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Towards Sustainable Museum Conservation Practices: A Study on the Surface Cleaning of Contemporary Art and Design Objects with the Use of Biodegradable Agents

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Abstract: Green contemporary art conservation cleaning methods are explored as sustainable museum practices, ensuring the conservator's health and reducing the environmental impact. The performance of selected biodegradable cleaning agents, namely deionised (DI) water, a chelate based on trisodium salt of methylglycinediacetic acid (MGDA), Trilon® M, a non-ionic surfactant based on alkoxylated fatty alcohols (Plurafac® LF900), and two solvents, limonene and ethyl lactate, was evaluated for the surface cleaning of polymethyl methacrylate (PMMA), polylactic acid (PLA), polypropylene (PP), and plasticized polyvinyl chloride (pPVC). Plastic mockups were used untreated or artificially soiled, simulating particulate matter or sebum stains produced by handling. Furthermore, the efficacy of ink removal from the plastic's surface was evaluated. Surface examination was carried out using optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM), while µ-Raman and gloss measurements complemented the cleaning assessment methodology. The cleaning agents' potency depends on the type of plastic, precluding a general cleaning protocol. However, their cleaning efficacy is very promising, enriching the available choices for the cleaning of plastics, using sustainable materials and practices. This study offers valuable information to the conservation field regarding the effects of the selected biodegradable cleaning agents on each type of plastic, their application method, and their cleaning efficacy for the removal of different types of soil and ink.

Keywords: sustainable conservation; plastics; museum and design objects; biodegradable cleaning agents; SEM; AFM; µ-Raman; glossimetry

1. Introduction

Inherent to the field of cultural heritage preservation is the social responsibility that requires the development of more sustainable approaches suitable for both human health and the environment, following the United Nations and climate change policies [1,2]. Conservation and restoration practices involve conservation treatments that require the use of various materials and techniques, aiming to ensure the stability of cultural heritage and art objects. Such practices have been developed and established on the basis of conservation ethics and principles, such as reversibility and compatibility. However, very often, materials that present a potentially high risk to the health of the conservator and the environment are applied. In this context, in the last few years, an effort has been made towards the integration of practices that are both healthy and environmentally safe, taking into account all the factors that contribute to their environmental impact, such as the life cycle assessment (LCA) of the products, waste management, and the carbon footprint of products' lifetime and all activities involved in the process [3–6].

It is beneficial for cultural heritage conservation when emerging sectors, such as the preservation of plastics, meet with environmentally benign practices. The understanding of plastic conservation treatment is still under vigorous investigation and the vast variety of approaches now encountered in museum, art, and design collections necessitates a thorough study of their properties and deterioration phenomena. Environmentally friendly systems can be incorporated into surface cleaning, which is of great importance in order to protect plastic materials from future deterioration and to preserve them in good condition.

1.1. Examples of Green Materials Used in Conservation

Obstructions faced in the transition towards sustainable conservation approaches include the accessibility to new products readily available in the market, the dissemination of the relevant information within the conservation community, the time required for testing and evaluation with regards to their efficacy, and the establishment of newly developed protocols in everyday laboratory practice. Nevertheless, during the last two decades, significant progress has been made towards the research and application of green and sustainable materials and methods in cultural heritage conservation. Green materials are derived from renewable sources or from the processing of agricultural crops, are non-toxic with low volatile organic compounds, easily disposed, and they significantly reduce contaminated waste [7].

Although carried out mostly at laboratory scale and inevitably designed and tested specifically for each case study, several green materials have already been introduced in the art conservation field, and these include but are not limited to cleaning agents using green biodegradable solvents [8–10], ionic liquids [11,12], biogels [13–17], biodegradable surfactants [18,19], bio-based chelates [20–22], enzymes [23–25], biocides based on bacteria [26–30], and essential oils [31–33].

1.2. Cleaning Applications on Plastics

A systematic study on the cleaning of plastics was carried in the context of the collaborative project entitled "Preservation of Plastic Artefacts in Museums" (POPART) [34]. The study focused on several different types of plastic, including cellulose acetate (CA), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), high impact polystyrene (PS), high density polyethylene (HDPE), and expanded polystyrene. A variety of wet and dry cleaning methods was investigated, using available materials that have been routinely applied mostly for the cleaning of traditional paintings. Additionally, dry cleaning tools and wet cleaning carriers, including different types of brushes, sponges, feathers, as well as supercritical carbon dioxide (sCO_2) were tested. The results showed a strong dependence on the specific type of plastic and the type of soil to be removed. Solvents proved more efficient for oily soil and the aqueous agents for the carbonaceous soil. Most of the mechanical cleaning tools, when used dry, may easily cause irreversible mechanical damage, with scratches that may be visible even under the naked eye [35]. All cleaning tests were comparatively evaluated, taking into account the changes induced on the plastic surface, e.g., scratches, changes of gloss, and the angle of contact. In the context of the project's scopes and considering the selected set of cleaning agents, several suggestions were given, excluding the most damaging cleaning systems and proposing the least damaging combinations of cleaning agent and carrier for every type of plastic and soil.

Several studies that followed were dedicated mostly on the cleaning of PVC and PMMA. Fricker evaluated some of the cleaning agents used within the POPART project using a synthetic microfiber cloth (80% polyester, 20% polyamide) for application on PMMA and PS. During the study, a combination of microscopic and spectroscopic techniques were used to evaluate the physicochemical changes, deterioration phenomena, and cleaning residues [36,37]. The results showed scratches induced both by the mechanical action of both the cloth and the soil particles and the presence of surfactant residues even after meticulous rinsing. Another study reported the use of hydrogels and solvent gels in order to control the solvent diffusion during the cleaning on PMMA- based objects [38,39]. W/o microemulsions based on a biodegradable alcohol ethoxylate non-ionic surfactant (Ecosurf 3) mixed with a silicone-based solvent was used for the cleaning of soiled and sticky

Pierre Cardin PVC and polyurethane boots from 1966 to 1969. The same microemulsion, also incorporating chelating agents (ethylenediaminetetraacetic acid and citric acid), was tested for the cleaning of a heavily soiled PVC rain-smock designed by Mary Quant in 1963 [40]. Further studies were carried out on plasticized PVC, using both dry and wet cleaning methods with water, solvents, non-ionic and ionic surfactants, an aqueous solution of KOH, and two commercial cleaning products, applied with cotton commercial cloths made of polyamide and polyester [41,42]. It was shown that in most cases both physical and chemical alterations occurred on the plastic surface, including changes on the topography, removal of the plasticizer, and, in some cases, migration of the plasticizer from the bulk of the plastic film. All solvents resulted in extracting the plasticizer upon minimal time of exposure, while DI water and KOH aqueous solution did not. Despite the numerous cleaning agents tested so far, none of them have proven to be both innocuous and efficient in respect of physicochemical alterations induced, cleaning residues left on the plastic's surface, and cleaning efficacy for the removal of soils.

1.3. Green and Sustainable Approaches for the Cleaning Treatment of Plastics

Among the materials evaluated so far for the surface cleaning of plastics, green approaches include the use of polysaccharide gel, such as agar, gellan, and xantham gum and, as already mentioned above, the use of biodegradable surfactants, following protocols that are being used for the cleaning of paintings. However, polysaccharide gels, when mixed only with water and applied as a rigid cold film, do not remove a sufficient amount of soil, while in other instances they have been used in combination with solvents, such as acetone, isopropanol, ethanol, and petroleum ether, in order to enhance the cleaning result [39,40,43]. On the other hand, most of the biodegradable surfactants tested [44] need to be used in combination with hydrocarbons as co-solvents. Interestingly, a recent study that tested the efficacy of soil removal from plasticized PVC, employing the Chemistry Scoring Index (CSI) sustainability matrix, combined with practicality factors (workability, ease of application etc.), and aiming to conclude the most effective cleaning system in terms of cleaning efficacy and environmental sustainability factors, reported that an SDS (sodium dodecyl sulphate)-based microemulsion and the HPMC (hydroxypropyl methylcellulose) gel presented the highest scores [44]. With the aim of using green methods for the conservation of plastics, supercritical CO_2 was proposed and tested [in the context of the POPART research project [34]. However, it was abandoned due to discoloration and irreversible physical and mechanical alterations induced on the plastics. A more recent study has focused on the use of sCO_2 method both for soil removal and for consolidation purposes in combination with different types of consolidant for synthetic latex-based foams [45,46]. This paper presents a research study focused on the use of explicitly biodegrabable solvents and aqueous cleaning systems for the surface cleaning of plastic surfaces. Four different types of plastic were tested, i.e., PMMA, plasticized PVC, polypropylene (PP) and poly(lactic acid) (PLA). The first three plastic types are among the most commonly found in museum collections [47]. PLA is widely used in 3D printing technology and is a relatively new material in art, used in 3D artworks and design objects. It is compostable or chemically biodegradable, and thus sensitive to environmental factors as well as to some solvents [48]. With a toolbox of three different imaging techniques (OM, SEM, AFM), glossimetry, and Raman spectroscopy, the initial screening of the cleaning materials was based on the impact of the cleaning treatments on untreated plastic samples, such as physicochemical and topographical changes and cleaning residues. After selecting the safest cleaning agents for each plastic, cleaning tests evaluated their efficacy on artificially soiled plastic surfaces.

