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Synthesis and characterization of hybrid aminopropyl silane-based coatings on stainless steel substrates

S.M. Hanetho [a], I. Kaus [b], A. Bouzga [c], C. Simon [c], T. Grande [a], M.-A. Einarsrud [a],*

[a] Department of Materials Science and Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway
[b] SINTEF Materials and Chemistry, 7465 Trondheim, Norway
[c] SINTEF Materials and Chemistry, 0314 Oslo, Norway

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ABSTRACT

Transparent and homogeneous hybrid aminopropyl silane-based coatings on steel were prepared by the sol–gel method using hydrolyzed γ-APS as a precursor. The coatings were fabricated by dip coating, and the effect of pH, water/silane ratio and solvent/silane ratio during the coating process was investigated with respect to thermal stability, coating thickness, roughness, contact angle and abrasion resistance. The thickness of the coatings was controlled by the preparation conditions as well as the viscosity of the sols and varied between 0.17 and 4.1 μm. The coatings were in general smooth and the roughness was in the order of a few nanometer. The coatings possessed hydrophilic character with contact angles of water from 65 to 80°, while organic pentadecane wetted the coatings. The abrasion resistance improved with decreasing pH of the water used during hydrolysis of the silane. The abrasion resistant properties of the coatings were characterized with respect to delamination and smearing. Thicker coatings were delaminated while thinner coatings were smeared and displayed lubricating properties. The coatings were thermally stable up to 350 °C, and also displayed a low pore volume and a low surface area.

1. Introduction

Hybrid inorganic–organic materials combine the advantages of the flexibility and good impact resistance of the organic moiety and high mechanical strength, good chemical resistance and high thermal stability of the inorganic component [1–3]. The properties of hybrid coatings can thus be designed by taking advantage of the fundamental different properties of these two components. Interesting applications for hybrid materials include wear and corrosion protection of metals, optics [4], primer solution [5], dental fillers [6], bone cement [7], water-repellent glass [8], transparent and abrasion-resistant coatings with fire-retardant properties and for the prevention of wax deposition during transport in oil and gas pipelines [9]. Hybrid inorganic–organic coatings can also be used to modify and improve the surface properties of metals such as steel [10].

The sol–gel method is versatile and is applicable for synthesizing hybrid inorganic–organic coatings. The method is gentle in terms of a low temperature, and the coatings may be readily applied to most metallic substrates. Sol–gel silica systems are preferred because they may provide good hydrophilic wetting and good adhesion to the substrate surface [1]. Strong covalent bonds in the hybrid inorganic–organic material can be formed either by mixing organic components directly into the inorganic matrix in the sol–gel systems, taking advantage of the functional groups within the polymer which react with hydrolyzed inorganic precursors, or by utilizing alkoxysilanes as precursors wherein one or several alkoxy groups attached to the silicon are substituted by alkyl groups [10–13]. This approach can be applied for synthesizing sols for metal coatings, and for instance, Li and Ba [14] coated aluminum with a triethoxysilane-based sol. The corrosion resistant behavior was improved during electrochemical/potentiodynamic polarization [14]. However, the most common use of substituted alkoxysilanes is as adhesion promoters between two different materials, and organofunctional silanes like 3-(aminopropyl)triethoxysilane (γ-APS) have been used to facilitate good bonding and to improve adhesion to organic coatings with any kind of substrate [15–17]. γ-APS based sols have been developed [18] and used as the basis for the preparation of wear resistant coatings by the addition of nanoparticles [19]. Coatings based on aminopropyl silane have currently been studied as barriers for preventing wax deposition [9]. The hybrid aminopropyl silane-based coatings showed good ability to reduce the thickness of the waxy layer which deposited compared to plain steel and commercial paints. Männle et al. [18] developed a sol–gel synthesis route for γ-APS, but the properties of the γ-APS-based coatings have not previously been characterized.

In this work we demonstrate the feasibility of using hybrid aminopropyl silane-based sols for the preparation of coatings on steel substrates. Steel is commonly used for oil and gas pipelines; however, corrosion and wax deposition cause unwanted shutdowns due to maintenance. Thus the possibility of coating the steel surfaces with γ-APS-
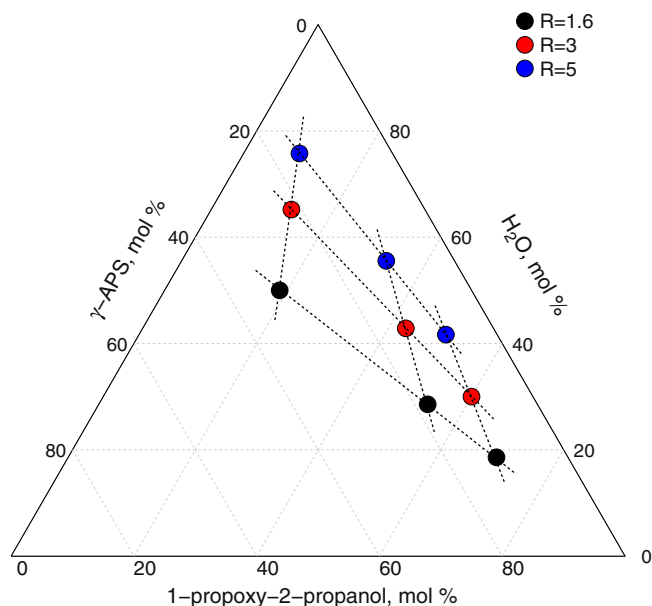
Fig. 1. Composition of the different hybrid aminopropyl silane-based sols.

based systems was explored. Generally, for tetraethoxysilane, the hydrolysis reaction is promoted at low pH levels. Due to this, it was desirable to investigate the feasibility of pH reduction in a relatively concentrated γ-APS in order to control the hydrolysis and condensation reactions. The coatings prepared by using different γ-APS-based sols have been characterized with respect to homogeneity, smoothness, thickness, wear resistance in addition to their wetting by water as well as an organic liquid.

