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Use of mid-infrared fiber-optic reflectance spectroscopy (FORS) to evaluate efficacy of nanostructured systems in wall painting conservation

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ABSTRACT Mid-infrared fiber-optic reflectance spectroscopy (Mid-IR FORS), a sensitive, non-invasive technique for determining chemicals present on a surface, has been used to test efficacy of oil-in-water microemulsions and micellar solutions in cleaning of painted surfaces. The target of the application of these innovative nanostructured systems was the selective removal of an undesired polymeric layer from a fresco surface. The experiments were carried out by first coating frosted glass slides and painted mortar simulating a real fresco with four acrylic and vinyl polymer varnishes commonly used in wall painting restoration. Spectra of the samples were then collected by means of microreflectance single-beam infrared spectroscopy and Mid-IR FORS before and after the application of the aqueous dispersed systems based cleaning agents. Sharp, strong peaks due to the stretching of the estereous C=O bond of the polymers in a wavelength range between 1730 and 1750 cm^{-1} were used as marker for the presence of these organic materials. Through Mid-IR FORS semiquantitative spectroscopy, the efficiency of the treatment has been clearly demonstrated, indicating that the nanotechnology approach represents a new, safe, and very efficient way of removing aged polymers from fresco surfaces.

PACS 82.35.Gh; 82.70.Uv; 82.80.Gk; 87.64.Je

1 Introduction

Polyacrylic resins and other synthetic varnishes, popular over the past few decades in fresco conservation, highly alter the physico chemical properties of the work of art [1]. Originally intended to protect surfaces from pollution, strengthen the mortar supports of the fresco, and improve adhesion of paint to the support [2, 3], it is now known that there are a number of circumstances in which synthetic polymers can be harmful to paintings and must be removed. Resins cause damage mainly by increasing brittleness of the fresco surface by two different simultaneous phenomena. One phenomenon is micro-crack formation both in the protective polymer layer of a painted surface and in the porous matrix. It is known that much damage to porous materials is

induced by the mechanical stresses due to the repeated cycles of crystallization/solubilization of salts that are present within porous matrix [4]. The salt crystal pressure p_c on the pore wall is expressed by the following equation [5]:

$$p_c = p_e + \gamma_{LV}\,\kappa_{LV} + \gamma_{CL}\,\kappa_{CL}^E\,, \qquad (1)$$

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, while κ_{LV} and κ_{CL}^E are the curvatures of these interfaces. Being, the curvature of the crystal $\kappa_{CL}^E = 2/(r_p - \delta)$, the crystal pressure is strictly related to the pore radius r_p. As the application of a surface polymer layer causes the shift of the pore size distribution toward narrower values [1], it can cause a remarkable increase in the mechanical stress in the porous matrix. The other simultaneous alteration is yellowing due to formation of oxidation products from the resins. This causes an alteration of the polychromy of the paint, changing the aesthetic quality of the artwork [6]. These reason often necessitate the removal of polymer varnishes.

Solubilization of the acrylic and vinyl polymers is commonly achieved by using organic solvents of appropriate polarities (less polar for acrylic and more polar for vinyl substances). The toxicity, the spreading into the works of art and porous structures of the works under restoration, limits the use of these simple organic solvents.

Systems that can locally remove the polymer with minimal interaction of underlying paint layers and a minimal environmental impact are necessary. Recently oil-in-water microemulsions and micellar solutions have been applied to solvating and removing these acrylic polymers with minimal impact on the paint layers. The efficacy of microemulsions and micellar solutions as solubilizing agents and a wide range of compositions it is possible to obtain [7–11], indicate that these systems can be used to selectively extract many organic substances of different chemical nature (grease, proteins, synthetic polymers etc.) that are often present as pollutants on the surface of works of art.