2. Materials and Methods

2.1. Sample Types and Preparation

Samples of transparent PP, plasticized transparent PVC, colorless PMMA, and 3D printed white PLA were used for testing the effects and the efficacy of the selected biodegradable cleaning agents, as described below. PP, PVC, and PMMA were commercially available, while the PLA was 3D printed at the desired dimensions by Planfab, a Greece based printing service company, using PLA filament produced by the MCPP company (Mitsubishi Chemical Corporation, Tokyo, Japan). The chemical composition of the specimens was confirmed by Raman spectroscopy. The white pigment in the PLA was identified as titanium dioxide (TiO_2) [49,50] and the plasticizer in the PVC was identified by the main Raman peaks as dioctyl terephthalate (DOTP) [51,52] (Raman spectra in Supplementary Figures S1 and S2). PMMA, PVC, and PLA have a thickness of 3 mm, and PP of 0.5 mm. Samples of the four different types of plastics were prepared in two different dimensions. A set of small samples with dimensions 2×2 cm^2 was used for the evaluation of the cleaning tests under SEM and AFM. Larger samples of 6×20 cm were used for the gloss measurements and for the spectroscopic analysis (Supplementary Figure S3).

2.2. Cleaning Tests

2.2.1. Artificial Soiling

The cleaning tests were initially applied to the control samples in order to investigate the effects of each cleaning agent on each type of plastic as a preliminary screening so as to proceed with the removal of soil. Artificially soiled samples were prepared using two types of soil, in order to simulate particulate matter (PM) and stains from oily substances and fingerprints (sebum). The methodology of the soiling preparation and application was based on the recipes given from the POPART project [34], with modifications of the components' analogies and the application mode. The PM soil was applied using a solution of 5% carbon black pigment of approximately10 μm particle size boneblack pigment (47200 IvoryblackJU from Kremer Pigmente GmbH& Co. KG, Aichstetten, Germany)in mineral oil and was applied using a soft brush. The sebum soil was prepared using a solution of 2% palmitic (hexadecanoic) acid in 1-propanol and it was applied by spraying the surface of the samples. The two types of soil will be referred tohereinafter as carbon and sebum soil respectively. For testing the efficacy of cleaning agents on ink removal, blue (STAEDTLER Lumocolor®) and green (STABILO OHPen Universal) permanent inks were used to write on the plastic samples.

2.2.2. Cleaning Agents and Application Methods

The cleaning agents tested include deionised (DI) water, agar gel, a chelate based on trisodium salt of methylglycinediacetic acid (MGDA) available as Trilon® M, a non-ionic surfactant based on alkoxylated fatty alcohols (commercial product Plurafac® LF900) and two solvents, limonene and ethyl lactate (Table 1). Ethyl lactate and limonene are known environmentally benign solvents, efficient in grease and oil removal [53,54], and their use in art conservation has also been reported [8,55]. Agar gel was tested using two different types of application, as hot viscous film and as cold eraser. In the former case, it was applied using a spatula, at approximately 40–45 °C for PP, PVC, and PMMA and at 35 °C for PLA, due to PLA's lower glass transition temperature [56]. The film was left to dry on the surface of the samples for 5 min and then it was removed, by peeling it off. In the latter case, cold agar gel, which had been poured in a syringe, was rubbed slightly onto the surface, as an eraser, following a methodology proposed by Cremonesi [57]. For the selection of the milder cleaning medium to be used for the rest of the biodegradable cleaning agents, sterilized pure cotton in the form of cotton bud and Evolon® CR [58], a non-woven highly absorbent microfilament fabric of 70% polyester and 30% polyamide, specially manufactured for conservation, were tested. These were initially used dry on all types of plastic, applying 10 forward and back rolls or rubs, respectively. The microfilament fabric was considered milder, as it will be discussed in Section 3.1. In order to follow the same procedure for all cleaning agents and samples, pieces of the microfabric were cut in specific dimensions and wetted with measured quantity of the cleaning agent (3×3 cm, 0.40 mL for the big samples and 2×2 cm, 0.10 mL for the small samples). Each cleaning agent was applied on untreated samples by wetting the Evolon® CR cloth and gently rubbing the surface 15 times (forward and back). A clearance step with DI water followed the application of agar, the chelate, and the surfactant, applying a water wetted cloth 15 times, after having tested that a 10-time application clearance was not adequately eliminating the cleaning residues. The cleaning tests that were carried out for the removal of the soil included an additional final step of wiping the surface with dry Evolon®CR cloth, in order to eliminate the water and any residues of the cleaning agents. Duplicates of each sample were tested. After the evaluation of the effects of each cleaning agent on the different plastics under study, those considered to be safer, with respect to the physical and chemical integrity of the plastics, were selected and applied for the cleaning of the artificially soiled samples. Taking into consideration the information retrieved from the evaluation of the untreated samples and after some preliminary tests on soil and ink treated samples, the parameters for the soil and ink removal were set. A maximum of 30 passages for the main wet cleaning step was decided and 15 passages for the wet clearance of the agar film, the surfactant, and the chelate. A final dry clearance step, gently applying the cotton or the cloth five times, was carried out after testing all the cleaning agents, in order to remove them completely and eliminate further action on the plastic surface.

Table 1. List of the cleaning agents used for the cleaning tests.

Cleaning Agent	Cleaning System Details	Application Mode
Deionised water	buffered to pH 6 and conductivity 6 mS/cm (ammonium acetate) [59]	
Agar powder (ACROS)	4% agar in DI water	a. Hot viscous film b. Cold Eraser
Trisodium salt of methylglycinediacetic acid (MGDA—Trilon® M by BASF)	2% in DI water	a. Cotton buds of sterilized 100% natural cellulose b. Evolon®CRmicrofilament fabric (Freudenberg Performance Materials—Deffner&Johann)
Non-ionic surfactant based on alkoxylated fatty alcohols (Plurafac®LF900 by BASF)	1% in DI water	
(R)-(+)- Limonene (Sigma-Aldrich)		
(-)-Ethyl L-lactate (Sigma-Aldrich)		

2.3. Methodology for the Surface Examination

2.3.1. Microscopy Techniques

For each sample, several images were collected using the following equipment. Optical microscopy (OM): A Zeiss Axioplan 2 Imaging microscope equipped with a Nikon D700 camera was used for the visual observation of the samples. Microphotos were recorded using the incident light source at magnifications 50–200×. Atomic force microscopy (AFM): A Bruker Innova AFM system operating in tapping mode with silicon probes was used. Images of 10×10 μm^2 areas (from at least 4 randomly selected areas of the sample) were collected in height, amplitude, and phase mode, using the Bruker Nanodrive v.8.0 and analyzed with the Bruker Nanoscope Analysis v.1.40 software. The tapping amplitude images gave the most comprehensive information, showing changes in the topography of the samples. Scanning electron microscopy (SEM): A JEOL JSM-6390LV scanning microscope was used. Operating conditions were: Accelerating voltage 5–20 kV, probe current 45nA, and counting time 60 s. The samples were coated with carbon using a Jeol JEE-4X vacuum evaporator.

