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Effect of functional groups (methyl, phenyl) on organic–inorganic hybrid sol–gel silica coatings on surface modified SS 316

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Abstract

Organic–inorganic hybrid sol–gel based silica coatings derived from hydrolysis and condensation of organically modified silane precursors like phenyltrimethoxysilane and methyltriethoxysilane along with tetraethoxysilane were deposited on different surface pre-treated (as-cleaned, plasma-treated, shot-blasted) SS 316 grade stainless steel substrate, using dip coating technique. The coatings were heat treated at 150 °C for 2 h in air. The pre-treated surfaces were characterized using X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy. The water content of the sols was determined by Karl Fischer titration to evaluate the degree of completion of hydrolysis and condensation reactions. Cured coatings were characterized to evaluate thickness, water contact angle, pencil scratch hardness, gloss, and shrinkage in coating thickness. Impact test was carried out on pigmented coatings derived from sols synthesized using the two silane precursors. The corrosion resistance and water durability tests were carried out to compare the coatings derived from using different precursors and different surface pre-treatments. The corrosion tests were carried out for 1 h and 24 h exposure to a 3.5% NaCl solution by electrochemical polarization measurements. It was found that coatings from methyl substituted organically modified alkoxysilane exhibited better hydrophobicity, scratch hardness, impact resistance and barrier properties with respect to corrosion, when compared to those derived from phenyl substituted trialkoxysilane. The difference in performance of coatings was explained on the basis of difference in hydrolysis and condensation rates between the two organically modified silane precursors used for the sol synthesis.

Keywords: A. Films; A. Plasma pre-treatment; A. Sol–gel processes; C. Corrosion

1. Introduction

Organic–inorganic (O–I) hybrid coatings combine the properties of organic polymeric materials with those of ceramics; where the inorganic components increase properties like scratch resistance, durability, impact strength, and gloss of the coating, while the organic moieties increase the flexibility, critical thickness and impart low temperature curability of coating. O–I hybrid coatings find extensive applications as hard coatings on plastics, colored coatings on glass [1,2] and barrier coatings for corrosion protection [3,4]. Usually, the hybrid coatings are generated from sols synthesized using organically modified silanes along with silicon tetraalkoxides. The organic groups can be polymerizable e.g. vinyl, acryl, epoxy or non-polymerizable like methyl, ethyl, phenyl etc. The nature of organic group strongly influences the rates of hydrolysis and condensation reactions, which in turn has a strong bearing on the properties of coatings derived from the sols. There are investigations reported on the effect of methyl and phenyl groups of methyl/phenyl trialkoxysilane on their rates of hydrolysis and condensation reactions [5–9]. However, there is no comparative evaluation of the properties of coatings derived from methyl and phenyl modified trialkoxysilanes.

SS 316 grade stainless steel is widely used as the structural material for various industrial applications like desalination plants, oil/gas pipelines, chemical industries etc. and sol–gel barrier coatings are often investigated for improving the corrosion resistance of SS 316 in halide containing environments [10–16]. Nevertheless, published

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literature on the corrosion properties of coating from Phenyltrimethoxysilane (PhTMOS) is not available to the best of our knowledge. Hence, one of the objectives of our work was to investigate the effect of different organic functional groups like Methyl (aliphatic) and Phenyl (aromatic) on the properties like hydrophobicity, impact strength, corrosion protection of coatings derived from hydrolysis and condensation reaction of phenyl trimethoxysilane $PhSi(OMe)_3$ and methyltriethoxysilane $MeSi(OEt)_3$, along with tetraethoxysilane $Si\text{-}(OEt)_4$.

Surface pre-treatment plays an important role in improving the wettability and hence, continuity and uniformity of coatings. More importantly, it also affects adhesion of the coating to the substrate, which indirectly influences the performance of coatings, especially scratch and corrosion resistance of coated objects, that are utmost important from a technology development point of view. There are two distinctly different pre-treatment processes namely: the plasma pre-treatment and shot blasting which are viable and adoptable for large-scale applications. Plasma pre-treatment is a method where no physical change in the structure of the substrate material occurs except cleaning by removal of organic matter and inducing reactive species on the surface by free ions and molecules of the plasma. On the other hand, shot blasting method induces mechanical deformation due to kinetic energy of the moving blasting media. Change in the surface morphology increases the effective surface area of the substrate thereby enhancing adhesion of the coating to the substrate besides removal of oxide layers from the surface. In some of our earlier studies, it was found that atmospheric air-plasma surface pre-treatment prior to coating deposition improved the corrosion resistance of coatings on aluminum and mild steel [17,18]. Hence, the effect of two different types of surface treatment on properties of coatings derived from the two different organically modified precursors (methyl and phenyl modified trialkoxysilanes) was also systematically studied in the present investigation.

