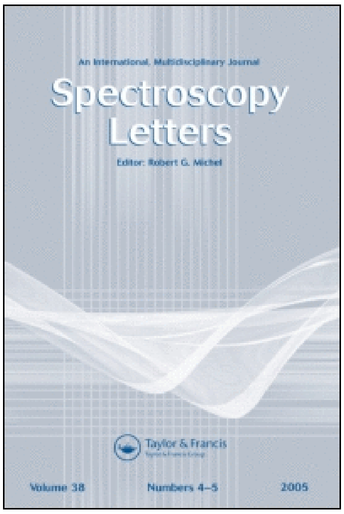

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Monitoring of Pictorial Surfaces by mid-FTIR Reflectance Spectroscopy: Evaluation of the Performance of Innovative Colloidal Cleaning Agents

Emiliano Carretti[a]; Francesca Rosi[b]; Costanza Miliani[c]; Luigi Dei[a]
[a] Department of Chemistry and Consortium CSGI, University of Florence, Sesto Fiorentino (FI), Italy [b] Department of Chemistry, University of Perugia, Perugia, Italy [c] CNR-ISTM (Institute of Molecular Science and Technologies) Perugia Unit, Perugia, Italy

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Monitoring of Pictorial Surfaces by mid-FTIR Reflectance Spectroscopy: Evaluation of the Performance of Innovative Colloidal Cleaning Agents

Emiliano Carretti
Department of Chemistry and Consortium CSGI, University of Florence,
Sesto Fiorentino (FI), Italy

Francesca Rosi
Department of Chemistry, University of Perugia, Perugia, Italy

Costanza Miliani
CNR-ISTM (Institute of Molecular Science and Technologies)
Perugia Unit, Perugia, Italy

Luigi Dei
Department of Chemistry and Consortium CSGI, University of Florence,
Sesto Fiorentino (FI), Italy

Abstract: This study reports the use of mid-FTIR reflectance spectroscopy to evaluate the efficiency of an innovative method to remove aged polyacrylic resins from porous carbonate surfaces. Acrylic copolymers have been extensively used in recent decades as protectives and consolidants of frescoes. However, their aging produces both yellowing and serious degradation of painted layers, necessitating their removal. The evaluation of the performance of a method aimed to remove such aged polymers is often a crucial and critical problem. The innovative technique proposed here is based on the use of mid-FTIR reflectance spectroscopy in optical fibers to check the reliability of an innovative colloidal cleaning agent, namely an oil-in-water microemulsion, constituted of a four-component system consisting of water as the continuous

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Address correspondence to Luigi Dei, Department of Chemistry and Consortium CSGI, University of Florence, via della Lastruccia, 3 I-50019, Sesto Fiorentino (FI), Italy. E-mail: dei@csgi.unifi.it

phase, sodium dodecyl sulfate as the surfactant, 1-pentanol as the cosurfactant, and *p*-xylene as the dispersed phase. The efficacy of this innovative method has been tested first in the laboratory and then on the surface of a Renaissance fresco by Spinello Aretino in the Cappella Guasconi at San Francesco Cathedral (Arezzo, Italy). Through mid-FTIR reflectance spectroscopic measurements performed *in situ*, the efficiency of the treatment has been proved, demonstrating that the nanotechnology approach represents a new, safe, and very efficient way of removing aged polymers from fresco surfaces.

Keywords: FTIR spectroscopy, fiber optics, cultural heritage conservation, nanotechnology

INTRODUCTION

Polyacrylic resins have been extensively used in the conservation of frescoes since the 1960s to restore strength of weathered mortar, to improve paint layer adhesion, and to protect painted surfaces from pollution.[1,2] Their aging nowadays poses significant unforeseen problems.

First of all, polyacrylic resins, as consequence of photo-aging, may yellow due to the formation of oxidation products [3] or conjugated double bonds systems.[4,5] The yellowed protective layer needs to be removed to restore the original chromatic appearance of the painting.

Second, in mortar samples simulating a real fresco it has been observed that physicochemical properties such us capillary rise, wettability, and water vapor permeability are all highly affected by the presence of acrylic resins. In fresco conservation, all these properties are extremely important, therefore the presence of acrylic polymers in some specific cases can account for degradation reoccurrence after restoration.

Third, it is well-known that much damage to porous materials is due to the mechanical stresses connected with the repeated cycles of crystallization/solubilization of salts into the porous matrix.[6] The salt crystal pressure p_c on the pore wall is expressed by the following equation:[7]

$$p_c = p_e + \gamma_{LV}\kappa_{LV} + \gamma_{CL}\kappa^E_{CL}$$

where p_e is the pressure in the liquid, γ_{LV} and γ_{CL} are the surface tensions at the liquid/vapor and at the crystal/liquid interfaces, respectively, and κ_{LV} and κ^E_{CL} are the curvatures of these interfaces. Being, the curvature of the crystal κ^E_{CL} expressed as the ratio $\kappa^E_{CL} = 2/(r_p - \delta)$, the crystal pressure is strictly related to the pore radius r_p. As the application of acrylic copolymers causes the shift of the pore size distribution toward narrower values,[8] it can cause a remarkable increase in the mechanical stress in the porous matrix. Finally, resin removal is necessary when the painted surfaces need to be re-restored.