2.3.2. Raman Spectroscopy

Raman spectra were collected using a LabRamHR (Horiba, Kyoto, Japan), single stage, micro-Raman spectrometer equipped with a Peltier-cooled CCD detector. For the excitation of the spectra, a Fandango (Cobolt) diode-pumped laser at 515 nm was used and the laser power was kept at ~1mW.The spectra resolution of the system was ~3.5 cm^{-1} and a standard 100×, N.A. 0.9 objective was employed, yielding a laser spot diameter of ~1 μm for point analysis. Raman spectra were collected around surface features appearing on the samples after cleaning, in order to clarify the local chemical composition.

2.3.3. Gloss Measurement

A Rhopoint NOVO GLOSS 20/60/85 gloss meter was used for measuring the gloss of the plastic surfaces before and after the cleaning tests. Three readings were conducted on each sample and the average was calculated and used, keeping the same relative positioning of the gloss meter with respect to the sample for the measurements before and after the cleaning treatment. For the transparent plastics, in order to avoid any reflections originating from the lower surface of the plastic, a matte black photographic foil was placed under the sample with a drop of water in between the two surfaces to optically bond the transparent plastic to the black foil. For the plastics that gave gloss values at the reflectance angle of 60° higher than 70 SGU (high gloss), the gloss was measured at 20°. For values lower than 10 SGU (low gloss), the angle of 85° was used for improved resolution according to [60].

3. Results–Discussion

3.1. Cleaning Application Method Effect

The two cleaning media tested on the plastic surfaces, namely cotton swab and microfilament fabric Evolon® CR, consist of different fiber types, as described in the materials section. Additionally, the application method differs. The cotton swab is rolled on the surface while, when using the Evolon®CR cloth, the surface is gently rubbed. The nature of the material, the mechanical action, and the pressure applied affect the possible alteration that may occur on the plastic surface. A study on the dry cleaning of plasticized PVC [41] showed that the use of cotton swabs induced the much faster migration of plasticizer towards the surface compared to other synthetic cloths made from polyester and polyamide fibers. Other studies also support the use of synthetic microfiber cloths instead of cotton swabs for sensitive surfaces [61,62]. In the present study, the evaluation of the cleaning media was carried out by testing the dry application of both the cotton and the Evolon® CR cloth and examining the plastic surfaces with OM, SEM, and AFM. Both cleaning media left fiber residues on the surface. The cotton swab left scratching marks on the surfaces, especially on the softer ones, such as those of PLA and PVC. This effect was better depicted in the AFM images (e.g., for PLA in Figure 1a–c), and with SEM but was not noticeable under the optical microscope. This fact implied that changes occurred in the nano scale. Nevertheless, it cannot be ruled out that such negligible changes could evolve into more significant alterations compromising the surface integrity of the plastics. On the contrary, the amount of fiber residues was lower when the swab or the Evolon® CR cloth was wet with the cleaning solution and any fiber left could be removed during the clearance step. Consequently, it was decided that the use of the Evolon® CR cloth is safer for the treatment of the plastic surfaces. All the cleaning tests that will be described below were undertaken using the microfilament fabric Evolon® CR.

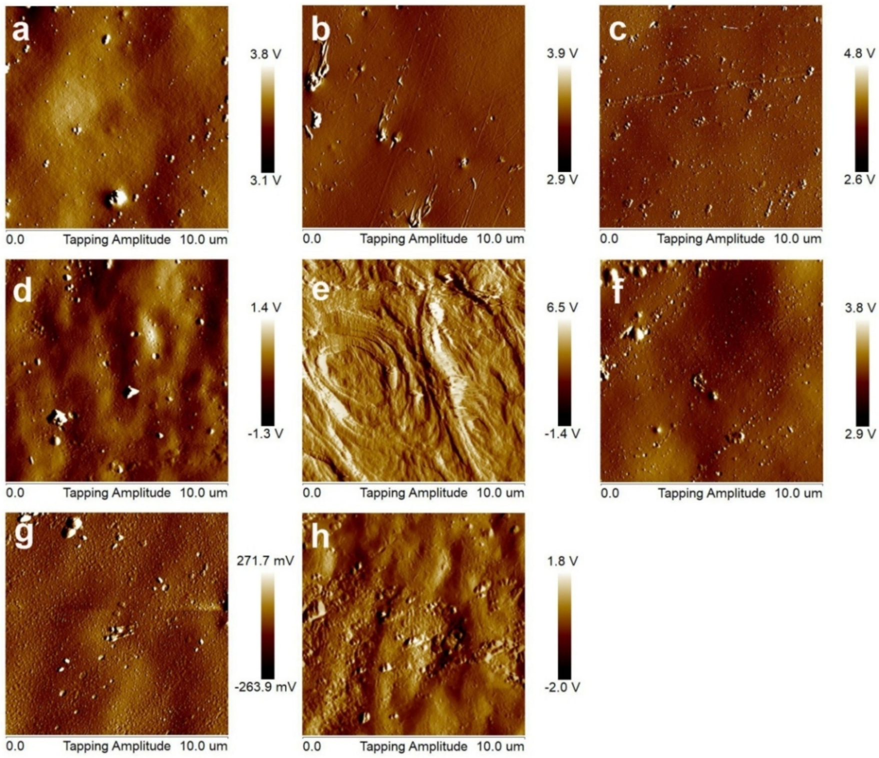

Figure 1. AFM tapping amplitude images of PLA: (**a**) control sample, and (**b**–**h**) non-soiled samples, treated with b) cotton swab showing scratching lines, (**c**) Evolon® CR cloth showing fiber residues, (**d**) DI water applied with cloth showing surface swelling, (**e**) ethyl lactate applied with cloth showing severe surface deformation, (**f**) limonene applied with cloth showing mild surface impact, (**g**) agar gel film showing mild surface impact and (**h**) agar gel eraser showing surface alterations and cleaning residues.

3.2. Cleaning of Untreated and Artificially Soiled Samples

Each cleaning agent was initially tested on non-soiled samples. Subsequently, the ones considered safe for the plastic surface were tested on artificially soiled samples. The details of each cleaning application are given in Supplementary Table S1. Below, the results are presented and discussed for each cleaning agent used.

3.2.1. DI Water

After the treatment with DI water, no changes were noticed on the surface of PMMA and PP. It was considered a safe agent for these materials and it was tested for the removal of carbonaceous soil. Water was not tested against sebum soil because of the hydrophobic character of palmitic acid. However, its cleaning action was not sufficient against carbonaceous soil either, leaving noticeable residual soil. Indeed, in the Raman spectrum collected from such surface features of the PP sample after water cleaning, the intense and broad carbon bands at ~1340 cm^{-1} and ~1590 cm^{-1} were clearly evident (Figure 2a). Thus, the addition of a chelate or a surfactant was judged necessary as an attempt to improve water's cleaning efficiency (vide infra).

