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PROTECTION OF HISTORICAL GLASSES BY HYBRID SOL GEL COATINGS

Introduction

The protection of historical windows is usually achieved by the installation of protective glazing – glass or plastic slabs installed on the external surface of the windows[1] – or by using acrylic resins on the altered glass surface. In the first case the protective effect by physical and chemical attacks is usually obtained with a negative impact on the esthetics of the monuments, also inducing a reduction of sound and light transmission, with a consequent darkening of colors[2]. The acrylic resins, normally used also for other very different substrates as frescos, wood and metals have the advantage of good adhesion, theoretical reversibility and ease of use by restorers. On the other hand, the main problems of these materials are the incompatibility with the inorganic substrate, the occurrence of yellowing phenomena and their thermal instability, mainly because of their low glass transition temperature (T_g) values.

In this work we studied silica-based protective hybrid coatings obtained by sol gel process to achieve the chemical and physical compatibility with the glass substrate. The addition of organic

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[1] Romich 2004.

[2] Ibid.

functionalities gives the surface water repellency, since water is the most dangerous alteration agent for glass[3].

Materials and Methods

Sols have been obtained mixing TEOS (Tetra-ethyl-orto-silicate), organically functionalized Si-alkoxides (Tab. 1), isopropanol, water and HCl (pH =2) as catalyst in round bottom flasks for about 4 hours at room temperature (Tab. 2). The deposition on the surface of very alterable medieval-like glass samples[4] (containing about 25 wt% of K_2O) was performed by dip-coating technique and the deposited films have been characterized by UV-VIS, FT-IR, TGA and performing static contact angle α was measurements (following the indications of the UNI 11207:2007 Protocol).

Coatings have been aged under UV-light and SO_2 saturated atmosphere to test their light and chemical stability[5]. Color and contact angle data were collected before and after the ageing experiments. Colorimetric measurements were performed by means of a spectrophotometric scanner using a D65 illuminant. As reference, a white standard certified by a metrological laboratory was used, in the same optical geometry as for the image acquisition. Color values were obtained in the CIE L*a*b* space and were used to obtain the average color difference ΔE*[6]:

Results and Discussion

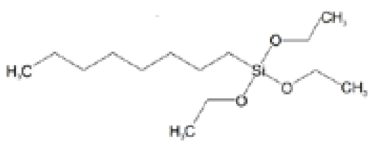
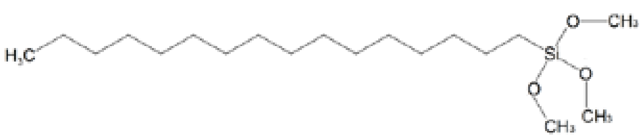
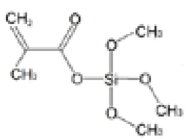
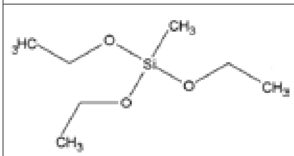
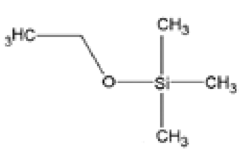
Table 2 reports all the tested sol compositions. Some of them have been immediately excluded since the deposited coatings appeared opaque and/or inhomogeneous, while characteristics as

3 Melcher and Schreiner 2004.
4 De Ferri et al. 2012.
5 DIN 50018:1997 Standard norm.
6 Oleari 1998.

transparency, homogeneity and absence of color are fundamental when working on transparent glass.

The transparent films have been characterized by UV-VIS absorption: Fig. 1 reports the spectrum of the 20% OTES film, confirming the absence of absorption features in the spectra.

FT-IR spectra were collected on the dried hybrid gel to get information about their degree of poly-condensation. The ratio between the intensities of the Si-O-Si anti-symmetric stretching (about 930 cm^{-1}) and of the Si-OH stretching (about 1030 cm^{-1})

	Octyl-triethoxy-silane (OTES)
	Hexadecyl-trimethoxy-silane (HDTMS)
	Methacryl-trimethoxy-silane (MTMS)
	Methyl-triethoxy-silane (MTES)
	Trimethyl-ethoxy-silane (TMES)

Tab. 1 - Structural formulae of the organically functionalized Si-alkoxides added to TEOS for the synthesis of the hybrid sols.

