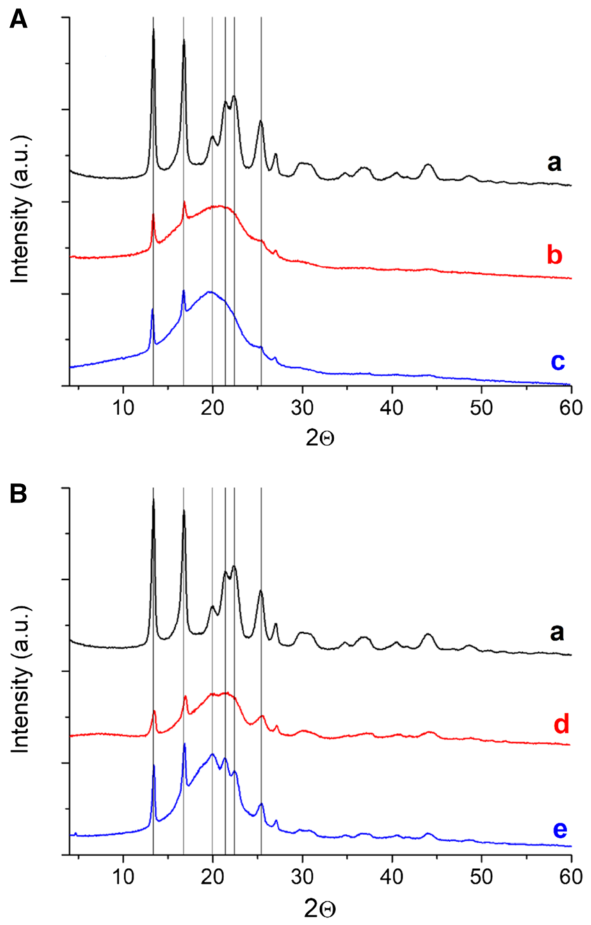

Fig. 3 WAXS diffractograms of pristine PHB powder (a) compared with **A** wet gels PHB-DMC/BD(3:1) (b) PHB-DMC/BD(1:1) (c) and **B** dried gels PHB-DMC/BD(3:1) (d) PHB-DMC/BD(1:1) (e). Vertical lines are drawn to guide the eye about the position of pristine PHB (a) crystal phase reflections

Evaluation the cleaning efficacy and biodiesel residuals

The evaluation of the cleaning efficacy of the gel was carried out on standard bronze samples, which were melted and covered with a beeswax-based by restorers of Opificio delle Pietre Dure in Florence (Fig. 6a).

These samples allowed us to assess the applicability of the gel on substrates presenting morphologies and compositions comparable to a real case of study. Thus, representative evaluation on the performances of the cleaning system was achieved. To this end, several areas were treated with the DMC/BD 3:1 gel, selected on the bases of rheological measurements as the most suitable cleaning system for restoration purposes. Treated areas were characterized by infrared microscopy in total