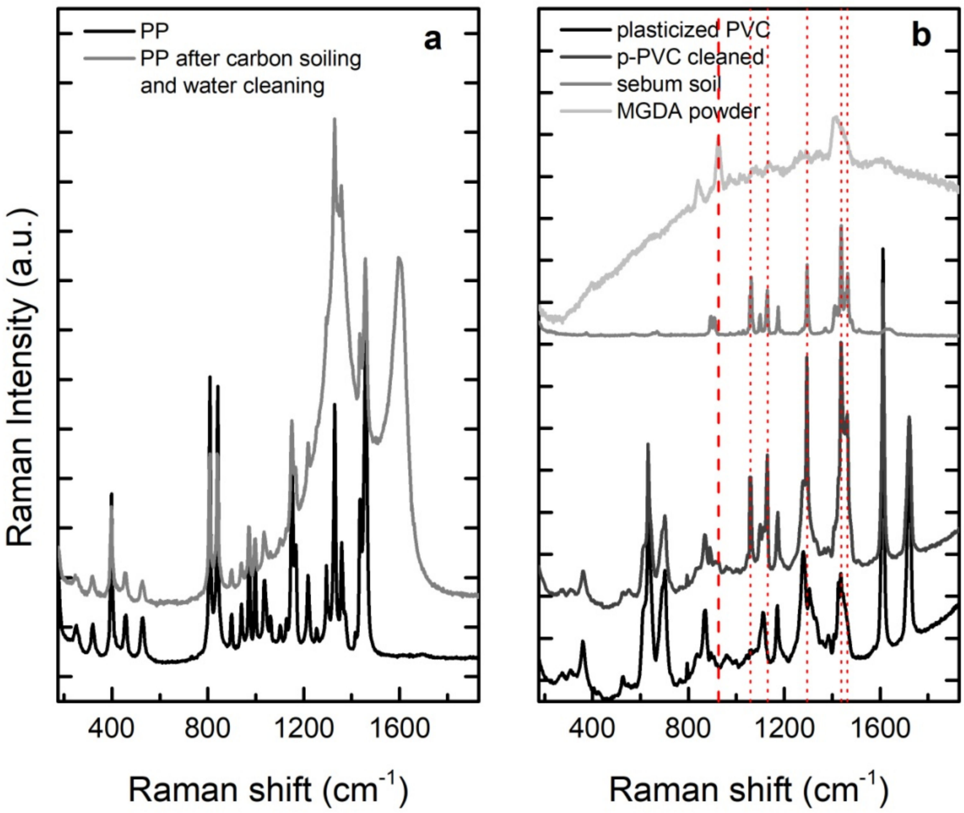

Figure 2. Raman spectra of (**a**) Polypropylene control and water cleaned sample, where the remaining carbon soil residues were evident (broad peaks at ~1340 cm^{-1} and ~1590 cm^{-1}) and (**b**) Plasticized PVC control and sebum soiled sample after cleaning with chelate MGDA, where residues of the agent and the soil were evident. The peaks attributed to the surface residues of the soil and of the cleaning agent are indicated with dotted and dashed lines respectively.

Contrary to the case of PMMA and PP, the use of DI water had an impact on the topography of the PLA. The topography change and the roughness increase (average relative roughness values 0.063 V and 0.3 V for the control and the water treated non-soiled sample respectively) observed in the AFM image (Figure 1d) indicated an interaction of the material with water that led to local surface swelling. A recent study has shown that 3D printed PLA tends to absorb more water than injection moulded PLA due to the higher porosity structure of the PLA specimen produced via 3D printing [63]. Therefore, the water sensitivity of the otherwise hydrophobic PLA [64] was most probably attributed to the morphology of the sample and not to the nature of the polymer itself.

The hydrophobic nature of plasticizer in PVC reduces the contact of water with the PVC surface and leads to less sufficient cleaning when only water is used [42]. The presence of plasticizer in the specific PVC type tested here was confirmed by the intense peaks of the plasticizer in the Raman spectrum (Raman spectrum in Supplementary Figure S2). Moreover, the surface plasticizer was in some cases diversely distributed, possibly because the exudation of the plasticizer towards the surface and areas with higher concentration appeared glossier when viewed with the naked eye. When such areas were examined with SEM, a wrinkled pattern was detected (Figure 3b). A similar wrinkled pattern has been observed in plasticized PVC surface in the literature [65]. Respectively, in AFM, the areas of dense plasticizer presence were characterized by dispersed distinct particles protruding from the surface. A comparison between the AFM images of the control PVC sample and the water treated one showed the appearance of directional lines attributed to the rubbing pressure on preexisting dust (aggregated particles on the control surface) that could not be removed by water (Figure 4b). Otherwise, the surface effect of pure water was considered mild, allowing the test of aqueous cleaning solutions on PVC. No changes in the Raman spectrum of the PVC sample before and after water cleaning were recorded, indicating that no plasticizer was removed.

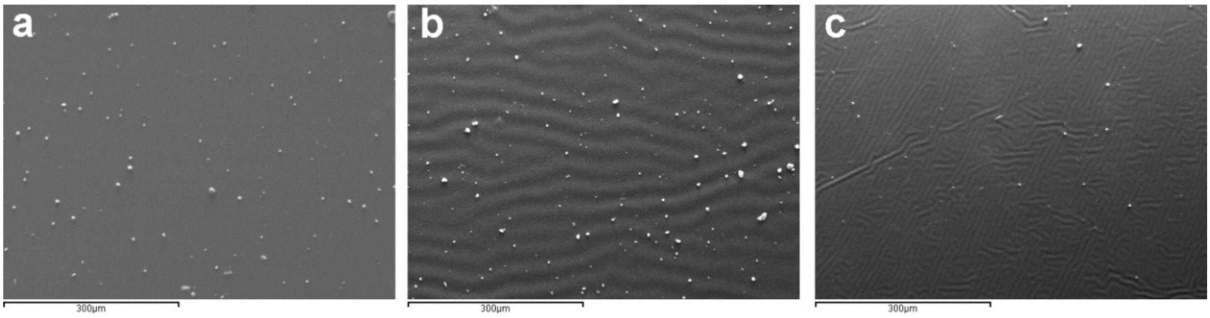

Figure 3. SEM images of plasticized PVC: (**a**) control sample, (**b**) observed wrinkled pattern in the control sample and (**c**) non-soiled sample treated with limonene.

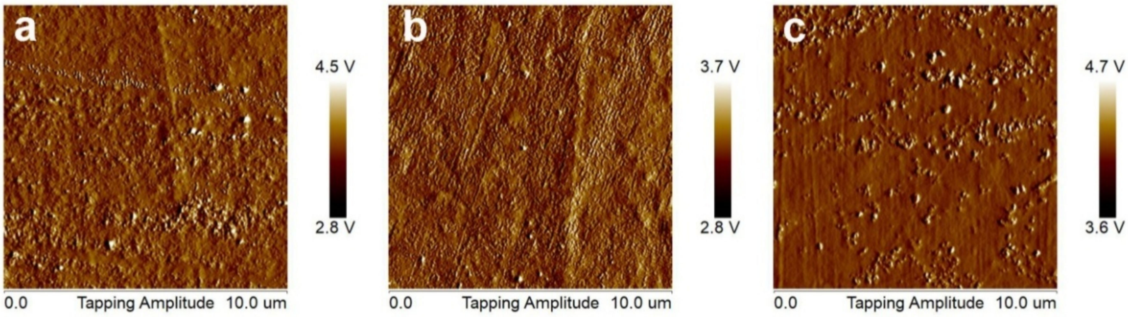

Figure 4. AFM tapping amplitude images of plasticized PVC: (**a**) control, (**b**) non-soiled sample treated with water and (**c**) non-soiled sample treated with limonene.

3.2.2. Chelate MGDA Solution

Chelate compounds have been previously used as cleaning agents and the increase of the cleaning efficacy compared to pure water has been attributed to a combination of factors, such as metal ion chelation, deflocculation, and the dispersion of oily soil [66]. In our case, cleaning residues was the main drawback of the MGDA chelate, even after the clearance step, as it can been seen in the SEM images obtained for the PP sample (Figure 5b). It seems that the presence of MGDA cleaning residues is not related to the roughness of the surface, since considerable amounts of residues were found in both PP (rough) and PMMA (flat and smooth) surfaces. The residue issue is possible to tackle by modifying the clearance step, increasing the number of rubs performed with the water wetted cloth. However, based on the aforementioned remarks regarding the water interaction with PLA surface, this increase of aqueous contact might be inappropriate for this plastic enhancing the swelling effect. Considering the cleaning efficacy, MGDA gave better results than water alone, but was not sufficient, especially regarding the cleaning of sebum soil. Indeed, in several Raman spectra of the PVC surface, peaks of the MGDA and the palmitic acid, besides those of the plasticized PVC, were detected (Figure 2b). Considerable amounts of sebum were left also after the cleaning of PP.