Composition	Organic fraction (wt%)	Homogeneity/ transparency	α (±3°)	$α_{UV}$ (±3°)	$α_{SO2}$ 10 ppm	$α_{SO2}$ 60 ppm	$α_{SO2}$ 120 ppm	ΔE*	$ΔE^*_{UV}$	$ΔE^*_{SO2}$ 10ppm	$ΔE^*_{SO2}$ 60ppm	$ΔE^*_{SO2}$ 120ppm
5% HDTMS+ 95% TEOS	8.6	✓	104	104	104	100	93	2.6	0.6	0.5	1.31	2.11
10% HDTMS +90%TEOS		X										
20% HDTMS +80%TEOS		X										
5%OTES+95%TEOS	5.6	✓	100									
10% OTES+90%TEOS	11	✓	101									
20%OTES+80%TEOS	20	✓	105	104	105	100	93	1.8	1.7	0.74	0.74	2.19
30%OTES+70%TEOS	27	✓	103									
40%OTES+60%TEOS	34	✓	103									
5%HDTMS+20% OTES+75%TEOS	31	✓	107	107	108	102	95	2.2	1.1	0.41	1.46	1.32
10%HDTMS+10%OTES+80%TEOS	35	✓	97									
20%MTMS+80%TEOS	14	✓	38									
60%MTMS+40%TEOS	31	✓	48									
10% MTMS+10% OTES		X										
15% MTMS+5% EDTMS		X										
20%MTES+80%TEOS	2.7	✓	81									
60%MTES+40%TEOS	6.6	✓	79									
10% MTES+ 10% OTES		X										
40% MTES+ 20% OTES		X										
20%TEMS+80%TEOS	9	✓	94									
60%TMES+40%TEOS	29	✓	86									
10% TMES + 10% OTES		X										
10% TMES+ 20% OTES		X										
40% TMES+ 20% OTES		X										
5%TMES+15%MTES+80%TEOS	4	✓	93									
15%TMES+45%MTES+ 40%TEOS	11	✓	91									

Tab. 2 - Composition of the sols, optical appearance, amount of organic fraction (wt%), static contact angle (α±3°) and ΔE* values before and after the UV and SO_2 ageing experiments and ΔE* values before and after the application of the coatings

peaks was evaluated (Fig. 2): this ratio increases with increasing the amount of organic functionalities, meaning that the structure is more linked and, as a consequence, the poly-condensation degree is higher.

This result was confirmed by the TGA data collected on the gels powder showing that the amount of OH group in the TEOS gel is higher than in the 40%OTES gel.

Since the main aim of this study was the production of water repellent coating, contact angle measurements have been performed and Table 2 reports the obtained results. On the basis of these values and of the amount of the organic component, three sol compositions were selected for the accelerated ageing tests. Generally the best results are obtained with the addition of Si-alkoxides functionalized with long linear chains: the 5% HDTMS sol shows the lower amount of organic component and displays high static contact angle values; the 5%HDTMS-20%OCTES composition gives the highest contact angles and the 20% OCTES sol was chosen as an intermediate composition.

Colorimetric measurements show that the L*a*b* parameters, and consequently the ΔE* value, do not vary significantly, before and after the deposition of the coatings and after the UV-light ageing. The same holds also for the static contact angle values (Tab. 2).

The ageing under SO_2 saturated atmosphere evidenced that the coatings are quite stable for low concentrations of SO_2 (10 and 60 ppm), while they start losing the water repellency after the exposure to 120 ppm, even if the colorimetric data do not change significantly (Tab. 2).

Conclusions

The water-repellent hybrid coatings designed for the protection of exposed historical windows seem matching quite well the requirements for the Conservation of Cultural Heritage field since they do not give reaction by-products or unreacted fractions that could damage the ancient substrate, are transparent and colorless, and chemically and light stable.