In this paper, non-invasive mid-infrared fiber-optic reflectance spectroscopy (mid-IR FORS) has been applied to monitor the presence of polymer on painted inorganic supports (Fig. 1) [12, 13] before and after their cleaning

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FIGURE 1 Painting on mortar (mock-fresco), coated with polymer, and with microemulsion compresses applied. Detail of fiber-optic reflectance probe-head measuring the sample surface (*top right*)

Type	Water	SDS	1-PeOH	*p*-Xylene	PC
μE	85.4	4	8	2.6	/
Sol Mic	69	3.9	5.1	/	22

TABLE 1 Composition (w/w %) of micellar solution and microemulsion [4]

by means of dispersed systems. Here controlled laboratory conditions are applied for the first time in monitoring presence of polymer varnish on inorganic supports by non-invasive infrared spectroscopy. Past work with this technique has focused on the reliability and reproducibility of using mid-IR FORS for painted and powdered samples [12], as well as on using principal component analysis (PCA) for characterization of media and/or colorants [14]. Furthermore, using portable mid-IR spectrophotometers, we could perform on-site non-invasive analysis on objects that cannot be moved from their current locations [15].

For all the polymers investigated, (Paraloid B72®, Elvacite 2046® Primal AC33® and Vinavil®) this paper reports the trend of the area of the infrared peak due to the stretching of the C=O estereous bond (between 1725 and 1750 cm^{-1}) before and after the application of the dispersed systems. Systems on both mortar and frosted glass were analyzed. With the sensitive, non-invasive method of fiber optic infrared analysis, one can semi-quantitatively verify the amount of polymer left on the surface after the cleaning action.

2   Experimental

1-Pentanol (1-PeOH, purity > 98.5%), *p*-xylene (purity > 99.5%), and propylene carbonate (purity > 99.5%) were purchased from Merck, Darmstadt, Germany and used as received. Sodium dodecyl sulfate (SDS) (purity > 98.5%) supplied by Merck, Darmstadt, Germany, was purified from ethanol following previous procedures prior to use [16]. Pellets of Paraloid B72®, poly(ethylmethacrylate (EMA)/methylacrylate (MA)), (poly(EMA/MA)), with EMA/MA mole ratio 70 : 30 and average molecular weight 80 000, Elvacite 2046® (EA/MMA 60/40) and Primal AC33® (aqueous suspension of nBMA/iBMA 50/50) were supplied by Zecchi, Florence, Italy. Vinavil® (aqueous suspension of polyvinyl acetate) was purchased from VINAVIL, Italy. Water was purified with a Millipore MilliRO-6 and MilliQ (Organex System) apparatus.

10%, 5%, and 2% by weight concentrations of vinavil, primal, elvacite and paraloid were prepared by solvating the polymers in purified water (for the former two) and purified acetone (for the latter two).

Microemulsions and micellar solutions were prepared by desolving the surfactant (SDS) in the needed amount of water (see Table 1), then the cosurfactant (1-pentanol) and the dispersed phase (*p*-xylene in the case of microemulsion and propylene carbonate in the case of micellar solution) are added until a clear system is obtained.
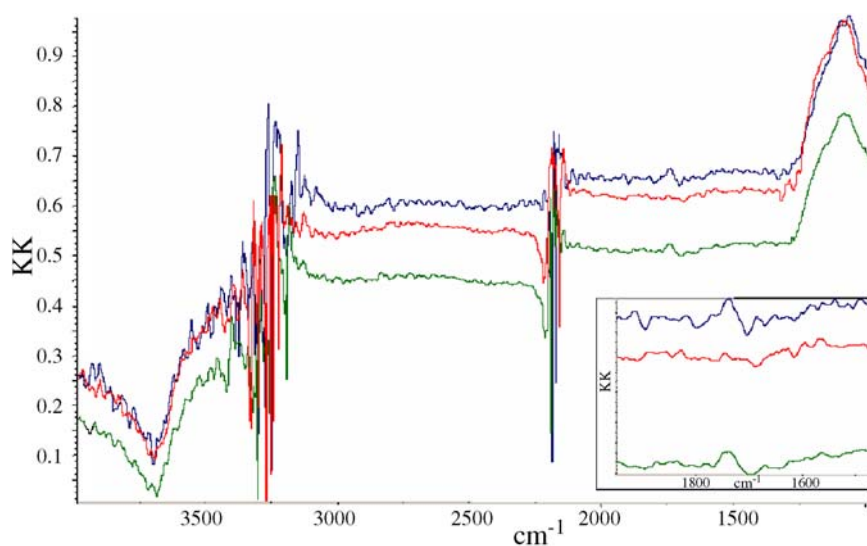
2.1   *On glass*