Recently, acrylic resins have not been found to follow the principle of reversibility, which requires that all the incompletely physicochemically compatible materials used in conservation treatment should be removable without causing damage to the art object. Due to oxidation processes, acrylic resins undergo simultaneous cross-link and depolymerization, and these latter processes do not make acrylic resins any more soluble.

Today, the removal of aged acrylic resins is carried out by applying solvents with increasing solubility parameter using the compress technique.[9] The main limitations of the current method are 1) the volatility and the toxicity of organic solvents used in nonaerated places, and 2) the spreading of solubilized materials into porous artwork. In order to overcome these limitations, we have focused our research on microheterogeneous systems, specifically oil-in-water microemulsions.[10] One of the first cleaning systems based on the use of microemulsions was successfully set up in 1991 by Ferroni et al. during the recovery of frescoes by Masaccio and Masolino at the Cappella Brancacci in Florence. In this pioneer workshop, hydrophobic organic deposits, mainly composed of candle wax, were selectively removed from the fresco surface using a dodecane-in-water microemulsion.[11]

Considering the high efficiency of the dispersed systems as solubilizing [12–16] and extracting [17] agents and the wide range of components that can be employed in their preparation, it is possible that dispersed systems can be used for the removal of a wide variety of organic matters such as waxes, grease, synthetic polymers, proteinaceous materials and so forth. The oil-in-water microemulsion approach seems to overcome the above-mentioned limitations of the traditional method. The penetration of the solubilized material into pores is avoided by solubilizing the polymer both into the core of the oil microdroplets and at the interface between them and the continuous aqueous phase. In fact, the hydrophilic nature of the cleaning agent matrix blocks the penetration of the extracted acrylic resins as they have affinity toward the dispersed phase.

Moreover, the oil-in-water microemulsion approach produces a remarkable impact reduction for both the environment and the conservators, considering that the organic solvent contained in the microemulsion systems is very low.[18–21]

The aim of this work was to evaluate, for the first time as far as we know, the efficacy of this innovative cleaning method for extraction of aged acrylic polymers from porous matrices both on laboratory samples and in a real case study by means of a noninvasive technique based on the use of mid-FTIR reflectance spectroscopy with optical fibers.

The acrylic copolymer investigated was the binary copolymer of ethylmethacrylate/methylacrylate: poly(EMA/MA) 70/30, Paraloid B72, because it has been one of the most widely used in conservation since the end of the 1960s.[22–26] In this study the microemulsion was tested on mortar samples coated with poly(EMA/MA) 70/30, and the recovery of noncoated mortar physicochemical parameters was used to test the cleaning efficacy.

Microemulsion was also successfully tested in the removal of a 40-year-old poly(EMA/MA) layer covering a fresco by Spinello Aretino (16th century) at the San Francesco Cathedral at Arezzo, Italy.[10,27] Fiberoptic mid-FTIR measurements permitted nondestructive checks *in situ* not only for cleaning efficiency but also for the harmlessness of the tested method.

EXPERIMENTAL

1-Pentanol (1-PeOH, purity $>98.5\%$) and *p*-xylene (purity $>99.5\%$), were purchased from Merck (Darmstadt, Germany) and used as received. Sodium dodecyl sulfate (SDS) (purity $>98.5\%$), supplied by Merck, was purified according to the procedure reported elsewhere,[28] Poly(EMA/MA) was purchased from Zecchi (Florence, Italy). *p*-Xylene [p.a., $\geq 99.5\%$ (GC)] and quartz sand (40–100 mesh) were used as received from Fluka (Buchs, Switzerland). For the capillary rise absorption measurements, Whatman ash-less filter papers were used (Ø = 10 cm). Water was purified by a Millipore (Billerica, MA, USA) MilliRO-6 plus MilliQ (Organex System) apparatus: the resistance of the ultrapure water was $> 18\,\mathrm{M\Omega\,cm}$.

The porous samples used for the laboratory tests were prepared from a mixture of pure quartz sand with slaked lime in the 1:3 lime/sand volume ratio according to the literature data.[8] During the carbonation period, the samples were maintained under controlled environmental conditions ($T = 25°C \pm 1$ $RH = 52\% \pm 1$).

The copolymer as *p*-xylene solution (4% by weight) was uniformly applied on the sample surface. The coated samples were maintained at controlled environmental conditions ($T = 25°C \pm 1$ $RH = 52\% \pm 1$) for 48 hr and then dried at $45 \pm 5°C$ in an oven until a constant weight was reached. The average amount of coating was $9.80 \pm 0.01\,\mathrm{mg/cm^2}$.

The composition of the microemulsion tested as solubilizing agent for acrylic coatings is reported in Table 1.

The microemulsion was prepared by dispersing 1-pentanol in an aqueous solution of sodium dodecyl sulfate (SDS). 1-Pentanol was gradually added under stirring at 25°C. The system, initially opalescent, became suddenly limpid after a few minutes. Then, the dispersed phase (*p*-xylene) was

Table 1. Composition of the microemulsion tested

Components	% By weight
Sodium dodecyl sulfate	4
Water	86
1-Pentanol	8
p-Xylene	2

added, and the system was maintained under stirring until a macroscopically clear solution was obtained.