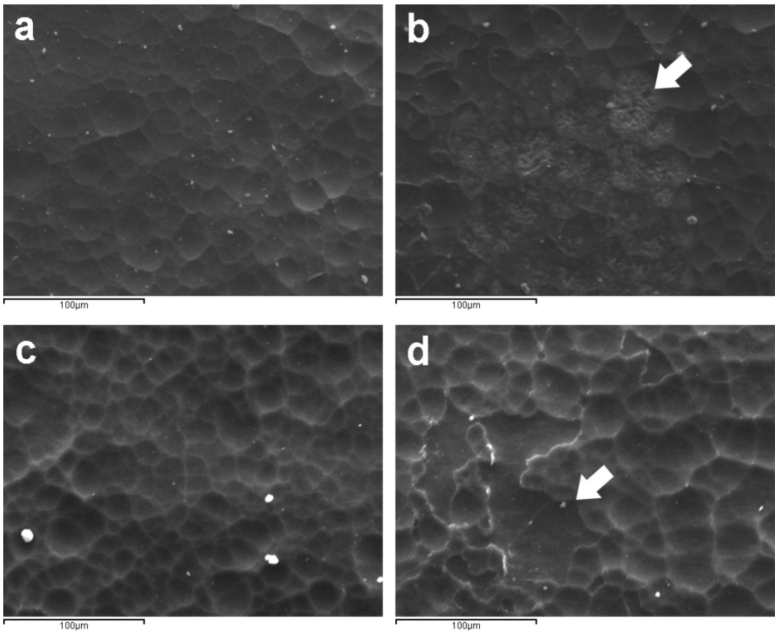

Figure 5. SEM images of PP: (**a**) control, (**b**) non-soiled sample, treated with chelate MGDA solution showing MGDA residues presence (indicated by the arrow), (**c**) carbon soiled sample after cleaning with ethyl lactate and (**d**) carbon soiled sample after cleaning with Plurafac®, showing deformations on the surface (indicated by the arrow).

3.2.3. Surfactant Solution (Plurafac® LF 900)

The solution with Plurafac® LF 900 exhibited a very good cleaning efficacy for all plastic types for the carbonaceous soil. Its effectiveness was most limited on the sebum soiled PLA, where the residual soil was much more distinct, most probably because of the rougher topography compared to the rest of the plastics, and consequently the entrapment of the soil, combined with the decreased cleaning efficacy of Plurafac® against sebum soil. The concern raised in the case of Plurafac® regarded the cleaning residues left on the PLA and PP that had a rougher surface texture. An increase of the number of clearance rubs from 10 to 15 on the PLA surface resulted in a significant reduction of the cleaning residues, although a more persistent clearance step with water could have an adverse effect on the PLA surface. However, the use of this biodegradable surfactant as a cleaning agent is very promising due to the remarkable effectiveness on carbon soil removal. A thorough experimentation on the clearance step conditions, setting thresholds regarding the effect on the surface integrity, will contribute towards the safe use of Plurafac® for 3D printed PLA objects. Besides, it should be noted that a light wiping of the PLA surface with a dry piece of the cloth immediately after the aqueous clearance step minimized the water absorption. As can be seen in the SEM imaging (Figure 6a,b), the cleaning of carbon soiled PLA with Plurafac® solution followed by a clearance step with DI water and dry Evolon® cloth led to a final PLA surface with almost identical features to the control one. Plurafac® solution proved to be the best cleaning agent for carbonaceous soil for the PMMA and it was also very effective when used with PP and PVC (Supplementary Figure S4). When used on PVC surface, the surfactant affected the appearance of wrinkled lines on the cleaned samples' surface. This alteration could be explained by a partial solubility of the surface plasticizer and its redistribution on the surface through the mechanical action. This is in accordance with a previous study testing organic solvents and detergents on plasticized PVC [42], where it was demonstrated that detergents extracted more plasticizer than water and less than organic solvents.

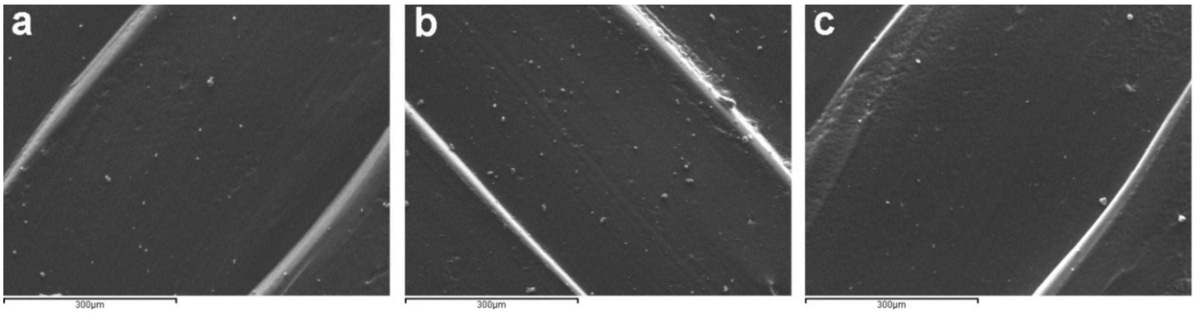

Figure 6. SEM images of PLA (**a**) control, (**b**) carbon soiled sample cleaned with Plurafac® solution, where no soil residues are evidenced, and after water clearance and wiping with dry Evolon® CR, which left no cleaning residues either and (**c**) carbon soiled sample cleaned with limonene with very good cleaning result.

3.2.4. Agar Gel

Agar gel was tested both applied as hot viscous film and cold, in the form of eraser on all four types of plastic. The application method was found to have an influence in the amount of cleaning residues left and the type of surface alteration. On PLA, agar gel was applied as film in a lower temperature (35 °C) than the usually used 40–45 °C [57] because in a previous study [67] we had noticed the sensitivity of the PLA and its surface deformation at temperatures around 50 °C, which is close to the T_g of the PLA (57 °C) [56].

Regarding the cleaning agent effects on the plastics, the use of agar film on PLA clearly reduced the swelling effect compared to water (average relative roughness values 0.08 V) (Figure 1g), since in this way the contact of the plastic surface with water was limited and controllable. Therefore, the surface distortion in this case was negligible. Moreover, the minor amounts of agar residues left on the surface were very easily removed during the clearance step in all four plastics. However, the clearance step was considered indispensable. On the other hand, when agar gel was tested in eraser form, the surface alterations on PLA occurred already from the cleaning step, probably due to the rubbing friction (Figure 1h). The rubbing friction was also responsible for the higher amount of agar cleaning residues observed after the application of agar eraser. In the case of PMMA, the eraser residues were smaller in size than the film residues but scattered over the whole surface, because of the rubbing action. After the clearance step, the scattered particles from the eraser were dispersed, mixed with the water, and left intense dragging marks. Increasing the duration of clearance step was not a considerable option because of the risk of scratching the surface of the plastic due to repeated mechanical action. Agar film was the only cleaning agent that did not alter the surface topography of PVC, especially regarding the plasticizer. This can be also attributed to the absence of mechanical action, since in the application of agar gel no rubbing with the Evolon® CR cloth was involved.

Based on the above observations, it was decided to systematically test the cleaning efficacy of the agar gel film, which in the case of sebum soil was very limited leaving too much of residual soil (Figure 7b). On the contrary, the efficacy on removing carbon soil was on average good, improved compared to water, but also affected by the topography, roughness, and the general type of plastic surface. Specifically, regarding PLA, soil residues remained mostly in the indentations that exist on the sample's surface due to the printing process, but the overall result was very satisfactory. Carbon soil was easily removed from the surface of PP and PMMA by the specific application procedure of agar gel hot film, with negligible residues left. Less effective was the agar gel film for the plasticized PVC surface cleaning, leaving quite an amount of soil residues. This result was because the carbon soil and the surface plasticizer cohered, inhibiting the soil removal, especially in the absence of mechanical action when agar gel film was used. In this case, agar gel in the form of eraser was tested as well and it was found that it gave a slightly improved cleaning result than agar film. The rubbing action of the eraser apparently allowed a better removal of soil, separating it from the plasticizer.