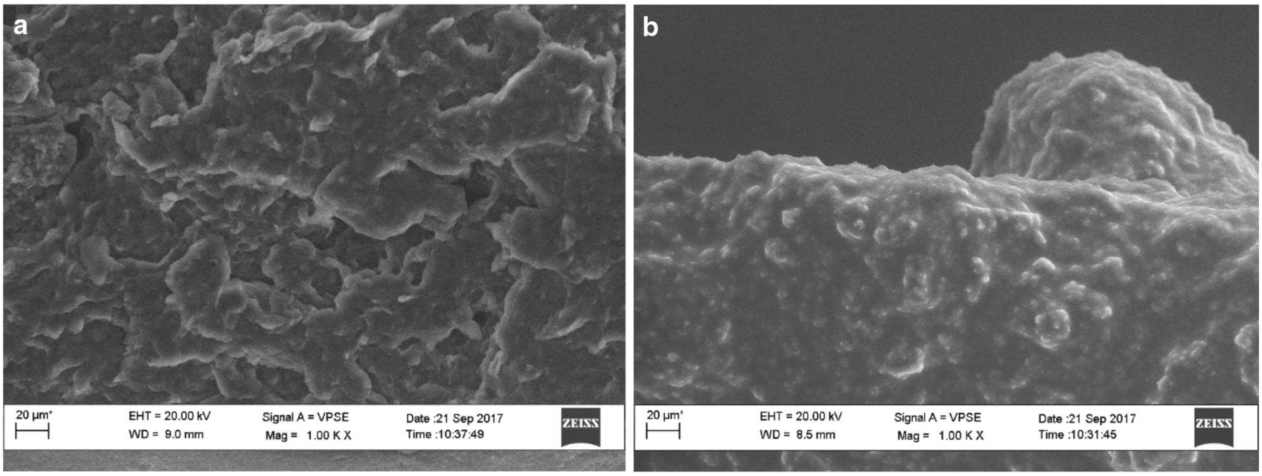

Fig. 4 SEM micrographs of dried gels PHB-DMC/BD(3:1) (**a**) PHB-DMC/BD(1:1) (**b**)

Table 2 Evaluation of the gel's retention power based on TGA results

Sample	Solvent fraction [%wt]	DMC in solvent mixture X_{DMC} [%wt]	TGA weight loss WL_{TGA} [%wt]	Δ^{b}_{DMC} [%wt]
Gel PHB-DMC/BD(3:1)	90.9	78.9	67.3[a]	15
Gel PHB-DMC/BD(1:1)	90.5	55.5	38.2[a]	31
DMC/BD(3:1)	100	78.9	72.3	8
DMC/BD(1:1)	100	55.5	51.7	7

[a] Evaluated discarding polymer fraction of the gel

[b] Evaluated as $\Delta_{DMC} = 100 * \frac{(X_{DMC} - WL_{TGA})}{X_{DMC}}$

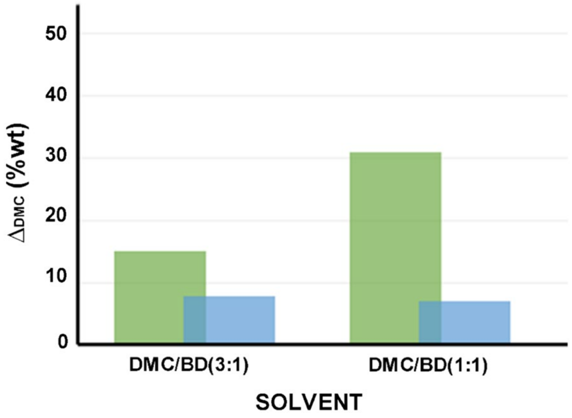

Fig. 5 Comparison of the solvent evaporation in the gel systems (blue bars) and in pure solvents (green bars) based on TGA experiments

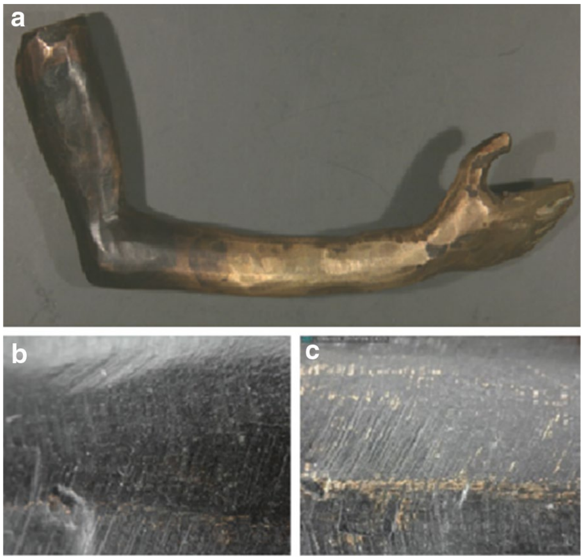

Fig. 6 **a** Bronze mock-up sample made by Opificio delle Pietre dure in Florence; Dino-lite microscope images **b** before and **c** after cleaning by PHB-DMC/BD(3:1) gel for 5 min

reflection mode to verify the absence of wax-residues after the treatment. All the areas were also documented with microphotographs to determinate changes in morphology (Fig. 6b, c).