Each frosted glass slide was coated with one of the polymer solutions. Multiple spectra were collected (to account for slight variance in concentration in different areas of the slide) by both infrared microreflectance and mid-IR FORS in the 4000–850 cm^{-1} and 5500–980 cm^{-1} regions, respectively.

Both microemulsion and micellar solution were applied on the surface of the polymer coated frosted glass by means of wood poultice compress technique [17]. The contact time was 50 min. Once the compress was removed, and excess residue was removed too by washing twice with distilled water and cotton, multiple microreflectance and fiber-optic relfectance (FORS) spectra were collected on each washed area and the FORS spectra averaged.

Microreflectance spectra in the mid-infrared region were collected using a BioRad FTS-40 spectrometer equipped with a BioRad UMA500 microscope (MCT detector) with 8 cm^{-1} resolution and 128 scans.

Mid-IR FORS spectra were collected using a REMSPEC Mid-IR fiber-optic reflectance probe connected to a Nicolet Protégé FTIR spectrophotomer. Fiber optic bundle cables consisted of seven sending and twelve receiving 500 μm fibers. The detector module was a liquid nitrogen cooled 0.5 × 0.5 mm mercury cadmium telluride (MCT) detector. The experimental setup consisted of 256 scans at 4 cm^{-1} resolution. A gold-coated glass was used as the reflectance standard surface in the spectra collected on glass. Noise typically associated with chalcogenide fibers (in the 2200–2050 cm^{-1} range) [13], atmospheric carbon dioxide, and atmospheric moisture had no overlapping effect in the region of interest for detection of varnish polymers in the range of 1750–1720 cm^{-1}. All spectra were analyzed using OMNIC 5.1 software. For samples on glass Kramers–Kronig corrections were applied to yield absorption spectra from the acquired data (Fig. 2). For each variable (i.e., 10% Paraloid B72® coating cleaned with *p*-xylene emulsion), three spectra were collected, the area under the peak typical of polymer (in the range 1750–1720 cm^{-1}) was measured, and the three values averaged.

FIGURE 2 Kramers–Kronig corrected spectra of Paraloid at 2% concentration on glass collected by mid-IR FORS (a: on glass, b: cleaned by micellar solution, c: cleaned by microemulsion). Detail of enlarged typical polymer peak (*bottom right*)

Reference samples to determine where infrared spectra peaks lie were prepared by collecting mid-IR spectra using the instruments mentioned before and one drop of each pure, dried polymer on gold-coated glass.
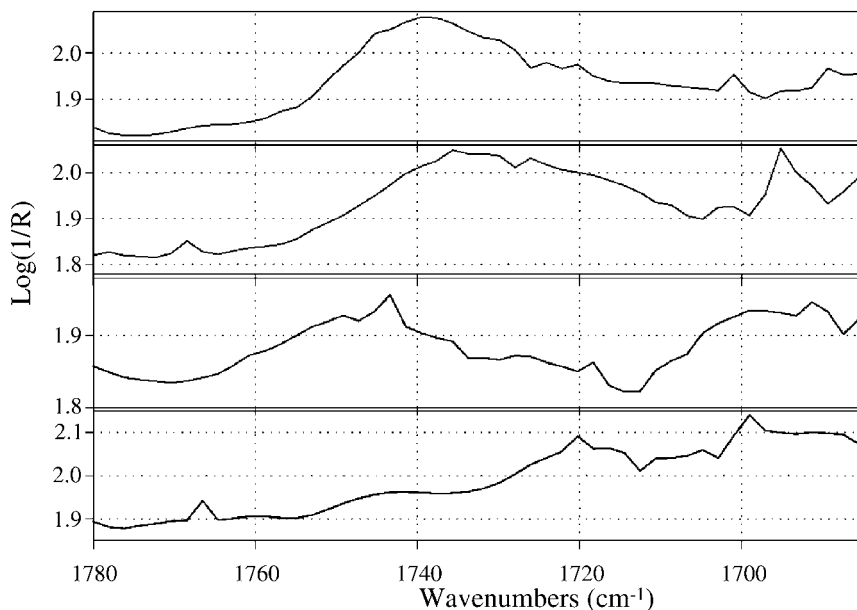
2.2   *On mortar*