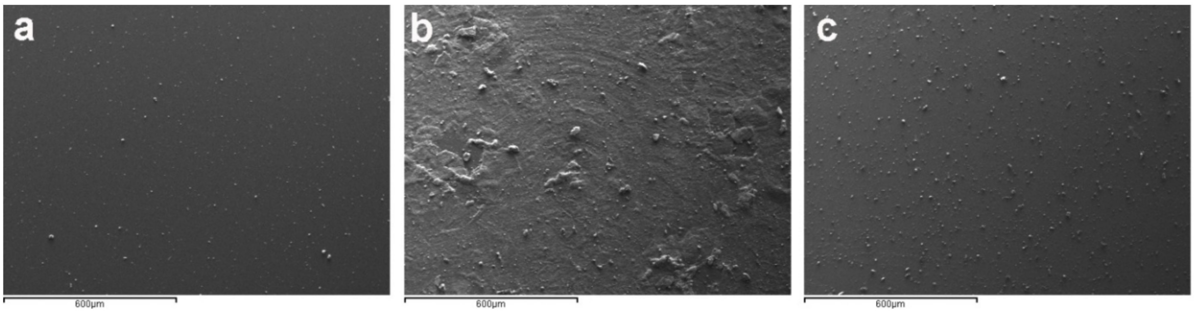

Figure 7. SEM images of PMMA: (**a**) control (non-soiled), (**b**) sebum soiled sample cleaned with agar gel film and (**c**) sebum soiled sample cleaned with limonene.

3.2.5. Limonene

The use of the biodegradable limonene on the PLA surface had a minimum effect on the surface. In this case, the swelling effect observed for the aqueous solutions was not detected in the AFM imaging (average relative roughness values 0.09 V, Figure 1f) and the amount of cleaning residues was negligible. When tested against carbon and sebum soil on the PLA surface, it was found to have a very good cleaning result for both types of soil (see Figure 6c for the carbon soil removal) leaving minor amounts of residue. On the PMMA surface, limonene residues were left after the cleaning step but were subsequently removed by wiping with a dry cloth. Its cleaning efficiency on PMMA was considered satisfactory for the carbon and sebum soil. The plastic surface treated with limonene looked totally clean with naked eye. However, some residual soil was visible under OM and more clearly under SEM (Figure 7c). Thus, this solvent is considered efficient for the cleaning of PMMA surfaces, perhaps with some modifications on the application method regarding the time of action. The application of limonene on the clean surface of PP caused some minor surface alterations that were observed only when using the AFM resolution, but not with OM or SEM, and this was not considered to deter the use of the solvent. Its overall effectiveness was good, although better against sebum soil, with no residues left, while a small amount of carbon soil residues was observed. Finally, for the plasticized PVC, it was observed that limonene interacted with the sample's surface and led to topography variations, like small wrinkles (SEM image, Figure 3c) or alteration of the surface particle distribution and morphology (AFM image, Figure 4c). In fact, we were rather skeptical towards the use of limonene on the plasticized PVC, considering the relatively small solubility distance between the solvent and the plasticizer (Ra: 5.47, see Supplementary Tables S2 and S3) according to the Hansen solubility parameters [68–71] and reports regarding the adverse effect of plasticizer exudation and/or loss on the properties and expected lifetime of PVC [72]. Nevertheless, the Raman spectra collected from the control plasticized PVC sample and the ones cleaned with limonene before and after the cleaning treatment, did not show any remarkable features ascribed to changes in the surface plasticizer. Therefore, the observed topography changes were attributed here to a possible redistribution of the surface plasticizer that probably would not downgrade the PVC properties. Limonene exhibited a very good cleaning efficacy for both types of soil and especially for the sebum soil. However, the effect of the limonene on the plasticizer remains alarming, and further investigations would be needed in order to conclude if the specific biodegradable solvent is safe for use on art objects made of plasticized PVC.

It must be also noted that, regardless of the cleaning agent, after the application of artificial sebum soil on the plasticized PVC and the subsequent cleaning of it, the wrinkled lines on the surface, attributed to the distribution of the plasticizer, were more intense compared to those on the control sample and on the carbon soil cleaned samples. This indicates an interaction between the sebum soil and more specifically between the hydrophobic palmitic acid and the hydrophobic plasticizer (respective solubility distance Ra: 4.66, see Supplementary Table S2), and it is not an alteration attributed solely to the cleaning agents.

3.2.6. Ethyl Lactate

Ethyl lactate was detrimental for the PLA surface, as can been seen in the AFM image (Figure 1e), and consequently it was rejected as a cleaning agent for 3D printed PLA objects. PLA film is not soluble in polar protic solvents, such as ethyl lactate, according to a study where the effect of various organic solvents was tested on PLA film [48]. However, in the same study, a high swelling degree was observed after 24-h immersion of PLA film in ethyl lactate accompanied by a decrease in its density. In the present research, it was shown that even a short contact between the solvent and the PLA can cause severe surface deformation and the alterations observed by the microscopic analysis can be attributed to a high degree of swelling. This fact implies the different behavior and higher sensitivity of a 3D printed PLA object compared to a uniform PLA film and the need to adjust experimental research on the nature of commercial and artistic objects for a better simulation of conservation treatments.

Regarding the rest of the plastics, ethyl lactate did not affect the surface of PP and at the same time showed an excellent cleaning result for both carbon and sebum soil, leaving at the same time almost no cleaning residues (Figure 5c). Similar behavior was observed for the PVC samples, where ethyl lactate effectively removed the two types of soiling. It also affected the surface plasticizer less than the other organic solvent, namely limonene, causing no changes in the surface pattern and indicating less solubility of the PVC plasticizer in ethyl lactate than in limonene. This observation is further supported by the higher solubility distance between the solvent and the plasticizer in PVC (calculated Ra value between ethyl lactate and DOTP: 9.50, see Supplementary Table S3) [71]. When ethyl lactate was tested on the PMMA surface, considerable amounts of cleaning residue were left and dry wiping was required in order to remove them. The solvent was tested only against sebum soil, and when the cleaned surface was examined under OM, circular stains of soil mixed with solvent residues were observed. Under SEM, a thin, continuous residual layer was also recorded.

An overview of the qualitative assessment regarding the cleaning efficiency of the biodegradable cleaning agents, based on the degree of soil removal and the soil and cleaning agent residues, is presented in Table 2. Additional photographs and microscopy images of the cleaned samples are available in Supplementary Figures S5–S15.

Table 2. Cleaning result of the tested cleaning agents on soiled plastic surfaces. SS: sebum soiled, CS: carbon soiled,—not tested, * insufficient cleaning, ** moderate cleaning, *** good cleaning, **** very good cleaning.

<table>
<tr><th></th><th></th><th>DI Water</th><th>Agar Gel Film</th><th>Agar Gel Eraser</th><th>Plurafac® Solution</th><th>MGDA Solution</th><th>Ethyl Lactate</th><th>Limonene</th></tr>
<tr><td rowspan="2">PLA</td><td>SS</td><td>-</td><td>*</td><td rowspan="2">-</td><td>***</td><td rowspan="2">-</td><td rowspan="2">-</td><td rowspan="2">****</td></tr>
<tr><td>CS</td><td>-</td><td>***</td><td>****</td></tr>
<tr><td rowspan="2">PMMA</td><td>SS</td><td>-</td><td>*</td><td rowspan="2">-</td><td>***</td><td rowspan="2">-</td><td>**</td><td rowspan="2">***</td></tr>
<tr><td>CS</td><td>*</td><td>***</td><td>****</td><td>-</td></tr>
<tr><td rowspan="2">PP</td><td>SS</td><td>-</td><td>-</td><td rowspan="2">-</td><td>***</td><td rowspan="2">**</td><td rowspan="2">****</td><td>****</td></tr>
<tr><td>CS</td><td>*</td><td>***</td><td>****</td><td>***</td></tr>
<tr><td rowspan="2">p-PVC</td><td>SS</td><td>-</td><td>-</td><td>-</td><td>***</td><td rowspan="2">**</td><td rowspan="2">****</td><td rowspan="2">**** (†)</td></tr>
<tr><td>CS</td><td>-</td><td>*</td><td>**</td><td>****</td></tr>
</table>

†: possible interaction with the plastic.