The microemulsion was applied by means of the wood poultice compresses technique.[9] The compresses were left in contact with the surface for 2.5 hr; during this time the temperature was maintained at 25°C. To avoid direct contact between the compress and the fresco, the painted surface was protected by Japanese paper sheets. Furthermore, to minimize the evaporation of the microemulsion components, the compresses were partially sealed to the painted surface using poly(ethylene) films. After the removal of the compresses, several washings by deionized water were done to remove any residue of the solid surfactant. All other microemulsion components are highly volatile, so they do not require to be manually removed.

Capillary absorption coefficients κ (expressed as $\mathrm{g\,cm^{-2}\,s^{-1/2}}$) [29] and water vapor permeability (expressed as $\mathrm{g\,cm^{-2}\,day^{-1}}$) [30] measurements were performed, as indicated in literature,[8] at controlled temperature and relative humidity ($T = 25°C \pm 1$ $RH = 52\% \pm 1$).

Contact angles values were also determined;[31,32] the measurements were performed with a NRL Ramé-Hart Inc. (Netcong, USA) goniometer interfaced with a PC. Water droplets (5 μL) were put onto the mortar surface using 10-μL Hamilton (Bonaduz, Switzerland) microsyringe, and the contact angle was determined 5 s after the deposition. Contact angle measurements were carried out for each droplet, and then the value at time equal to zero ϑ_0 was extrapolated.

SEM micrographs were performed using a Philips 515 (Rotterdam, NL) scanning electron microscope after graphitization of the samples with a JEOL JEE 4B (Japan) apparatus.

Reflectance FTIR spectra were recorded both in laboratory and *in situ* using a portable Jasco VIR 9500 (MD, USA) spectrophotometer equipped with a Remspec (USA) mid-infrared fiberoptic sampling probe. The bench, made up of a Midac Illuminator IR radiation source, a Michelson interferometer, and a liquid nitrogen-cooled MCT (mercury cadmium telluride), weighed about 35 kg and had an overall dimension of $50 \times 50 \times 50\,\mathrm{cm}^3$. The fiberoptic probe was a bifurcated cable containing 19 chalcogenide glass fibers, 7 of which carried the infrared radiation from the source to the sample, while the other 12 collected the radiation reflected off the surface. The chalcogenide glass fibers allowed the collection of spectra from 4000 to 900 cm^{-1}, having an excellent signal-to-noise ratio throughout the range, except in the 2200–2050 cm^{-1} region due to the glass fiber Se–H stretching absorption.

The fiberoptic probe was designed for normal incident measurements (0°/0° geometry) and did not allow off-line configurations. We tested that slight inclinations with respect to the 0°/0° geometry, due to repositioning errors, do not affect the spectrum sensitively. The distance between probe and surface was fixed at about 5 mm by a distance device. Again, we tested that distance repositioning errors do not affect relative absorption band intensity, even if the signal-to-noise ratio decreases with the distance. The investigated width of the sample area, as determined by the probe diameter, was about 4 mm. Single beam background reference spectra acquired on a aluminum mirror plate were perfectly reproducible and were not effected by repositioning errors or fiber stress. Background reference spectra were acquired frequently to properly correct the effect of environmental humidity. Sample spectra were the ratio of 200 sample to 200 background scans with resolution of 4 cm^{-1}. At least three spectra were made and averaged for each sample. When necessary, Kramers Kronig transform was calculated by the Jasco instrument software. Before performing the measurements, the cleaned surface was allowed to dry for about 3 hr.

RESULTS AND DISCUSSION

Acrylic copolymer films dramatically alter both the wetting and the transpiration properties of the solid porous surface on which they are spread.[8] So, to check how the interface properties vary with the cleaning compared, the trend of contact angle, water vapor permeability, and capillarity were measured on four samples that underwent the same treatments.

Figure 1 shows that the water vapor permeability of the porous material surface decreases by about 50% due to the polyacrylic resin application

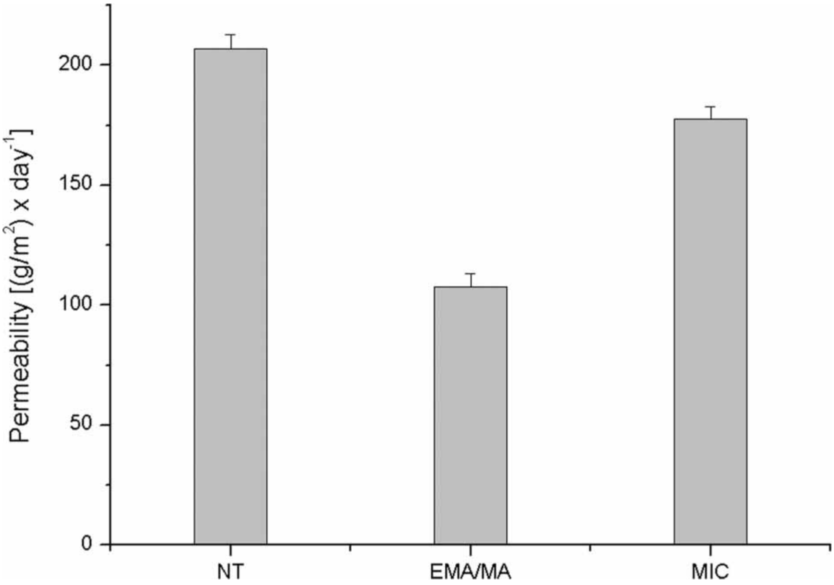

Figure 1. Water vapor permeability coefficient values for mortar samples untreated (NT), treated with acrylic copolymers [poly(EMA/MA)], and cleaned with the oil-in-water microemulsion (MIC).