Results obtained by μFTIR analysis showed an efficient removal of the coating in all areas in which the gel was applied. Thus, the diagnostic bands of wax at 1474 and 1465 cm^{-1} (CH_2 scissoring), the doublet at 731 and 721 cm^{-1} (CH_2 rocking), as well as the C=O stretching band at 1742 cm^{-1} were no longer visible after PHB-DMC/BD gel application (Fig. 7).

On the other hand, bands that characterizes to the original metal patina were better identifiable. The broad band at 1586 cm^{-1}, ascribable to copper carboxylate salts and possibly formed due to the interaction between fatty acids of wax with copper salts, become more intense. In addition, the O-H stretching at 3547 cm^{-1}, the N–O stretching at 1047 cm^{-1} and O-NO_2 symmetric stretching at 1342 and 1421 cm^{-1} may be referred to the copper hydroxyl nitrate ($Cu_2(OH)_3NO_3$), formed during the procedure of manufacture, based on the use of a silver nitrate solution. The weak bands ascribed to the C-H stretching are still present although with a significantly lower intensity. These bands could be related to the presence of organic materials used as a coating penetrated into the porosity of the substrate as well as to the presence of copper carboxylates. After the cleaning procedure, the surface appeared to be less uniform and details on the manufacturing have become visible. In addition, no bands related to the presence of BD residues were detected.

Comparative tests, performed with neat BD simple applied with a cotton swab, seem to confirm the ability of BD in the removal of wax coating (Fig. 8). However, while the CH_2 rocking bands at 721 and 729 cm^{-1} disappeared, wax and BD residues cannot be excluded due to the presence of bands at 1746 cm^{-1} (C=O stretching bands), at 1195 and 1175 cm^{-1} (O–CH_3 stretching and C–O–C symetric stretching) (Fig. 8b). This result can be explained by the less controlled action of BD, which

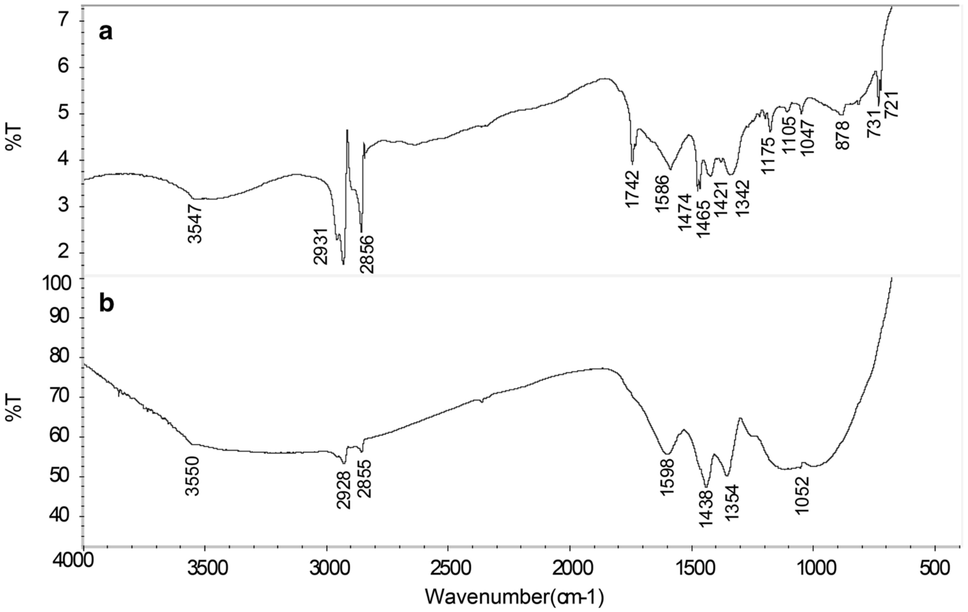

Fig. 7 Total reflection spectra of bronze mock-up sample made by Opificio delle Pietre dure in Florence collected from a treated area with PHB-DMC/BD(3:1) gel **a** before cleaning; **b** after cleaning