The experiment on glass was then repeated on a mock-fresco painting; also in this case the contact time was 50 min. The residues of the cleaning systems were removed by H_2O rinsing as described above until the complete disappearance of the foam. The Kramers–Kronig function, used to correct high reflectance properties of the surface being studied, was only applied to conditions where Vinavil® was present on mortar. The area under single peaks typical of acrylic or polyvinyl resin (at 1724–1748 cm^{-1}) was calculated for each spectrum and averaged for each condition (Fig. 3).

The same mortar sample underwent a second cleaning and spectra were collected again in the same manner.

3   **Results and discussion**

As concentration of polymer used in coating both glass and painted mortar surfaces decreases, a general decrease in average area beneath carbonyl peak is observed, as reported in Fig. 2 (2% Paraloid B72® solution on glass) and 3 (10% Paraloid B72® solution on mock-fresco painting). In fact, Fig. 2 indicates that after the application of both the microemulsion and the micellar solution the area of the peak at 1740 cm^{-1} due to the presence of Paraloid B72® decreases (about 60% and 80%, respectively) indicating the partial efficacy of the extraction. A better performance can be achieved in two different ways. It is possible to increase the application time up to two hours, but also by means of a second application. In particular, in the case of mortar, Fig. 3 shows that

FIGURE 3 Absorbance (log $1/R$) spectra of Paraloid 10% concentration on mortar collected by mid-IR FORS. From *top* to *bottom*, the spectra show: Paraloid 10% on mortar, micellar-cleaned portion of paraloid 10% on mortar, portion after first cleaning by microemulsion, same portion after second cleaning by microemulsion
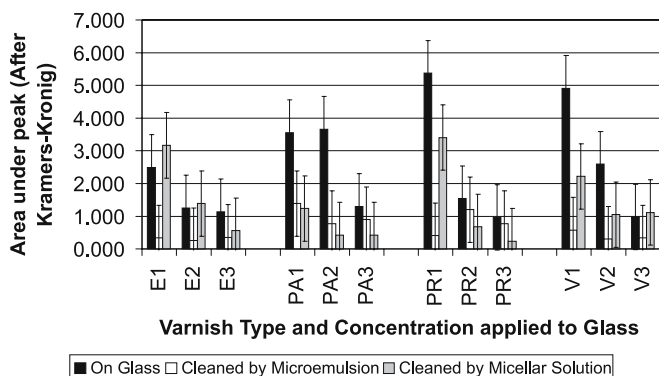
FIGURE 4 Numbers 1, 2, and 3 represent polymer concentration of 10%, 5%, and 2% in solution by weight respectively. Kramers–Kronig function was applied to E (Elvacite), PA (Paraloid), PR (Primal), and V (Vinavil) coated portions of frosted glass slides
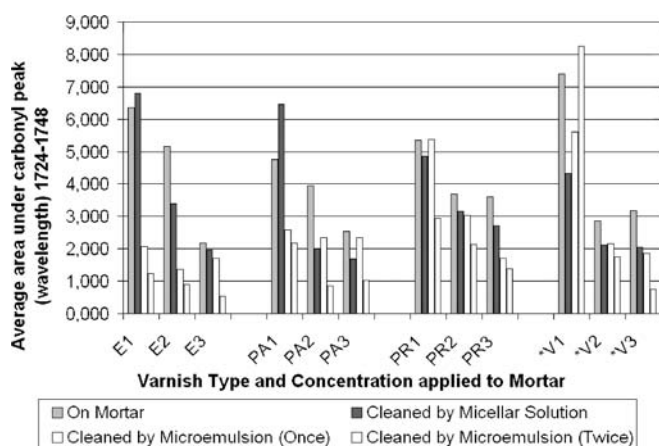
FIGURE 5 Numbers 1, 2, and 3 represent polymer concentration of 10%, 5%, and 2% in solution by weight respectively. Graphical values represent average area under peaks at 1724–1748 cm^{-1} collected by FORS spectroscopy for E (Elvacite), PA (Paraloid), and PR (Primal). Additional Kramers–Kronig function was applied before averaging peak area for V (Vinavil) coated portions of mortar

