Study of the stability of siloxane stone strengthening agents

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ABSTRACT

The commercial organosilicone compounds *Rhodorsil Consolidante RC90* and *Rhodorsil Consolidante RC80*, commonly used as stone strengthening agents for the conservation of artefacts, were tested to ascertain their chemical nature, the mechanisms involved in the polymerization reactions and their stability under oxidative stress. The resins were first chemically characterized by means of GC/MS, FTIR and EDXRF techniques, then applied to slides and subjected to controlled photo-oxidative and thermo-oxidative weathering. The film's morphology was observed by SEM determinations, while DTA-TG techniques were used to determine polymer thermal stability. The features examined prompted a number of considerations on the effects of the resins applied on stone materials and were the reference point for speculation on the chemical nature and the performance of *Sogesil XR893*, a silicon resin which is no longer available on the market.

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1. Introduction

Organosilicone compounds have been widely used as protective and consolidating agents to preserve stone materials from inevitable weathering due to environmental exposure. Good chemical stability resulting from the high strength of the silicon—oxygen bond, together with low surface tension, good elasticity and resistance to thermal stress foster their application on different stone substrates [1]. Silicone resins, such as polysiloxanes and alkyl-alkoxy-silane, have been applied in Venice since 1960, on various stone surfaces during well-documented restorations. The first consolidation treatment using organosilicone compounds in Venice took place in 1967 and was applied to the marble statue of St. Alvise, located on the main façade of the church dedicated to the saint. The statue was treated by vacuum impregnation in autoclave using the silicone resin *Sogesil XR893* [2]. To the best of our knowledge the resin, which was produced by Rhone Poulenc and is no longer available on the market, was a methyl-phenyl-polysiloxane dissolved in benzene with a solid content of 50%. Right away, it was judged very promising and began to be used

elsewhere in the city: in the following year it was employed for the consolidation of the four angels supporting the Holy Sepulchre altar in the Church of San Martino, during the restoration of the Ca' D'Oro in 1969 and in 1977—78 for the consolidation of the statues located on the gable-end of the façade of Basilica of San Marco [3]. No datasheet is available to indicate the chemical composition of the resin actually used. Moreover no studies have been carried out to illustrate the characteristics of the resin or the mechanisms of the polymerisation process. However, several years after the applications cited above, authoptic observations were carried out to evaluate the efficiency of the past treatments: all the stone surfaces showed a good state of conservation and no new fracture planes were observed [4]. Nowadays the fact that the resin is not commercially distributed prevents detailed study of its chemical stability. In the intervening years however, other silicone-based commercial products based such as tetraethylorthosilicate (TEOS) and poly-dimethyl-siloxane (PDMS) have been studied in detailed laboratory examinations [5—7]. In general, analytical tests have demonstrated that the most important problem of silicone resin is related to the cracking of the derived gel, due to the evaporation of the solvent upon the gelification process, or in the case of products based on TEOS, to the TEOS/organometallic catalyst ratio [5]. In order to solve this drawback, alternative mixtures of acrylic and silicone polymers [8] or, more recently, mixed systems of epoxy-silicone resins have been synthesized in organic-inorganic formulation with acid catalysts [9].

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Nowadays, in the restoration field, a new silicone resin, *Rhodorsil Consolidante RC90*, has replaced the old Sogesil XR893. The chemical nature of these two resins is quite different, as shown in the literature [10]: in fact RC90 differs from XR893 because of the presence of TEOS as the main component, combined with a tin-siloxane catalyst and a methyl-phenyl resin. The consolidation effects of RC90 such as changes in porosity and pore size distribution, water absorption coefficient, mechanical resistance and colorimetric features have been well-documented [11–13].

Another silicone resin commonly used in the restoration field, is *Rhodorsil Consolidante RC80*, which is different from RC90 only in that it contains a methyl instead of a methyl-phenyl resin [14]. The effectiveness of *RC80* on stone surfaces has been examined [13,15].

Nevertheless, despite their applications, the features of both Rhodorsil resins and the polymerization process remain unclear.

This study aims to achieve a better understanding of the chemical nature and stability of *Rhodorsil Consolidante RC90*, by comparison with *Rhodorsil Consolidante RC80*, in a thermo-oxidative and photo-oxidative environment. Among the techniques used, Fourier Transform Infrared Spectroscopy (FTIR) has been invaluable for understanding the sol–gel processes, as well as any polymer structural changes due to UV radiation and thermal-oxidation. Thermal analysis (DTA-TG) was used to assess the resistance of the resins to heat [16]. The results obtained have clarified the hydrolysis reactions involved in the polymerization process and ascertained the general high stability of the resins, supplying users with useful information concerning the performance of the consolidants. Furthermore, the different thermal stability and resistance to UV radiation of RC90 and RC80, has revealed the important role played by the methyl-phenyl resin in the ageing process, and provide reasonable explanations for the causes of failure of the old *Sogesil XR893*. These hypotheses were tested by study of a fragment of a column of the Ca' D'Oro façade, treated in 1963 with the XR893 resin.