(from 207 to 108 $g\,m^{-2}\,day^{-1}$). Although the transpiration of the water through the surface was not completely annulled, a drastic increase (between 40% and 50%) of the time needed to permeate through the porous support was observed. The decrease in the rate of water transpiration is one of the principle negative side-effects related to the use of polymer-based coatings in art conservation.

Permeability measurements were also repeated after the application of the oil-in-water microemulsion. The value of this parameter after the extraction of the copolymer was close to the pure mortar value, which meant that the most of the organic layer was removed and that the permeability of the mortar was almost recovered.

In Fig. 2, capillary coefficient κ values of the mortar samples are reported before and after the application of the surface poly(EMA/MA) layer, and also after cleaning by means of oil-in-water microemulsion. After the surface deposition of the copolymer, a loss of about the 90% of the capillary absorption power was observed: κ decreased from an initial value of $0.092\,g\,cm^{-2}\,s^{-1/2}$ for the bare mortars until $0.008\,g\,cm^{-2}\,s^{-1/2}$ for the coated samples (see Fig. 3). The decrease in both the water absorbed (the value of the asymptote in Fig. 3) and of the rate of capillary suction (the slope of the initial straight line) demonstrates that a marked alteration is induced by the deposition of the copolymer in the physicochemical properties of the interface. A further datum confirming this observation

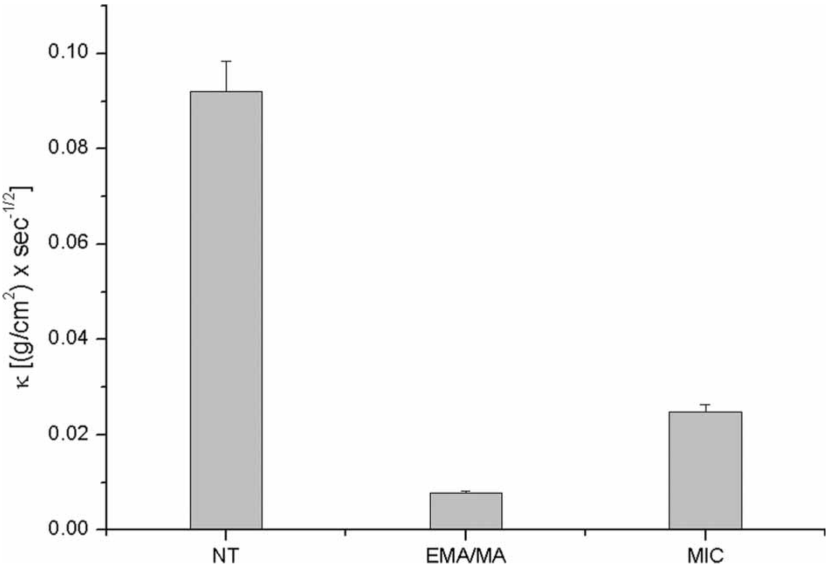

Figure 2. Capillary absorption coefficients for mortar samples untreated (NT), treated with acrylic copolymers [poly(EMA/MA)], and cleaned with the oil-in-water microemulsion (MIC).

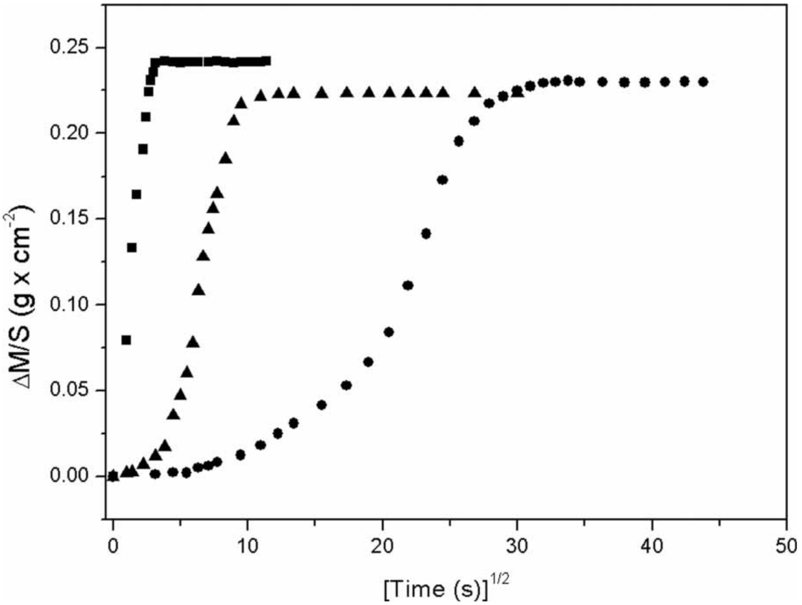

Figure 3. Capillary rise curves for mortar samples untreated (squares), treated with acrylic copolymers (triangles), and cleaned with the oil-in-water microemulsion (circles).

