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Structural studies of sol–gel urea/polydimethylsiloxane barrier coatings and improvement of their corrosion inhibition by addition of various alkoxysilanes

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ABSTRACT

A sol–gel organic–inorganic hybrid precursor, bis[(ureapropyl)triethoxysilane]bis(propyl)-terminated-polydimethylsiloxane 1000 (PDMSU, for short), was tested as a corrosion barrier coating for AA 2024 aluminium alloy. The PDMSU coatings were prepared in either ethanol (PDMSU/EtOH) or propanol (PDMSU/PrOH) solvents. XRD measurements of xerogels showed the diffraction peak of amorphous silica domains at 21.5° and a broad peak at approximately 12.2°, which could be associated with the presence of the polyhedral silsesquioxane structural units (T^2 and T^3) determined in our previous investigations from the ^{29}Si NMR spectra. The structure of thin coatings on AA 2024 prepared by heat-treatment at 140 °C was studied with the surface-sensitive IR reflection–absorption (IR RA) spectroscopic technique. Results revealed that in both coatings the poly(dimethylsiloxane) (PDMS) chain segments were projecting from the metal surface, however, this effect was more pronounced for the PDMSU/PrOH than for the PDMSU/EtOH coatings. Information gathered from the structural studies (IR, IR RA, ^{29}Si NMR and XRD) enabled some correlations to be drawn between the coatings' structure and the effectiveness of the corrosion inhibition, which was assessed from the potentiodynamic and salt-spray measurements. Results showed the improved corrosion inhibition of PDMSU/PrOH coatings attributed to their denser and more compact sol–gel network and also to their higher hydrophobicity, i.e. lower surface energy determined from the contact angle measurements. Addition of various tetraalkoxysilanes and alkyltriethoxysilanes further improved the corrosion inhibition of PDMSU coatings due to more extensive cross-linking. The salt-spray tests showed that tetraethoxysilane and phenyltriethoxysilane were the most effective additives.

1. Introduction

During recent decades, hexavalent chromium compounds were among the most effective and frequently used corrosion inhibitors of various metals and alloys. Recent environmental regulations in numerous industrialized countries, however, have led to their replacement because of their highly toxic, allergenic and carcinogenic properties [1,2]. These restrictions instigated the search for new corrosion inhibition possibilities. Among them barrier coatings on metal surfaces were extensively investigated due to their ease of manufacture and application, acceptable costs and a wide range of product possibilities. Corrosion protection coatings were prepared using various polymers (polyamides, alkyds, acrylics, epoxies, polyurethanes and polyesters) [1] and conductive polymers (polyaniline and polypyrrol) [1,3], but in the recent years publications discussing sol–gel corrosion protection coatings emerged [1,4–15].

One of the challenges for the sol–gel community became the preparation of protective coatings for aluminium alloys, vitally important in the aircraft industry. During the first phase of research it was found that conventional inorganic SiO_2, TiO_2 or mixed SiO_2/TiO_2, SiO_2/Al_2O_3, etc. sol–gel coatings with a thickness above 1 μm did not result in better corrosion protection, but that cracking occurred because of increased internal stress [1,4]. The use of organically modified alkoxysilane precursors was proposed, since the increased flexibility of the organic groups should offer the possibility to produce thicker coatings [1]. The benefit of organically modified alkoxysilanes also lies in the fact that the structure of the final products can be tailored at the molecular level by the addition of water, catalysts and additives [5]. The compactness and extensive cross-linking of the siloxane networks depend on precursor choice, preparation conditions and thermal treatment of the as-deposited

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coatings. The preparation of dense and compact structures is important, because the corrosion protection of barrier coatings crucially depends on their structure and permeability to water, oxygen and pollutants [6,7].

Specifically, for the corrosion inhibition of aluminium alloys various single end-capped alkylalkoxysilanes (*n*-decyltriethoxysilane or *n*-octadecyltriethoxysilane [8]), functionalized alkylalkoxysilanes (γ-mercaptopropyltrimethoxysilane (γ-MPS) [9]) and mixtures of 3-glycidoxypropyl trimethoxysilane (GLYMO) with either tetramethoxysilane (TMOS), tetraethoxysilane (TEOS) or methyltriethoxysilane (MTEOS) [7,10,11] have been used, and their corrosion inhibition tested in salt spray chamber and by employing various electrochemical techniques. Metroke et al. [12] have shown that the corrosion inhibition of organically modified silane (ormosil), prepared from TEOS, vinyltrimethoxysilane and 3-(trimethoxysilyl)propylmethacrylate, can be increased by addition of various alkyl-modified silanes. Contact angle, EIS and salt-spray measurements revealed that the corrosion resistance and hydrophobicity of the coatings increased with the alkyl-modifier concentration and the alkyl chain length. When the same ormosil coatings were made in various solvents (non-polar, aprotic polar, alcohols), corrosion resistance properties were found to depend on the stability of the solvent-induced re-esterification products [13]. Nevertheless, it can be concluded that single end-caped precursors, even though performing well when used under topcoats, could not pass the corrosion tests when used as a single protective layer, i.e. without a topcoat [14].