2. Experimental

3-(Aminopropyl)triethoxysilane (γ-APS, Sigma-Aldrich, >97%) was mixed with 2,2,6,6-tetramethylpiperidine (Tmpp, Sigma-Aldrich, ≥99%) and dissolved in approximately 50% of the total amount of 1-propoxy-2-propanol (PnP, Sigma-Aldrich, 99%) in argon atmosphere in a chemical clean room (ISO class 7). Deionized water of 15 MΩ cm was used for hydrolyzing the sols. If required, water was adjusted to different pH values by the addition of hydrochloric acid (HCl, VWR International, >25%). Water was then mixed with the remaining part of 1-propoxy-2-propanol and added dropwise to the γ-APS solution. The solution was

subsequently magnetically stirred and heated to 80 °C (90 °C for the sols containing HCl as the reaction kinetics were slower) under reflux and kept at this temperature for 60 min. The solution was cooled under reflux. Three parameters were varied during the experiments in order to determine the impact of the sol chemistry on the final coating properties: water/silane ratio (R), solvent/silane ratio (S) and pH of water during the hydrolysis reaction, hereby denoted as hydrolysis pH. The compositions studied are included in the ternary diagram in Fig. 1. The sols are referred to as h–xR–yS where h reflects that the sol is a hydrolyzed aminopropyl silane, x represents the water/silane ratio, R, and y denotes the solvent/silane ratio, S. An HCl-suffix is attached to the sols and coatings hydrolyzed with a water-HCl mixture, and these are denoted "acidic", while the sols and coatings hydrolyzed with neutral hydrolysis water are termed "neutral". Furthermore, the water/silane ratio was 1.6 (here defined as hypostoichiometric with respect to hydrolysis), 3 (here defined as stoichiometric with respect to hydrolysis) or 5 (here defined as hyperstoichiometric with respect to hydrolysis). A summary of the composition of the sols is provided in Table 1. The silane concentration was calculated as the amount of γ-APS present in the sol and is given as mol% silane.

Substrates of stainless steel (E. A. Smith Stål og Metall AS, AISI SS 304, thickness = 0.5 mm, $3 \cdot 5$ cm^2) were ground and polished to a mirror shine. The sols were aged at 4 °C for 24 to 48 h before they were applied to the substrates. Coating of the substrates was performed with a dip coater (KSV DCX2) in a clean room (ISO 7) in nitrogen atmosphere to avoid reactions between the basic amine groups and carbon dioxide from ambient air. The withdrawal speed was varied between 5 and 20 mm/min. The coatings were thermally cured in a chamber furnace (Carbolite HT/28CR) at 140 °C for 2 h with a subsequent hold at 160 °C for 3 h. The heating rate was 10 K/h from ambient temperature to 140 °C and 20 K/h the remaining temperature increases up to 160 °C. The cooling rate was 100 K/h. One part of the sol was gelled in a beaker and dried at ambient conditions. Subsequently, thermogravimetric analysis (TGA, Netzsch STA449C on 19 TASC 414/3) was conducted on the dried gels with a heating rate of 120 K/h.

A Micromeritics Tristar 3000 analyzer was used to measure the nitrogen adsorption and desorption isotherms of a selection of the hybrid aminopropyl silane-based gels at 77.3 K. The gels were dehydrated at 250 °C under vacuum prior to the analysis.

The viscosity of selected sols was measured at 5 °C under nitrogen atmosphere using the Haake Mars Modular Advanced Rheometer System (Thermo Scientific) with a cup cone geometry. The sols were stored at 5 °C for 4 months prior to the viscosity measurements.

^{29}Si NMR signals of a selection of the hybrid aminopropyl silane-based sols aged 24 h or 4 months at 5 °C were recorded with a Bruker Ultrashield 400 MHz Plus system equipped with a 5 mm PABBO-BB

Table 1
Amount of precursors used for the preparation of the different hydrolyzed aminopropyl silane-based sols, water/silane ratio (R), solvent/silane ratio (S) and pH of the distilled water used during the hydrolysis reaction.

Sol	Precursors (mol)		Silane (mol%)	$R = \frac{n_{H_2O}}{n_{Si}}$	$S = \frac{n_{solvent}}{n_{Si}}$	Hydrolysis pH
	γ-APS	Tmpp				
h-1.6R-0.6S	0.4338	0.002152	31.2	1.6	0.6	6.2
h-1.6R-3S	0.1084	0.0005381	17.8	1.6	3	6.2
h-1.6R-6S	0.1084	0.0005381	11.6	1.6	6	6.2
h-3R-0.6S	0.4338	0.002152	21.7	3	0.6	6.2
h-3R-3S	0.4338	0.002152	14.3	3	3	6.2
h-3R-6S	0.4338	0.002152	10.0	3	6	6.2
h-5R-0.6S	0.4338	0.002152	15.1	5	0.6	6.2
h-5R-3S	0.4338	0.002152	11.1	5	3	6.2
h-5R-6S	0.4338	0.002152	8.3	5	6	6.2
h-1.6R-0.6S-HCl	0.2169	0.001097	31.2	1.6	0.6	0.8
h-1.6R-3S-HCl	0.4338	0.002152	17.8	1.6	3	0.8
h-1.6R-6S-HCl	0.4338	0.002152	11.6	1.6	6	0.8
h-3R-0.6S-HCl	0.4338	0.002152	21.7	3	0.6	0.8
h-3R-3S-HCl	0.07229	0.0003587	14.3	3	3	0.8
h-3R-6S-HCl	0.4338	0.002152	10.0	3	6	0.8