2. Experimental

2.1. Materials and synthesis

PhTMOS (Phenyltrimethoxysilane 98 wt%), MTES (Methyltriethoxysilane 98 wt%), and TEOS (Tetraethoxysilane) from GELEST Inc., USA were used as-received and Iriodin® Black Mica and Carbon Black Pigments from Merck, Germany were used along with the sols for making the colored coatings. SS 316 flat sheets manufactured by Jindal Stainless Steel Way Ltd., India and having composition in wt% as Cr-16.65, Ni-10.07, Mo-2.08, Mn-1.06, Si-0.35, C-0.018, S-0.004, P-0.036, Cu-0.34 and remaining Fe, and dimensions 100 mm × 100 mm × 1 mm were used as substrates for the coating experiments. An acid catalyzed hydrolysis and condensation was carried out using PhTMOS or MTES, TEOS, HCl, and H_2O in the mole ratio of 1:0.25:0.25:4. Acidified H_2O was added to PhTMOS (or MTES), TEOS mixture under continuous stirring and the mixture was further stirred for 20 h at a temperature maintained between 20–27 °C. Pigmented sols were prepared by sonicating a mixture of black mica pigment and the sol. The amount of pigment added was 15 wt% of solid content of the sol along with 1 wt% carbon black.

2.2. Substrate pre-treatment

The SS 316 substrates were degreased using isopropyl alcohol (IPA) and dried with hot air. Surface pre-treatment of the substrate was carried out using atmospheric air plasma treatment equipment (Plasmatreat GmbH, Germany). The plasma produced using compressed air was used for activating the surface by inducing highly active species. A nozzle to substrate distance of 10 mm was used as the optimized parameter for the plasma treatment process while the plasma exposure time was 10 s.

Another surface pre-treatment was carried out by shot blasting technique using induction suction shot blasting equipment (Model:SB9182 supplied by M/s MEC shot blast equipment Pvt. Ltd. India). Spherical glass beads were used as the blasting medium. Compressed air pressure was fixed at 3.5 bar and working distance was maintained at 10 cm. Shot blasted substrates were cleaned by ultrasonication in IPA prior to coating.

2.3. Coating deposition

Coatings were generated using dip coating technique, on as-cleaned and pre-treated SS 316 surfaces employing withdrawal speeds from 1 mm/s to 10 mm/s. The pigmented sol was sonicated for 10 min to uniformly disperse the pigment particles prior to spray coating deposition.

2.4. Characterization

The viscosities of sols were measured using a Viscometer (Anton Paar Rheolab QC, Austria). Water content in the sols was measured using a Karl Fischer Titrator (Metrohm KF Titrino). XPS spectra were recorded using Omicron Nanotechnology GmbH (model ESCA+) X-ray Photoelectron spectrometer for as-cleaned and plasma treated surfaces. Hitachi scanning electron microscope model S/3400N was used for surface morphology studies of as cleaned, plasma-treated, shot blasted surfaces as well as the surfaces of coated substrates. Water contact angle (WCA) and surface tension of sol were measured using a Drop shape analyzer (Krüss GmbH, Germany) and thickness of coating was measured using an optical thickness measurement equipment model F20 supplied by Filmetrics Inc., USA. The scratch hardness was measured using pencil test according to ASTM-D3363-05; coating impact strength measured using Tubular Impact tester according ASTM-D2794 and adhesion of the coatings measured by a tape test using a cross hatch cutter according to ASTM-3359-02. Gloss of the coating at 60° was measured using Digital

Gloss meter (Photoelectric instruments Pvt Ltd., India). The durability of coatings with respect to hydrophobicity was evaluated on the basis of contact angle measurements, after immersion of the coated substrate in water for 40 days. Electrochemical tests were carried out using a Solartron electrochemical interface SI 1287. Polarization studies of the coated SS 316 substrate was carried out at 25 °C in a N_2 purged 3.5% NaCl solution with an exposure time of 1 h and 24 h. Potentiodynamic scans were recorded by applying potentials from -1 V to $+0.6$ V with a scan rate of 1 mV/s. The results obtained were analyzed using CORRVIEW2 software and compared with those obtained for bare SS 316 substrates.