was the time needed for each sample to reach the asymptote in Fig. 3: this parameter varied from ~9 s for the pure mortar until up to about 900 s for the poly(EMA/MA)-coated sample (Fig. 3). The appearance of an induction time (about 150 s) was also observed, indicating an initial resistance to water capillary suction at the solid–liquid interface. The efficacy of the application of the microemulsion as a solubilizing agent is indicated in both Figs. 2 and 3 described above. First of all, the capillary absorption coefficient κ went back up to $0.025\,\mathrm{g\,cm^{-2}\,s^{-1/2}}$ (Fig. 2), then the capillary power was almost recovered. In this direction, at the same time, the rate of capillary suction increased, too (Fig. 3), and a drastic decrease in the induction time (until ~4 s) was observed.

Furthermore, the wettability of the surface was immediately reduced by the application of the copolymer; the contact angle at the interface water/porous matrix, increased about 60% after the copolymer deposition (from 32° ± 7° up to 88° ± 3°; Fig. 5). This trend was confirmed by the contact angle values collected from the surface of a frosted glass both before and after the application of a surface layer of poly(EMA/MA).[10] After the application of the microemulsion, a strong decrease in the contact angle was observed. This demonstrated a good solubilization of the acrylic copolymer in the microemulsion system with the consequent detachment and removal of the hydrophobic film from the surface of the substrate. Gravimetric

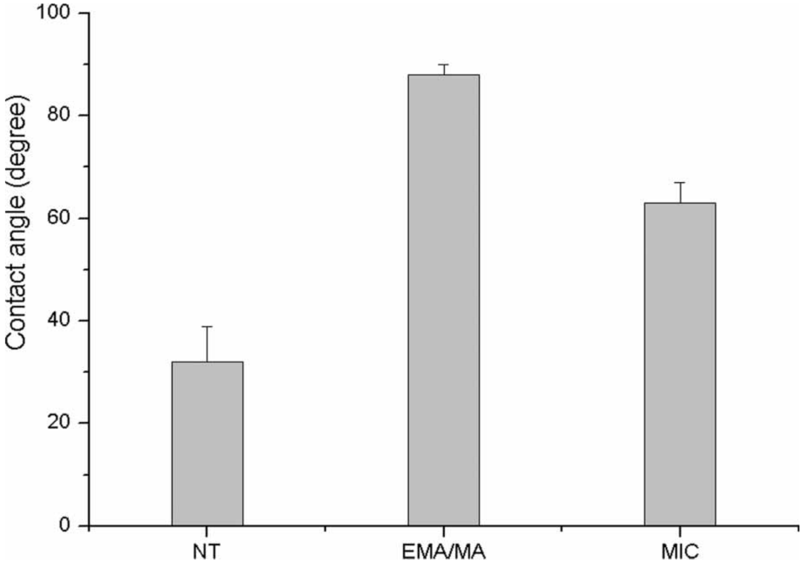

Figure 4. Contact angle measurements for mortar samples untreated (NT), treated with acrylic copolymers [poly(EMA/MA)], and cleaned with the oil-in-water microemulsion (MIC).

measurements further confirmed polymer solubilization: the acrylic copolymer extraction was always $>95\%$.

However, the slightly different values of all the physicochemical parameters investigated after the cleaning procedure, with respect to the untreated mortar, can be associated with the residual fraction of the acrylic copolymer ($<5\%$) that remained in the porous matrix. For example, it could modify the three-phase contact line of the water drop on the surface to prevent attainment of the before-treatment wettability value. The residual copolymer still in the porous matrix prevented the complete recovery of the original values both of permeability and capillary rise property.

The morphology of the mortar surface was investigated by SEM. The main effect after the acrylic copolymer layer deposition was with respect to the pure mortar (Fig. 5a)[33] the surface appeared smoother (Fig. 5b) and partial occlusion of the pores with diameter in the range of tenths of micrometers occurred. After the cleaning process, the mortar surface morphology looked like that of nontreated sample and the pores were reopened (Fig. 5c). In agreement with the data discussed above, the SEM observations confirmed that the application of the microemulsion partially caused the recovery of bare mortar properties.

