



Preparation of a TiMEMO nanocomposite by the sol–gel method and its application in coloured thickness insensitive spectrally selective (TISS) coatings

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ABSTRACT

An organic–inorganic nanocomposite was prepared via sol–gel processing from 3-(trimethoxysilyl)propyl methacrylate (MAPTMS) and titanium(IV) isopropoxide (TIP) precursors (TiMEMO) in the form of a viscous resin, and used as a binder for the preparation of coloured thickness insensitive spectrally selective (TISS) paints and corresponding solar absorber coatings. The spectral selectivity of TiMEMO-based TISS paints was optimized by varying the concentrations of binder and different pigments: black, coloured (red, green and blue) and aluminium flakes, the latter imparting low thermal emittance, which was correlated to the presence of titanium in the TiMEMO sol–gel host. The formation and the ensuing structure of the sol–gel TiMEMO hybrid was studied in detail and the nanocomposite structure of the TiMEMO binder formed was assessed from infrared and ²⁹Si NMR measurements, which confirmed the formation of Ti–O–Si linkages established after the hydrolysed precursors condensed into a compliant resinous material. XRD measurements provided additional information about the existence of small coherent domains of silsesquioxane units in the sol–gel host. The abrasion resistance of the non-pigmented TiMEMO binder deposited in thin film form on a PMMA substrate was assessed by the Taber test, and its hardness compared with other resin binders which have been used for making TISS paint coatings. The surface properties of the non-pigmented TiMEMO binder and the ensuing TISS paint coatings were determined from contact angle measurements. The results showed that the water contact angles of non-pigmented TiMEMO binder increased from 70° to 125–135° for the corresponding pigmented TISS paint coatings, inferring the influence of surface roughness on surface energy in the presence of pigments. SEM measurements revealed a striking similarity in the surface morphology of the TISS paint coatings with some other surfaces exhibiting the Lotus effect.

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1. Introduction

Despite fast growing needs for spectrally selective coatings stemming from the fact that in Europe nearly 50% of fossil fuels are nowadays spent for heating buildings (www.esttp.org), surprisingly, relatively small numbers of new selective coatings have been developed for these specific applications. Since the early 1950s, when Tabor [1] proposed and demonstrated the usefulness of selective surfaces for increasing the photothermal efficiency of solar collectors, many types of absorber have been reported and produced [2,3] but only a few became available commercially.

The European solar thermal market is today dominated by black highly selective ($a_s = 0.93–0.94$, $e_T = 0.04–0.07$) but expensive thickness sensitive spectrally selective (TSSS) sputtered

cermet coatings, such as TiNO_x, Alanod Sunselect and BlueTech. A cheaper black TSSS paint coating [4,5] prepared via the coil-coating technique is produced by Chromagen (Israel) but the market is relatively small. However, none of the mentioned coatings is suitable for solar façade absorbers. TSSS coatings are neither mechanically nor corrosion resistant enough to assure the long service life of unglazed solar façade collectors. An additional drawback to the widespread use of solar façades lies in the black appearance of solar absorbers. According to Weiss [6], more than 85% of architects would prefer colours other than black, even if a lower efficiency would have to be accepted. Accordingly, the main focus of this study was to develop coloured selective paint coatings with various hues suitable for unglazed solar absorbers.

Thickness insensitive spectrally selective (TISS) paint coatings represent the material of choice because they combine the advantages of paints (longevity, chemical resistance achieved by a high thickness of the applied layer, variety of colours and simple application) with spectral selectivity, which does not depend on

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the thermal emittance of the substrate. The latter is achieved by the addition of metallic flakes (Al, Cu and Ni) to the paint dispersion, significantly decreasing their thermal emittance. The idea of making black TISS paint coatings was first reported by McKinley and Zimmer [7], Telkes [8] and Moore [9,10] and since then has been successfully realized by Hoeflaak [11]. His black TISS paint coatings made of black pigment, an organic resin binder and low-emitting aluminium flakes exhibited $a_s = 0.84\text{--}0.90$ and $e_T = 0.41\text{--}0.47$.

Coloured TISS paint coatings (various shades of blue, green and red) prepared in our laboratory [12–15], were made by embedding appropriate amounts of aluminium flakes, and coloured and black pigments in silicone [14] or polyurethane [15] binders. However, in order to prepare even better coloured TISS coatings, new resin binders with infrared absorption lower than those of the already used polyurethane and silicone binders, higher abrasion resistance and possibly antisoiling (i.e. hydrophobic and oleophobic) properties are required. Sol–gel organic–inorganic hybrids [16–18] seem to be suitable because the sol–gel processing can be done at low temperature and because of the variety of commercially available sol–gel precursors.

Sol–gel based materials have not been frequently used as binders for selective coatings. Rincon et al. [19] reported TSSS coatings prepared from tetraethoxysilane (TEOS) in combination with titanium(IV) isopropoxide (TIP) with added carbon soot and carbon nanotubes as pigments. However, high curing temperatures (300–600 °C) were needed to fully cure TSSS selective coatings. Posset et al. [20,21] reported TISS coatings made by mixing Al flakes with single end-capped 3-isocyanatopropyltriethoxysilane or 3-(triethoxysilyl)propyl succinic anhydride, which is combined with a poly(vinylbutyral) copolymer bearing –OH groups. The ensuing TISS coatings have good mechanical properties due to the added sol–gel precursor, which enhanced the amount of silica (inorganic) phase, but this led to the increase of e_T values above 0.45. It is obvious that thermal emittance and mechanical hardness are interrelated properties; increasing the amount of the sol–gel inorganic phase in the binder mixture deteriorates the selectivity. Therefore, a sol–gel hybrid having an inherently low thermal emittance is needed.