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows the scanning electron microscopic (SEM) images of the surface of as-cleaned, plasma pre-treated and the shot-blasted SS 316 specimens. The original specimen is featured by its coarse grain size which is in the range of 10–30 μm (Fig. 1a). Since the plasma pre-treatment produces more chemical modification than physical modification, it is expected that SEM may not reveal any difference between an as-cleaned and pre-treated surface, as seen from Fig. 1b. The grain boundaries however appear clearer in plasma treated surface when compared to the as-cleaned one, probably due to removal of remnant organic matter during plasma treatment. The microstructure of the shot-blasted surface (Fig. 1c) obviously differs from that of as-cleaned and plasma pre-treated surfaces. Plastic deformation is evident in the surface in which the grain boundaries cannot be identified. The shot blasted surface is more roughened when compared to as-cleaned or plasma pre-treated surface.

3.2. X-ray photoelectron spectroscopy (XPS)

Since any change in surface oxidation state caused possibly by atmospheric air-plasma treatment, would be better revealed by XPS, the plasma-treated surface and as-cleaned surfaces were analyzed using XPS and results are shown in Fig. 2. The percentage compositions of the major elements determined after analysis of the XPS data are given in Table 1. Argon sputtering was avoided for cleaning the substrate inside high vacuum of XPS equipment, so as not to cause any changes in surface caused due to plasma treatment. Hence, the carbon and oxygen percentage due to remaining impurities contained in metal substrate and due to contamination of air used for plasma treatment by CO_2 and CO molecules were high [19,20]. Fe, Fe_2O_3 and Cr_2O_3 were detected on the untreated surface with binding energies equaling 706.74 eV, 710.57 eV and 576.48 eV, respectively.

After plasma treatment, the amount of Fe oxides distinctly increases due to formation of FeO and FeOOH corresponding to binding energies of 709.68 eV and 711.44 eV respectively, and Fe distinctly decreases corresponding to binding energy of 706.20 eV, as was reported on a plasma treated SS 304 surface [19]. Some non-stoichiometric CrO_x oxides occur after plasma treatment, with x below three, for binding energy corresponding to 575.75 eV [21].

3.3. Water contact angle

The water contact angles of the plasma treated surface were found to be $25 \pm 1°$, which were very much lower than $81 \pm 3°$ measured for the as-cleaned surface and $60 \pm 3°$ measured for the shot-blasted surface. The low WCA values indicate the high surface free energy of the plasma-treated surface. The change in WCA of the plasma-treated surface was also followed up as a function of time. It was found that 5 h after plasma pre-treatment, the WCA started to increase slowly and reaches $60 \pm 3°$ after 50 h. The slow increase in WCA with time implies a decrease of surface free energy due to bonding with air or dust particles in the ambience which decreases the surface wettability. Hence, coatings were deposited immediately after plasma pre-treatment.

3.4. Sol and coating characterization

The viscosities, water contents of sols and other properties of coatings measured for coatings derived from methyl

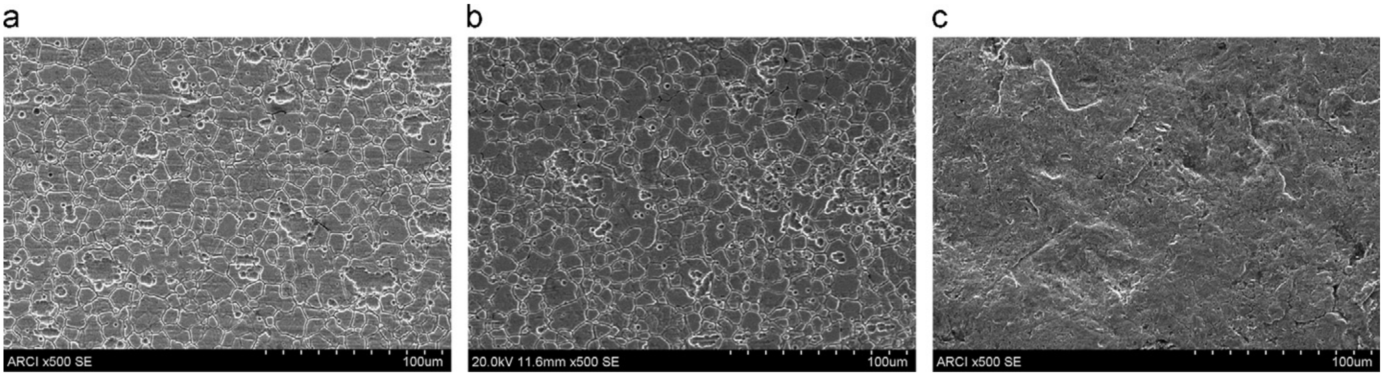

Fig. 1. SEM image of SS 316 substrate (a) as-cleaned surface (b) plasma pre-treated surface and (c) shot-blasted surface.