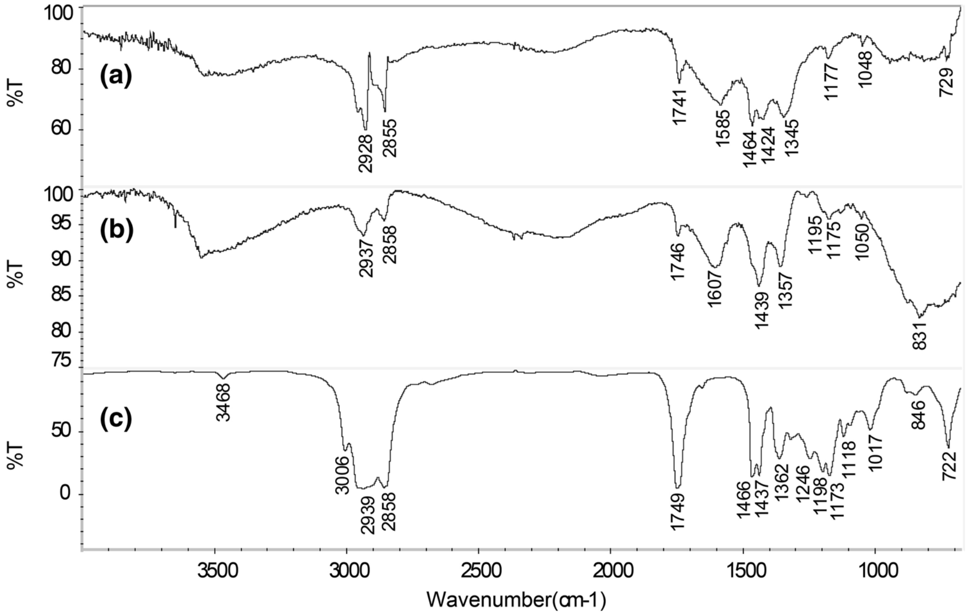

Fig. 8 Total reflection spectra of bronze mock-up sample made by Opificio delle Pietre dure in Florence collected from a treated area with neat BD **a** before cleaning; **b** after cleaning; **c** BD reference spectrum

was not confined to the gel matrix, and by a less effective cleaning action of the neat solvent.

The evaluation of solvent retention by the treated surface is a crucial point in the development of new cleaning systems [21]. Indeed, the persistence of solvent on the treated surfaces may led to harmful interaction, alterating the substrate and inducing further corrosion phenomenas. To better investigate the amount of residual biodiesel after cleaning, quantitative GC-MS analysis of biodiesel methyl esters (methyl esters of palmitic, linoleic, oleic and stearic acid) were carried out on *ad-hoc* samples obtained by covering an oxidated copper sheet with a layer of beeswax and treated with PHB-DMC/BD gel or neat BD. BD methyl esters were clearly visible and detectable after the cleaning with neat BD applied by cotton swab. The analysis performed on three sample replicas treated with the same procedure allowed to quantify the amount of BD in the substrate after the cleaning procedure (0.15 ± 0.03 mg/cm^2). On the other hand, no BD residues were detected after the application of DMC/BD gel for 5 or 15 min, confirming the gel capacity in solvent retention (Fig. 9), in accordance with FTIR investigations.

Application of the DMC/BD gel on a real case of study

After the preliminary evaluation of the gel performances in terms of cleaning efficiency and solvent retention, the PHB-DMC/BD gel was finally applied on the Pulpito della Passione attributed to Donatello. The metal surface presented a wax-based coating, probably applied during a past restoration campaign. The coating appeared extremely altered, possible due to the degradation phenomena that occurred over time (Fig. 10).