2. Experimental

2.1. Materials

The commercial products to be tested were *Rhodorsil Consolidante RC90* and *Rhodorsil Consolidante RC80* supplied by the Italian company *Siliconi Padova*. Both of them are composed of tetraethylorthosilicate (TEOS) combined with a tin-siloxane catalyst and a water repellent component, which is a methyl resin in the case of RC80 and a methyl-phenyl resin in the case of RC90. The solvent is white spirit with the addition of xylenes only in the case of RC90, presumably to improve dissolution of the methyl-phenyl resin [10–14].

The polymers were chemically characterized in liquid and dried form.

After the complete sol–gel changeover, films were subjected to UV radiation in a UV chamber equipped with four 8 W black light blue lamps, emitting in the near-UV range (315–400 nm; 3 mW cm^{-2}). The volume of the photoreactor was 25 ml. The films were also subjected to thermal-oxidation in a ventilated oven fixed at 60 °C [17]. These experiments almost simulate the ongoing degradation of resins exposed to outdoor conditions.

2.2. Investigation methods

RC90 and RC80 were chemically characterized in sol and gel form, following UV radiation and thermal treatment under laboratory conditions, the better to ascertain their chemical composition, microstructure and stability.

2.2.1. GC/MS measurements

The GC/MS analysis performed in this study was carried out using a TRACE GC 2000 Gas Chromatograph interfaced by the quadrupole Mass Spectrometer TRACE MS (Thermo Finnigan). The gas chromatograph was equipped with an HP5-MS column (length: 30 m, I.D.: 0.25 mm, film: 0.25 μm). The samples were injected in the split flow mode and the oven was set from 80 °C to 300 °C.

The identifications were supported by NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral Library, 2.0.

2.2.2. FTIR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) using a Perkin–Elmer 1000 spectrometer and a Jasco-Europe model FT/IR4200 instrument in the spectral range of 400–4000 cm^{-1} was used to characterize both the sols and the xerogels. The sol samples were initially placed inside an AgBr cell with a Teflon spacer (0.05 mm thick) between the windows. In the case of the xerogels, they were homogenized with KBr and pressed to obtain a pellet using a vacuum hydraulic press. Sols and xerogels were recorded in the absorbance mode with a spectral resolution of 4 cm^{-1} and 75 consecutive scans were summed and averaged before applying the Fourier transform, in order to obtain a good signal-to-noise ratio. The spectra of sols and xerogels were recorded at various time intervals during the curing and ageing of resins, as follows: (a) the sols and the derived xerogels of both resins were analysed at time intervals of 0, 18, 48, 83, 155, 216 and 384 h from the application time in the laboratory ambient; (b) spectra were recorded for the resins subjected to UV radiation at time intervals of 0, 24, 72, 216, 288 and 1152 h; (c) spectra were also recorded for the resins subjected to a thermal-oxidation at time intervals of 83, 155, 323, 491, 1163, 2123 h [18,19].

In order to evaluate an old conservation treatment based on XR893 silicone resin and to compare it with the results obtained from the application of RC90 resin on a stone surface, as better explained in paragraph 2.3, μFTIR analysis was carried out. The instrument used is a Jasco IRT-5000 Irtron Infrared Microscope. A micro scale of the polymeric films was sampled from the stone surface, using a needle, laid and pressed on a standard KBr pellet, then analysed in transmittance mode.

2.2.3. Thermal analysis

The thermal decomposition of the nanocomposite coatings was assessed by means of differential thermal analysis (DTA) and thermogravimetric (TG) analysis with a Setaram LabSysEvo 1600. The TG analysis was performed under air atmosphere at a heating rate of 10 °C/min from 27 °C to 1000 °C, on samples dried at 60 °C for one day.

2.2.4. EDXRF technique

An EDXRF unit with [55]Fe and [109]Cd and [241]Am radioactive sources, Si(Li) semiconductor detector (resolution 150 eV at 5.9 keV) was employed for the identification of the catalyst included in the resins. The EDXRF analysis was performed in powders originating from cured films of the resins.

2.2.5. Scanning electron microscopy

Morphological observations and detailed chemical microanalyses of dried films polymerized on a slide and coated with a thin gold layer, were carried out by Philips XL 30 SERIES SEM instrument. The semi-quantitative elemental composition was measured using an EDS coupled with EDAX X-ray dispersive spectrometer, equipped with a thin beryllium window. The accelerating voltage was 25 keV.