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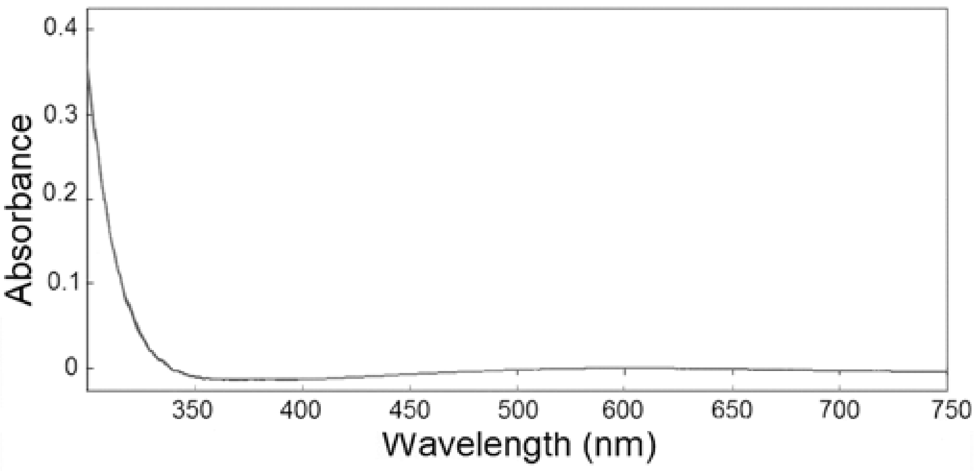

Fig. 1 - UV-VIS absorption spectrum of the 20% OTES film.

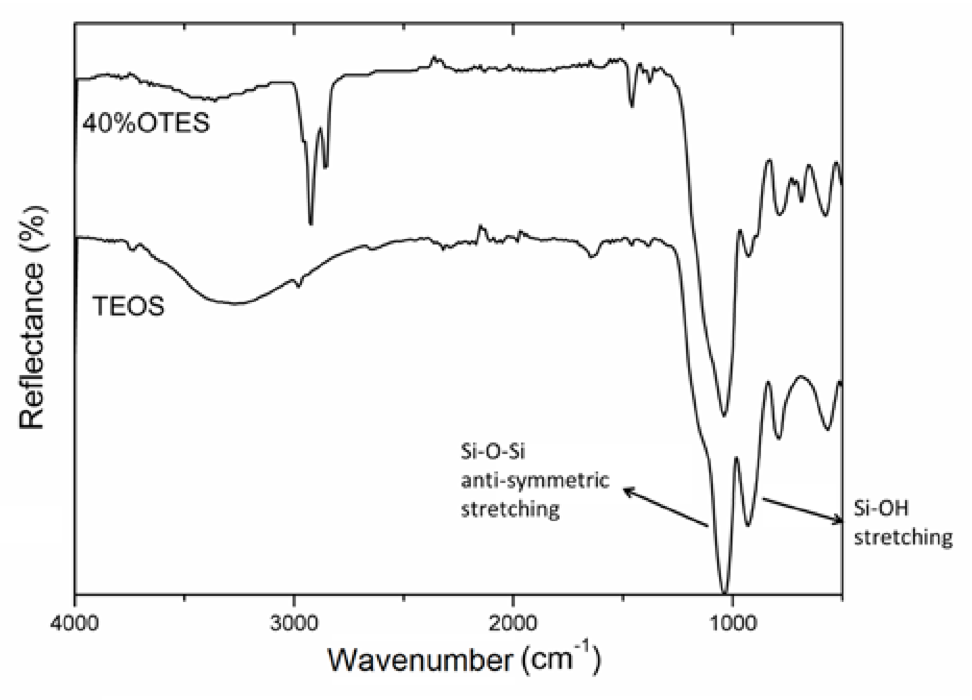

Fig. 2 - FT-IR spectra of the TEOS and of the 40%OTES powdered gels.