A supplemental observation regarding the PP samples was that after the application of the surfactant and the chelate solutions and the agar gel, deformation areas with a bubble-like disrupted surface were evident both under OM and SEM (Figure 5d). Water, limonene, and ethyl lactate treated samples did not develop these alterations and this fact rules out the mechanical action of cleaning since the above agents were also applied by Evolon® CR cloth. Besides, the same effect was observed after agar gel film treatment, where no rubbing with the cloth was involved. Additionally, the phenomenon seemed to be more intense for the carbon soiled and cleaned samples but not for the sebum soiled ones. For example, after the treatment of carbon soiled PP with limonene, these bubble-like disrupted areas were microscopically noticed while they were absent on the non-soiled and sebum soiled ones after the limonene treatment. Moreover, no differences were recorded in the Raman spectrum obtained for these areas, indicating that these were indeed a result of topography change that had occurred rather than a result of the presence of residues or exudation towards the surface of any bulk additives possibly present in the PP. To check if the phenomenon occurs at a higher degree with longer exposure of the plastic to the cleaning agents, samples of PP were immersed for 24 h in the cleaning solutions. No worsening of the effect was observed. At this point of research, no definite explanation could be given to this observation except that it was probably a random result of a combination of both the cleaning agent and the method of application. Furthermore, since these small, scattered deformation areas of PP bubble like surface did not seem to affect the gloss parameter (see below), they were not accounted for a rejection or not of a solution as a cleaning agent. Still, it is a useful observation for similar PP surfaces that a conservator should have in mind.

3.3. Gloss Measurements

Another parameter that was evaluated in order to characterize the effect of the biodegradable cleaning agents was the gloss of the plastic surfaces. The gloss values between the original surfaces and the non-soiled ones treated with cleaning agents were compared and they were very similar, allowing us to conclude that the cleaning agents did not adversely affect the gloss of the plastics, i.e., the aesthetic appearance of the object. Of course, an exception to this was the application of ethyl lactate on PLA, where a 50% decrease of the gloss was observed after the damaging effect of the solvent. Gloss values were also measured first on the original surfaces, before these being soiled and cleaned, and then, after the application on them of the soiling and their subsequent cleaning treatment. The values presented in Figure 8 are for the cleaning agents that exhibited satisfactory results. Regarding the PVC samples, due to the formation of the purchased PVC, which was rolled by the manufacturer, some of the samples preserved a curving that affected the accuracy of the gloss measurements. Thus, data are not presented for all the PVC samples but rather for the carbon soiled ones that were cleaned with the three most safe cleaning agents for this plastic, namely Plurafac® solution, limonene, and ethyl lactate. The general observation is that, after the cleaning treatment, the plastic surfaces' gloss values were very close to the original ones. However, the inadequate cleaning of the sebum soil with agar gel film on PMMA was depicted in the high decrease of gloss. Similarly, the increase between the gloss values before and after cleaning of the PLA samples may be also attributed to the residual sebum soil that renders glossier the printed PLA surface, which inherently has a very small gloss value. Conclusively, the most significant gloss variation was a result of inadequate cleaning and not of aggressive behavior of the cleaning agents affecting the plastics that could cause significant surface alterations, such as scratches or blemishing.

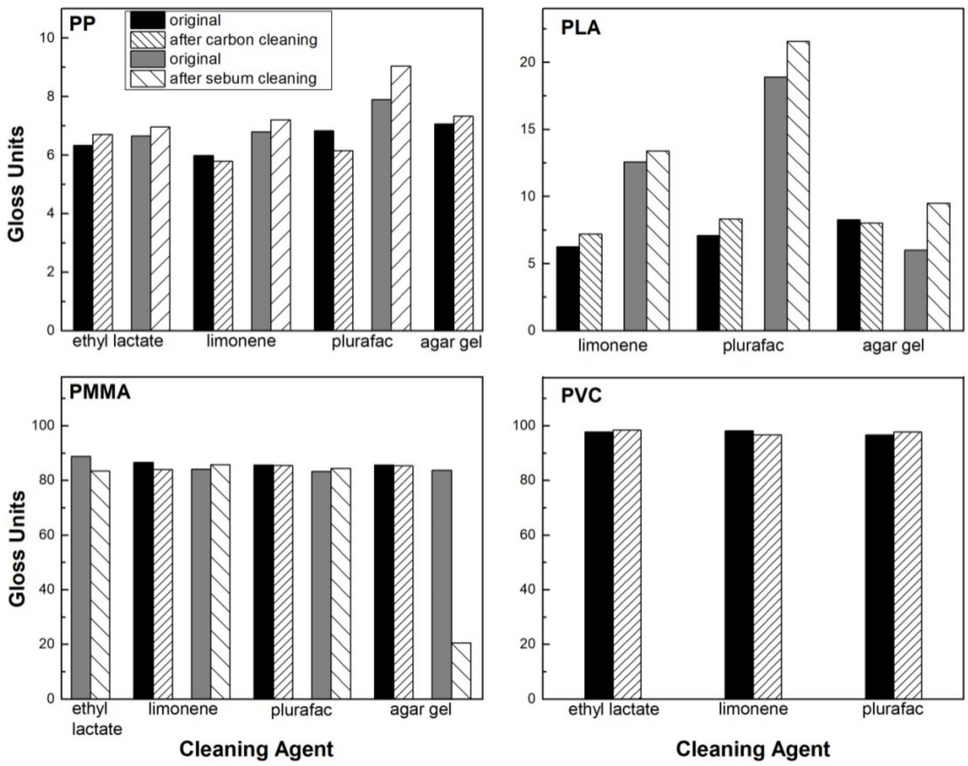

Figure 8. Gloss values of untreated PP, PLA, PMMA and PVC surfaces and after soil removal using biodegradable cleaning agents.

3.4. Ink Removal

After having collected all the encouraging data for the use of the specific biodegradable materials for the cleaning of plastic surfaces from soiling commonly encountered in museum objects and produced by air dust and handling of the objects, further tests were conducted on permanent ink removal. Permanent inks are often used for labelling and numbering museum objects together with a barrier coating [73]. There are cases where the conservators face the need to remove the ink in order to follow an alternative method of labelling [74]. During discussions with conservators, cases of plastic objects (e.g., plastic toys) in private collections marked directly on their surface were reported. Conservators have also expressed their concern about graffiti vandalism, especially in the case of outdoor art or design objects made of plastic. Ethyl lactate has been previously reported to efficiently remove ink from paint layers [8]. Since it has been proven to be safe for use on the plastics tested in the present research, except PLA, it would be interesting to evaluate its efficacy on ink removal from plastic surfaces as well. In parallel, Plurafac® solution was tested as well for comparison reasons. Blue (STAEDTLER Lumocolor®) and green (STABILO OHPen Universal) permanent inks were used to write on the samples. In general, both the selected biodegradable cleaning agents removed the inks sufficiently, with the ethyl lactate solvent being slightly more efficient, especially for the blue ink that was proved more resistant to removal. The removal of the inks from the PVC surface was trickier and incomplete, since the ink seemed to penetrate in the bulk of the sample. Plurafac® solution was an excellent cleaner for the green ink for the rest of the plastics while it did not completely remove the blue ink from the PLA (Figure 9) and PP surface.