In order to set up a noninvasive spectroscopic tool to be used *in situ* for the evaluation of microemulsion efficacy in removing acrylic polymers, mid-infrared fiberoptic reflectance measurements were performed in the laboratory

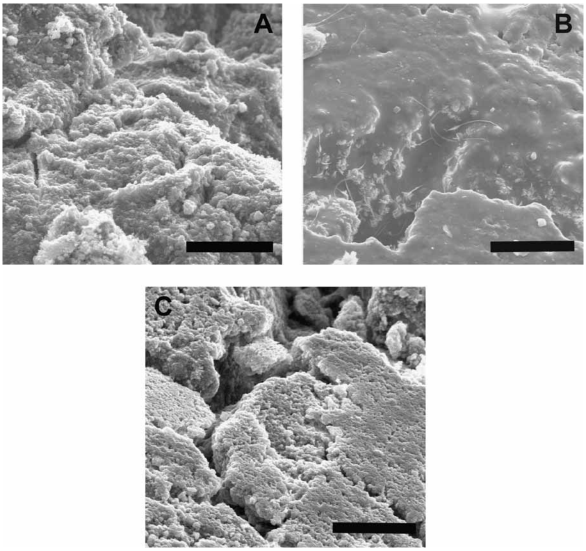

Figure 5. SEM micrographs of mortar samples treated with poly(EMA/MA): (A) untreated sample; (B) treated with poly(EMA/MA), (C) treated with poly(EMA/MA) and cleaned with the oil-in-water microemulsion. Bar = 50 μm.

on 1) bare mortar samples; 2) poly(EMA/MA)-coated mortar samples; and 3) poly(EMA/MA)-coated mortar samples cleaned using the tested microemulsion. IR external reflectance measurements present spectral distortion mainly related to the optical layout, sample concentration, and band strength. The optical layout depends on both the sampling geometry and the sample surface microstructure. Using a 0°/0° sampling geometry, both specular and diffuse reflectance are collected, hence the spectra show a mixed character, with a prevalence of specular features from smooth and flat surfaces and a prevalence of diffuse features from rough and coarse surfaces.

The reflectance spectrum of bare mortar surface is shown in Fig. 6a in comparison to a calcium carbonate standard transmittance spectrum. It exhibits primarily diffuse reflectance features owing to the rough surface microstructure of the mortar, as visible in the SEM micrograph of Fig. 5a. The combination bands at 1795 and 2520 are clearly visible, while the ν_3 stretching absorption (at 1420–1540 $\mathrm{cm^{-1}}$) shows an anomalous behavior due to a specular contribution distorted by the change of refractive index.[34] The absorptions in the range 2870–2995 $\mathrm{cm^{-1}}$ are due to combinations bands of CO_3^-, while sharp bands at 3640 $\mathrm{cm^{-1}}$ are assigned to the OH stretching of unreacted $Ca(OH)_2$. Spectra recorded at different points of bare mortar samples were quite reproducible regarding the relative intensity of CO_3^- bands, while the intensity of the $Ca(OH)_2$ band varied from 10% to 40%.

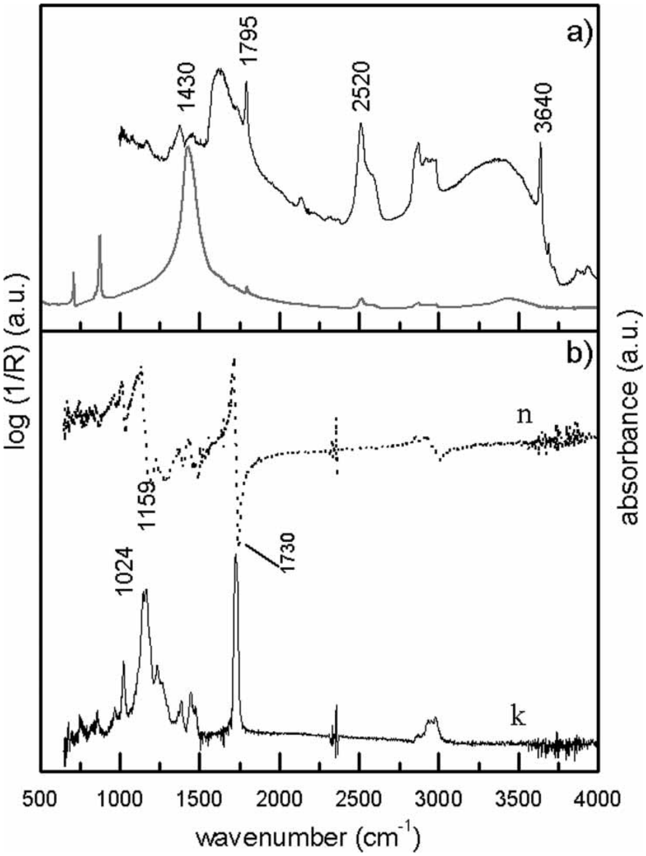

Figure 6. Reflectance mid-FTIR spectrum of mortar sample (a) and optical properties of poly(EMA/MA) (b).

A self-consisting poly(EMA/MA) film, 2-mm thick, was used as reflection standard; it showed a pure specular reflection behavior, hence the spectrum was treated by the Kramers–Kronig transform to obtain the refractive index (n) and absorption index (k). The optical properties of poly(EMA/MA) are reported in Fig. 6b. The principal absorption at 1730 cm^{-1} is assigned to the stretching of the C=O ester group. Because this signal lies in a spectrum region quite free from carbonate absorption, it was chosen to allow the cleaning treatment to be followed.