PHB-DMC/BD gel was sandwiched in between two sheets of rice paper and applied for 15 min on a representative area of a bas-relief. On-site spectroscopic investigations were carried out to monitor the cleaning effects using a portable spectrometer. IR spectra in total reflection mode were acquired before and after the cleaning procedure (Fig. 11). The untreated surface showed peculiar bands ascribable to the fatty materials present on the surface. In particular, bands at 1736 cm^{-1} (C=O stretching), 1480 cm^{-1} (CH_2 scissoring), 1188 cm^{-1} (C–O stretching), and at 786 cm^{-1} (CH_2 rocking) were visible. In addition, the presence of calcium carbonate at 716 cm^{-1} and

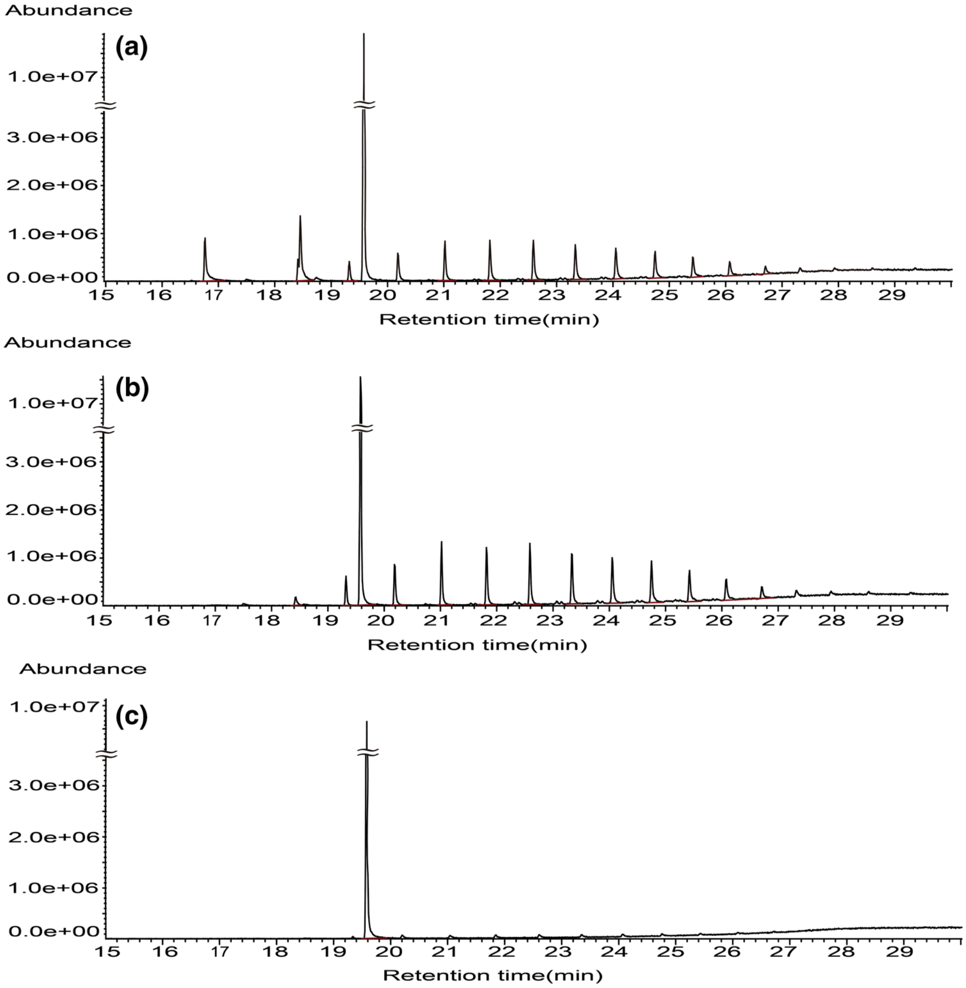

Fig. 9 Chromatograms of **a** cleaned sample with neat BD; **b** cleaned sample with PHB-DMC/BD(3:1) gel for 5 min; **c** cleaned sample with PHB-DMC/BD(3:1) gel for 15 min