In principle, there are two possible ways to avoid an excessive thermal emittance of sol–gel hybrids, which mainly originates from the massive infrared absorption of the Si–O–Si bonding, typical of linear (or branched) silsesquioxanes ($R_8(\text{SiO}_{3/2})_8$, R = organic group), characteristic condensation products of silanes. One possibility to overcome this is to use polyhedral oligomeric silsesquioxanes (POSS) [22], such as octahydrido POSS, having cyclic (cage-like) $H_8(\text{SiO}_{3/2})_8$ structure, known as low- k materials ($\epsilon_0 < 4.0$) in microelectronics. Another possibility, which we applied in this study, is to use binders which have an inherently low infrared absorption due to the presence of heavier atoms (or their clusters) randomly substituted within the Si–O–Si chains. Heavier atoms (titanium, for example) decouple the internal electric field established due to the strong dipole–dipole interactions of polar groups existing in linear or branched Si–O–Si chains. Moreover, such atoms when bonded to oxygens show vibrational bands below 1000 cm^{-1} , and thus do not contribute as strongly as Si–O–Si modes to the thermal emittance in the spectral range $1200\text{--}1000\text{ cm}^{-1}$. Accordingly, the binder for TISS paints was prepared from acryloxypropyltriethoxysilane (APTMS or MEMO, for short [23] and TIP, with an organic–inorganic hybrid structure (TiMEMO, for short).

The TiMEMO sol–gel hybrid is not new and has been used as “hard” coating to increase the abrasion resistance of acrylic (PMMA) and polycarbonate transparent panes [24–28]. However, practically no information could be found about the use of the TiMEMO sol–gel hybrid as a binder for pigmented coatings such as TISS paints, or about the interactions of TiMEMO with pigments, important in achieving non-agglomerated pigment dispersions and spectral selectivity.

In this paper we first report the preparation of TiMEMO organic–inorganic hybrids, accentuating the need for controlling the extent of hydrolysis and condensation reactions of the MAPTMS and TIP precursors, and their effect on the ensuing structure of TiMEMO binders. In order to demonstrate the suitability of TiMEMO binder for solar façade absorber coatings, the thermal infrared absorbance and abrasion resistance of TiMEMO were next measured and compared to those of other commonly used organic binders. Finally, some examples of selective coloured TISS paint coatings are given, demonstrating the advantages of the TiMEMO binder for achieving high solar absorptance and low thermal emittance in selective coatings. Interestingly, the presence of pigments dramatically decreases the surface energy values of the TISS paint coatings, as demonstrated by water contact angle measurements.

2. Experimental

2.1. Instrumental

IR absorption spectra of the sols and films deposited on silicon wafers by dip-coating (10 cm/min) were recorded on a Bruker IFS 66/S instrument with a resolution of 4 cm^{-1} using 32 scans for each sample. Solar absorptance (a_s) of coatings in the visible and near infrared spectral regions was determined from the reflectance spectra measurements performed on a Perkin Elmer Lambda 950 UV/Vis/NIR with an integration sphere (module 150 mm). Thermal emittance values (e_T) were obtained from the reflection spectra measured on a Bruker IFS 66/S spectrometer, equipped with an integrating sphere (OPTOSOL) using a gold plate as a standard for diffuse reflectance. A standard procedure was used for the evaluation of a_s and e_T values [29]. XRD spectra were obtained on a PANalytical X'pert PRO X-ray diffractometer (CuK α , $\lambda = 1.5406\text{ \AA}$), while ^{29}Si NMR spectra were recorded on a Varian Unity Plus 300 MHz with a Doty CPMAS head. XPS analyses were carried out on a PHI-TFA XPS spectrometer (Physical Electronics Inc.). The sample surfaces were excited by X-ray radiation from an Al source and the area analysed was 0.4 mm in diameter. The O 1s, Si 2p and Ti 2p spectra were acquired with an energy resolution of about 1.0 eV. Sample charging during XPS analysis was compensated by a low-energy electron gun–neutralizer.

SEM micrographs were obtained on a FE-SEM Supra 35 VP electron scanning microscope. Since the paint coatings contained conductive aluminium flakes, no additional preparation of the samples was needed to make micrographs. TEM micrographs were obtained on a JEOL 2000 FX transmission electron microscope, operating at 200 kV.

The thickness of the coatings was measured on a Taylor-Hobson Talysurf 2. The abrasion test was done on a Teledyne Taber abramer, Model 503, by rubbing the films with a pair of CS-10 wheels, with a 500 g load per wheel. The abrasion resistance of the films was graded using the difference of haze between the wear track and non-abraded regions after 500 cycles of abrasion. The contact angles were measured on a contact angle goniometer (Kreuss). Total surface energy values γ^{tot} were determined by introducing the contact angle values of water, methylene iodide and formamide test liquids into the van Oss relation [30]. The details regarding contact angle measurements were reported elsewhere [31].

2.2. Preparation of MEMO and TiMEMO binders

A typical procedure used for the preparation of the MEMO and TiMEMO nanocomposite binders is presented in Fig. 1. First,

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