The reflectance spectra of the stratified system made of poly(EMA/MA) film on the carbonate matrix is shown in Figs. 7a and 7b. As expected, only the 1730 signal of acrylic resin (stretching of C=O ester group) is easily differentiated from the substratum absorbance. When the acrylic layer is thick and smooth, the carbonyl signal shows a derivative shape, due to specular reflection (Fig. 7a). When the acrylic coating is thin and quite rough, as

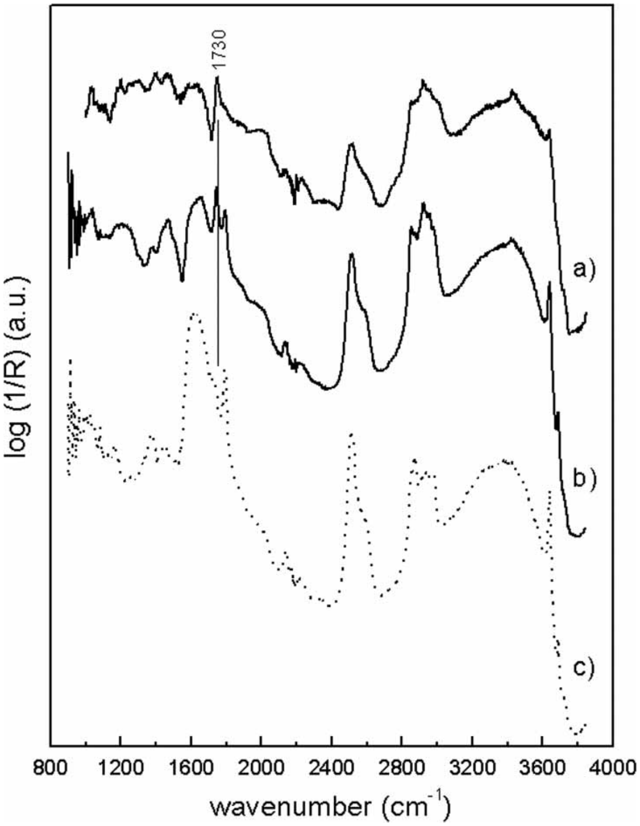

Figure 7. Reflectance mid-FTIR spectra of surface of poly(EMA/MA)-coated sample before (a) and after (b) the cleaning process. Dotted line spectrum is that of bare mortar sample (c).

shown in the SEM micrograph (Fig. 5b), the carbonyl signal exhibited a shape similar to an absorption band, due to diffuse reflection (Fig. 7a). Spectra recorded at different points of poly(EMA/MA)-coated mortar sample were reproducible when the acrylic layer is thick and smooth; diversely, on thin coatings consecutive spectra showed differences in the relative intensities of matrix and acrylic bands.

The disappearance of the 1730 signal can successfully account for the polymer removal, as shown in Fig. 7 where the spectrum from a sample cleaned with the microemulsion (c) is compared with that of a bare mortar sample (d).

Particularly, in Fig. 8 the diagnostic spectral regions of C═O stretching (1700–1850 cm^{-1}) and C–H stretching (2800–3000 cm^{-1}) are reported, showing a comparison between coated, cleaned and bare mortar sample. The ester stretching, clearly visible at 1730 cm^{-1} for the coated sample

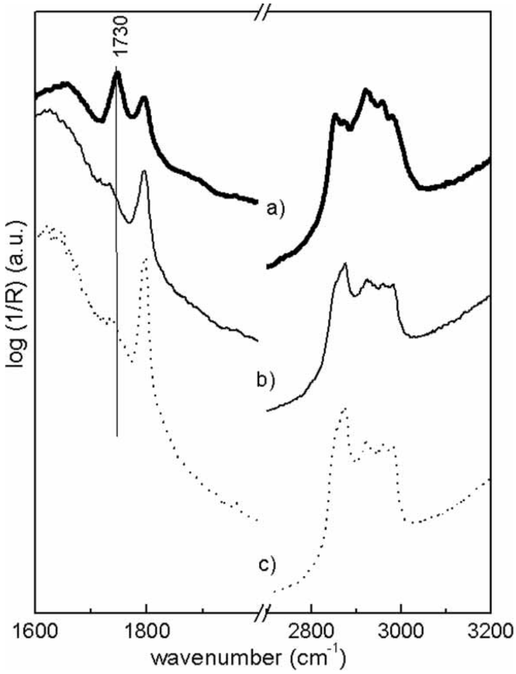

Figure 8. C=O and C–H stretching regions of spectra recorded on poly(EMA/MA)-coated sample: before the cleaning (a), after the cleaning (b), compared with that recorded on bare mortar sample (c).

(spectrum 8a), is almost absent for the cleaned sample (spectrum 8b). It has to be noted that the shoulder at 1720 cm^{-1} in the spectrum of cleaned sample is due to the carbonate matrix rather than to a residual polymer, being visible also in the spectrum of bare mortar sample (8c). As regards the C–H stretching region (Fig. 8), it is evident that after cleaning the spectral features changed (with a decrease of absorption at 2920 cm^{-1}), becoming similar to that of combination band of carbonate matrix.

Spectra recorded on different points of cleaned mortar sample were not always reproducible, showing in some case a weak absorption at 1730 and 2920 cm^{-1} due to residual polymer.