Fig. 10 Detail of the Pulpito della passione (Donatello, 1460, Florence), before (left) and after (right) the cleaning with PHB-DMC/BD(3:1) gel

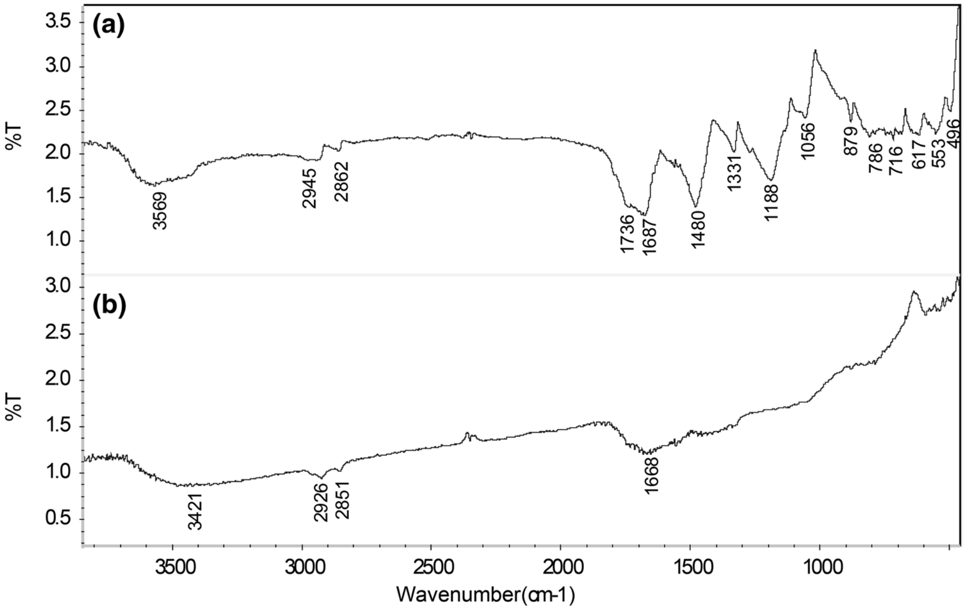

Fig. 11 Total reflection spectra collected from the Pulpito di Donatello on the treated area of with PHB-DMC/BD(3:1) gel **a** before cleaning; **b** after cleaning

879 cm^{-1} probably ascribable to atmospheric deposition, and calcium oxalates (band at 1331 cm^{-1}) were also detected. After the cleaning procedure, only traces of calcium oxalates were visible, demonstrating the high efficiency of the proposed system in removing the wax-based coating, without leaving solvent residues.

Conclusions

To date, scientific research has mainly focused on the proposal of new cleaning systems for painted surfaces, while little attention has been paid to the evaluation of new solutions for the restoration of indoor and outdoor bronzes.

We developed a new fully sustainable cleaning method based on the use of the PHB-DMC/BD organogel for the removal of wax coating from indoor bronze surfaces, increasing the number and types of PHB-based gels that can be used for restoration purposes. In particular, we demonstrated the possibility of tuning the hydrophobic/hydrophilic character of the gels for tailored applications.

Thus, Biodiesel was selected as a perfect candidate for the non-polar coatings, while DMC was selected thanks to its ability to solubilize PHB at 70–90 °C and to form a gelly phase when cooled down to room temperature.

FTIR and GC-MS analyses allowed to describe the efficacy of the gels and evaluating BD residues after the application. The results showed the good performance of new green gel proposed for the removal of fresh and aged beeswax coatings, avoiding problems related to solvent residues and ensuring safety for the works, the operators and the environment.

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Authors' contributions
All authors contributed to the analysis of the data and the drafting of the document. All authors have read and approved the final manuscript.

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Competing interests
The authors declare that they have no competing interests.

Availability of data and materials
The datasets used and analysis during the current study are available from the corresponding author on reasonable request.

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