the peak area decreases to 40% of its initial value after a second application of the xylene-based microemulsion indicating a high improvement of the extraction treatment. Furthermore, cleaning with both microemulsions and micellar solutions generally decreases the absorption of 1750–1720 cm^{-1} frequencies indicating the partial removal of the hydrophobic polymer. These trends can be seen on both glass (Fig. 4) and mortar supports (Fig. 5). Figure 4 shows the trend of the peak area when glass was used as a support. The main result is that the micellar solution has a performance that is better than the one of the microemulsion. This result can be due to the much higher content of active phase (propylene carbonate) into this system rather than xylene in the microemulsion one.

An opposite behavior is observed in the case of the mock-fresco (Fig. 5). In fact, on this support the microemulsion performs better than the micellar solution. This trend is probably due to the microscopical architecture of the two different systems. In the case of the oil-in-water-microemulsion the solvent (*p*-xylene) is fully located into the hydrophobic core of the xylene nanodroplets, then the interaction with the polymer is driven by an interaction at the microdroplet/water

interface [18, 19]. On the other hand, in the micellar solution, being a ripartition equilibrium of the PC (60/40 w/w) between the continous phase and the micellar interface [20], the driving factors are both the interaction of the polymer at the interface and the solubility of the polymer into the PC.

Therefore in the case of the frosted glass, where the washing after the removal of the compresses can be carried out without any risk of leaving residues into the porous structure (it does not exist apart from the surface roughness) the better efficiency is in agreement with the large amount of the solubilizing agent (propylene carbonate). In the case of the fresco specimen, however, the washing cannot succeed in completely removing the extracted polymers, due to the tendency of the porous matrix to re-adsorb the solubilized polymer. Thus in the microemulsion the solubilized polymers are more confined in an apolar pool (the nanodroplets). The risk of remaining entrapped into the porous structure is reduced relative to the micellar solutions, where the solubilized polymer is 'not protected' by the nanodroplets structure and can be more easily adsorbed into the first wall painting layers.

In certain cases, such as propylene carbonate cleaning of Vinavil®, it appears there is no significant difference between the signal from cleaned 5% polymer and cleaned 2% polymer. The same is true of Elvacite and polyvinyl samples cleaned with *p*-xylene microemulsion. This could signify that the value represented for each is the maximum amount of polyvinyl that can be removed by this cleaning agent.

As the microemulsion yielded positive results for several varnish conditions (either complete or partial cleaning of polymer varnishes), it was chosen to be used again for samples on mortar. A second cleaning of samples (Fig. 5) on mortar also indicates that more cleanings further decrease the signal peak size in mid-IR FORS spectra.

On these supports microemulsion cleans polymer varnish better than a micellar solution. In every case that the cleaning system was applied a second time, clearance remained unchanged or improved. In cases in which no significant difference was seen after a first application of cleaning system, a second application showed significant clearance.

4 Conclusion

These first laboratory experiments to monitor polymeric resin clearance by microemulsion and micellar solutions have shown that the nanostructured systems can be very powerful and effective as cleaning agents in wall-painting conservation with very low environmental impact. Use of non-invasive spectroscopy has shown preliminary semi-quantitative results, and has potential as a powerful tool in testing efficacy in situ of polymer clearance for restored works of art. Future experiments would include repeating this experiment on aged polymers.

dell'Arte, Florence, Italy and to Mr. Sabino Giovannoni for the preparation of the fresco specimens.

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