Microemulsion was also tested on a real workshop: the frescoes of the Renaissance fresco by Spinello Aretino in the Cappella Guasconi at San Francesco Cathedral (Arezzo, Italy). Through nondestructive mid-FTIR measurements performed *in situ*, the efficacy of the treatment as well as the long-term stability was proven.

The painting was coated with a thick layer of an acrylic resin during a restoration 40 years prior. The painting polychromy was so affected by the acrylic coating that all the colors appeared dark and shiny. As a consequence, the infrared reflectance spectrum of the surface exhibited a strong specular feature in the region of carbonyl absorption, as shown in Fig. 9a.

So, the necessity to remove the copolymer layer, in this case, was not only related to the need to reestablish the physicochemical status of the original fresco but more important to recapture its original beauty.

Microemulsion was applied following the wood poultice technique (2 hr of application, temperature between 20°C and 23°C) and washing the cleaned surface twice with isopropanol and several times with deionized water until the residual surfactant foam disappeared.

The reflectance spectrum of the cleaned surface showed clearly that the acrylic layer had been successfully removed, since the carbonyl signal at

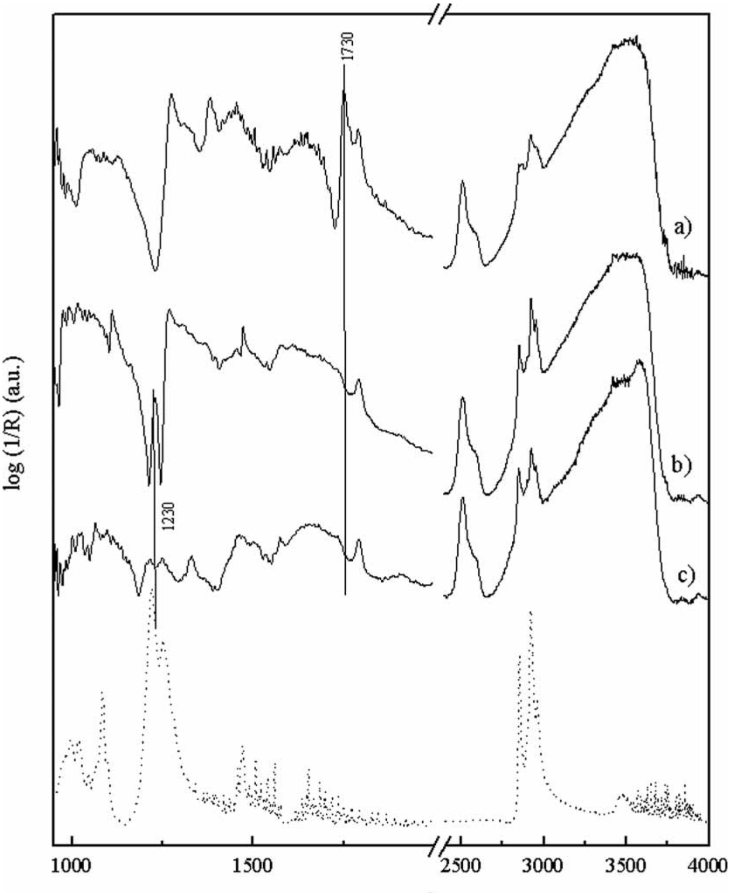

Figure 9. Reflectance mid-FTIR spectra of fresco surface: before the cleaning (a), after the cleaning (b), and after the ammonium carbonate treatment (c). Dotted line spectrum is that of sodium dodecyl sulfate.

1730 cm^{-1} disappeared completely (Fig. 9b). The results obtained were in agreement with those obtained from the analysis of microsamples taken from the fresco surface.[10] Additionally through the reflectance surface analysis, new signals at about 1230 cm^{-1} and 1080 cm^{-1} were observed, next to the carbonyl band disappearing. These bands, strongly affected by specular distortion, were assigned to the SO_4^- vibrations of residual surfactant by comparison with a sodium dodecyl sulfate spectrum (Fig. 9). After an additional treatment with saturated solution of ammonium carbonate, the resultant surface was perfectly clean as shown by the features of spectrum (c) in Fig. 9.

CONCLUSIONS

The cleaning method, consisting of SDS/1-PeOH/*p*-xylene/water oil-in-water microemulsion applied by the compression technique, is a reliable alternative for removing aged acrylic polymer from the surfaces of frescoes. Compared to the traditional method, the proposed approach is both more respectful of the artwork and safer for the conservator. General applicability of the new cleaning method was proven by cleaning a 40-year-old coating on a Renaissance fresco. Field application was nondestructively monitored by the IR spectroscopic technique. Determining the cleanliness in this way, it was pointed out that special attention must be paid to the removal of the surfactant used in the cleaning processes. Additionally, this work fosters the nondestructive validation of conservation treatments. In fact, using the mid-IR spectral range and chalcogenide fiber-optics, a spectroscopic instrument capable of surface fresco analysis was set up. Several appealing aspects of reflectance mid-FTIR spectroscopy are the ability to discriminate a wide variety of organic and inorganic components from carbonate substrate, rapid analysis time, and capability for *in situ* application.

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