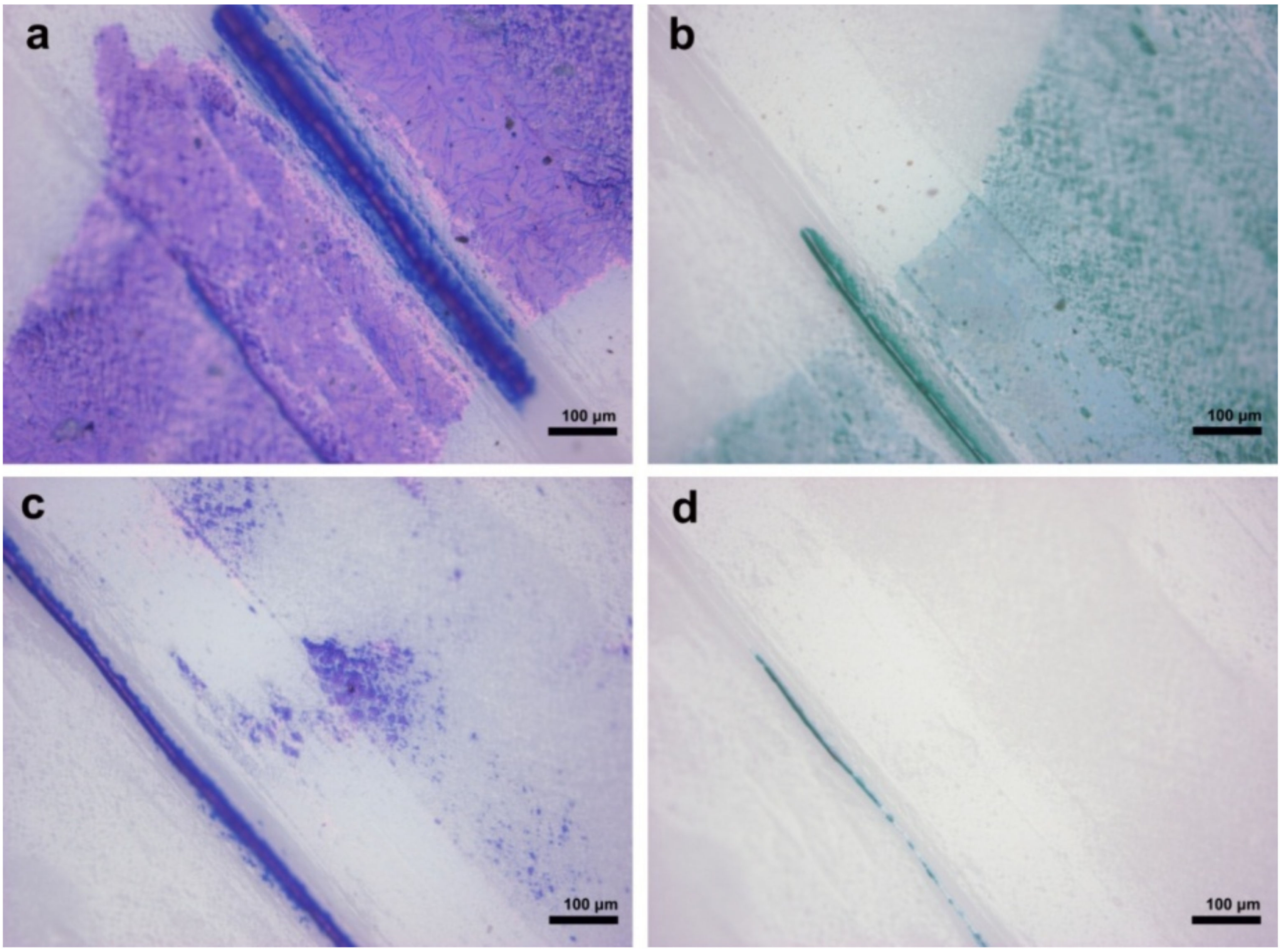

Figure 9. Optical Microscopy images of PLA (**a**,**b**) before and (**c**,**d**) after blue and green ink removal with Plurafac® solution.

4. Conclusions

The effect of the application of selected biodegradable materials for surface cleaning purposes on plastics, in the context of cultural heritage preservation, was studied. Besides water, agar gel, the MGDA chelate, the non-ionic surfactant Plurafac®LF900, and the organic solvents limonene and ethyl lactate were tested. The preliminary results obtained in this research using imaging techniques (OM, SEM, AFM) and Raman spectroscopy were very encouraging, showing, in general terms, the safety of these materials for the plastic surfaces with no remarkable changes to the morphology, chemical structure, or aesthetic appearance. Simultaneously, for most of the cases, a cleaning efficacy ranging from sufficient to very good, depending on the type of plastic and soil, was recorded. Evolon® CR microfiber cloth proved to be a safe material for the application of the cleaning agents, for all plastic types, preventing abrasion action.

The cleaning result of water was improved by the addition of the MGDA chelate and the non-ionic surfactant Plurafac®. Agar gel was efficient against carbon soil when applied as a hot (40–45 °C), viscous film, while in the form of eraser it caused morphological alterations and residue issues in most of the cases. The application temperature of the agar gel film depends also on the T_g of the plastic material, and it should not be very close to it. Plurafac® solution was shown to work well against carbon soil, i.e., for the removal of adhered particulate matter. Limonene solvent was both safe and effective for all plastics. However, a possible interaction with the plasticizer in PVC should be considered and further explored, preferably using quantitative analysis, for a better understanding of its use on plasticized PVC. Ethyl lactate adversely affected only the PLA. Its cleaning efficacy was very good for both sebum and carbon soil for the PP and PVC, but moderate for the PMMA. Regarding PVC, the plasticizer seems to be affected more or less by every cleaning agent tested. Due to the sticky nature of the plasticizer, which attracts dust, and its mobility in and out of the plastic bulk, preventive measures to avoid dust accumulation on PVC art objects would be highly recommended in order to minimize interventive cleaning treatments. Furthermore, the water sensitivity of 3D printed PLA that was demonstrated here necessitates the further investigation and adjustment of the aqueous treatment of this material in order to avoid water permeability and swelling effects. The surfactant solution and limonene solvent would be suggested as more appropriate cleaning agents, compared to ethyl lactate, for the surface cleaning of PMMA for the carbonaceous and sebum soil respectively. Positive results were also obtained from an exploratory use of Plurafac® solution and ethyl lactate for the permanent ink removal from the plastics.

It is of great importance that the type of plastic and the form of the object, e.g., 3D printed PLA, together with the topography and any additives such as plasticizers affect the overall cleaning result. Thus, a general cleaning protocol for all plastics is to be avoided and each case should be examined individually. The original topography and roughness of the plastic surface also influenced the amount of cleaning residues and the efficiency of the clearance procedure.

In this study, the specific effects and efficiency of each selected biodegradable cleaning agent were evaluated. As a future research step, a combination of them can be tested and evaluated, such as the addition of solvent in agar gel either for the improvement of the cleaning result or for the mitigation of the interaction between the cleaning agent and the plastic surface. Moreover, additional surface analysis techniques would certainly contribute to the development of safe protocols for the cleaning of plastics. Furthermore, life cycle analysis is also a significant parameter for the selection of cleaning agents in a sustainable museum and it would be interesting to use in future research. In the context of a sustainable approach to conservation practices for the benefit of the environment and human health, the results of the present research contribute by providing evidence for the suitability of biodegradable compounds as cleaning agents for the conservation of plastic museum objects.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/heritage4030115/s1, Figure S1: Raman spectrum of the commercial 3d printed PLA, Figure S2: Raman spectrum of commercial plasticized PVC, Figure S3: Control samples of (a) PLA, (b) PMMA, (c) PP and (d) PVC, Figure S4: OM images of PLA, PMMA, PP and pl.PVC carbon soiled samples before and after the cleaning with Plurafac® LF900 solution, Figure S5: Photographs of soiled and cleaned PLA samples, Figure S6: Photographs of soiled and cleaned PMMA samples, Figure S7: Photographs of soiled and cleaned PP samples, Figure S8: Photographs of soiled and cleaned pl.PVC samples, Figure S9: OM images of sebum soiled PLA, (a) control, and after cleaning with (b) agar gel film, (c) Plurafac® solution and (d) limonene, Figure S10: OM images of carbon soiled PMMA, cleaned with (a) DI water and (b) limonene, Figure S11: OM images of sebum soiled PMMA, (a) control and (b) after cleaning with ethyl lactate and (c) SEM image after cleaning with ethyl lactate, Figure S12: SEM images of carbon soiled PP, (a) control and after cleaning with (b) DI water and (c) MGDA chelate solution, Figure S13: OM images of sebum soiled PP (a) control and after cleaning with (b) MGDA chelate solution and (c) limonene, Figure S14: OM images of carbon soiled pl. PVC, cleaned with (a) MGDA chelate solution, (b) hot agar film and(c) agar in the form of eraser, Figure S15: OM images of sebum soiled pl. PVC, (a) control, and after cleaning with (b) MGDA chelate solution and (c) limonene, Table S1: Details of the cleaning procedure followed for the artificially soiled samples, Table S2: List of the Hansen solubility parameters of the selected compounds, Table S3: Ra values between the selected compounds.

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