In order to prepare dense, highly cross-linked and impermeable silsesquoxane networks, bis end-capped precursors with the general formula ($(RO)_3Si–(CH_2)_n–R'–(CH_2)_n–Si(OR)_3$; R–alkoxy; R′–alkyl chain, chain of sulphur atoms, amine group, etc.) were employed. The best corrosion protection was observed for 1,2-bis[triethoxysilyl]ethane (BTSE) [9] and bis[3-(triethoxysilyl)propyl]tetrasulfide (BTESPT) [9,14,15], which were adequate even without topcoats. Namely, bis end-capped precursors enable hydrolysis and condensation reactions on both sides of the molecules, which lead (compared to single end-capped precursors) to thicker, more homogeneous films on, for example, AA 2024 aluminium alloy, and to formation of a higher number of interfacial metallo-siloxane Al—O—Si bonds [9]. Furthermore, as for single end-capped precursors [12], we found – as shown in this study – that also for bis end-capped precursors the corrosion inhibition can be increased by the addition of simple alkylalkoxysilanes like TMOS, TEOS, MTEOS, etc.

In our laboratory we synthesized the bis end-capped alkoxysilane precursor bis[(ureapropyl)triethoxysilane]bis(propyl)-terminated-polydimethylsiloxane 1000 (PDMSU) (Fig. 1), which was first applied as a hydrophobic additive to proton conducting membranes for fuel cells based on a poly(propyleneglycol)urea/siloxane (PPGU) hybrid [16]. The water contact angle of these membranes increased above 90°, the swelling decreased and their long-term stability improved. This finding suggested the use of PDMSU as a water-repellent coating for various substrates. PDMSU was then tested as a hydrophobic impregnation for cotton fabrics, with contact angle values around 130° [17]. The water repellent properties of PDMSU were also confirmed for concrete and mortar, suggesting excellent bonding to inorganic substrates. This led us to investigate the corrosion inhibition of PDMSU for metallic substrates. Intentionally, a highly corrosively unstable aluminium alloy (AA 2024-T3) was first tested. It was found that the corrosion inhibition of PDMSU coatings [18] surpassed that of other single end-capped alkoxysilane hybrid coatings [7–12], and was comparable to the corrosion inhibition of BTSE [9] and BTESPT [9,14,15] coatings. This was not surprising because PDMSU, BTSE and BTESPT are all bis end-capped precursors, enabling hydrolysis and condensation reactions on both sides of the molecules, leading to the formation of a dense and compact coating structure and also to Al—O—Si interface bonding [18]. In addition, it is important to stress that in contrast to BTSE and BTESPT, PDMSU consists of long hydrophobic poly(dimethylsiloxane) (PDMS) chains with 12 repeating units. Due to the relatively long PDMS chains, the number of reactive silanol groups is limited and can be increased either by using shorter PDMS chains or by using PDMSU in combination with other single end-capped alkoxysilane precursors. In general, hydrophobicity beneficially affects the corrosion inhibition of coatings. Namely, it is crucial to prevent the ingression of water because water molecules can influence corrosion by sorption in the coating and the ensuing transport through the coating to the coating–substrate interface [19].

PDMSU is structurally similar to ureasils, in which urea groups link end-capped alkoxysilane groups to various polymers and are responsible for self-assembly of ureasil molecules [20,21]. The fact that PDMSU consists of PDMS polymer chains led us to investigate their orientation on AA 2024 alloy and to establish the possible correlations with the corrosion inhibition of PDMSU coatings. PDMS forms self-assembled Langmuir–Blodgett (LB) films [22], characterized by the orientation of PDMS chains parallel with respect to the substrate. The orientation of the PDMS backbone has been established from the IR reflection–absorption (IR RA) spectra obtained at an incidence angle of 85° in P-polarized light, giving a strong enhancement of intensity to the modes whose dipole moments lie perpendicular to the substrate. By considering the intensity of the main skeletal modes of PDMS, i.e. the ν_S(Si—O—Si) (1110 cm^{-1}) band characterized by the dipole moment oscillating perpendicularly to the chain axis, and the ν_A(Si—O—Si) band (1040 cm^{-1}) oscillating parallel to the chain backbone [23], it has been found that the PDMS backbone lies in the plane of the substrate. A similar orientation of the chains deposited on gold was found for PDMS copolymers containing propanethiol [23], showing IR RA (83°, P-polarization) spectra having similar features; orientation causes enhancement of the ν_S(Si—O—Si) band (1110 cm^{-1}) compared to the intensity of the ν_A(Si—O—Si) band (1040 cm^{-1}). In the spectra of cast films both bands are observed, albeit with different intensities as reported by Tsao et al. [23]. The relative intensity variation of the two bands is not as extreme as in the spectra of LB films, but distinct enough to allow the orientational studies. Accordingly, IR RA spectra of our barrier coatings having different thicknesses were measured and from the variations of the relative band intensities the preferential orientation of the PDMS chains in the coatings was established.

As already stated, the corrosion protection effect of sol–gel coatings is strongly affected by their structure, depending on the extent of hydrolysis and the ensuing condensation species, which form in the final sol–gel network. Water added to sols affects the number of silanol groups needed for condensation reactions [7,24] and for interface interactions between the precursor and substrate, while the type of solvent (and eventual presence of an excess of water) determines the sol's long-term stability via re-esterification reactions [25]. In the present work, either pure ethanol or a mixture of ethanol, propanol and an excess of water were used as solvents. We first present structural studies of PDMSU coatings, as obtained by transmission IR spectroscopy, X-ray diffraction and briefly the results of the ^{29}Si NMR spectra analysis are mentioned. SEM micrographs revealed the visual appearance of the PDMSU coatings of various thicknesses and their effectiveness in covering the surface of the AA 2024 substrate. With relation to the structure of the coatings an important accent in this study was given to the determination of the orientation of the PDMS chains with respect to the AA 2024 substrate. The corrosion inhibition of coatings on AA 2024 alloy was tested using potentiodynamic polarization curves and was substantiated by salt-spray test analyses. The salt-spray test, however, was also used to analyse the corrosion inhibition of