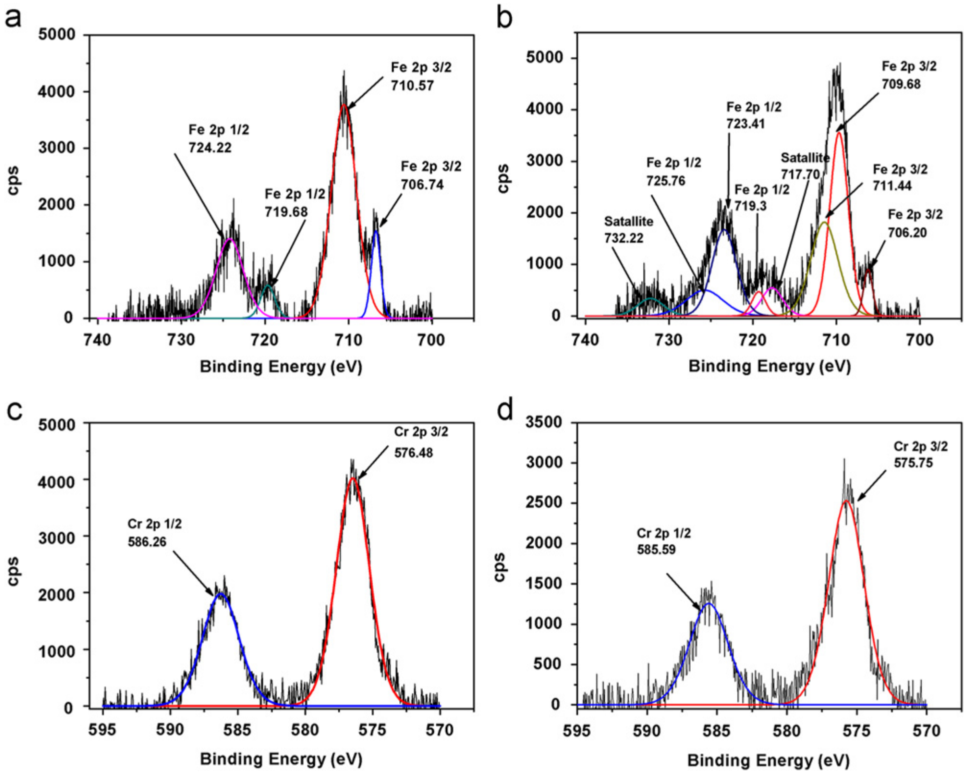

Fig. 2. XPS spectra (a) before and (b) after plasma pre-treatment for Fe; (c) before and (d) after plasma pre-treatment for Cr.

Table 1
XPS analysis of SS 316 surface before and after plasma treatment.

Treatment	Content composition			
	% Fe	% Cr	% C	% O
Untreated surface	2.23 Fe—14.34% Fe_2O_3—85.66%	2.22 Cr_2O_3—100%	47.90	44.21
Plasma treated surface	2.47 Fe—6.86% FeO—50.89% FeOOH—32.59%	1.51 Cr Non-stoichiometric in oxidation state < 3	48.73 Due to CO_2 from atmosphere	43.65 Due to oxides

or phenyl modified trialkoxysilane deposited on surfaces after each surface pre-treatment are shown in Table 2. The viscosities of sol were measured before coating deposition and it was found that both the sols had nearly the same viscosity. The water content however was higher for the sol synthesized using MTES. This indicates that more water condensation reaction has taken place in sol synthesized using MTES (abbreviated as M-T) when compared to that using PhTMOS (abbreviated as Ph-T), which means the 3-dimensional network is more complete in M-T sol than Ph-T sol. Accordingly, the coating from M-T sol shows higher pencil scratch hardness of 3H when compared to B from Ph-T sol as seen from Table 2. This higher hardness of M-T coating could be attributed to a complete network formation when methyl modified silane is used, due to the higher hydrolysis and condensation rates of MTES when compared to PhTMOS. Under acidic conditions, the hydrolysis of alkoxysilanes is reported to be initiated by the faster protonation of a leaving alkoxy group (formation of positive charge) followed by nucleophilic attack of water molecule leading to a penta coordinate transition state. The electron releasing nature of $–CH_3$ group, increases hydrolysis rate by stabilizing this positive charge. When the transition state becomes crowded due to a bulky phenyl group, the hydrolysis rate is reduced.

As regards the acid catalyzed condensation reactions, since they involve protonated silanol groups ($SiOH_2^+$), the electron releasing nature of $–CH_3$ groups can increase the condensation rates also when compared to the bulky phenyl group. Hence, the $–CH_3$ group favors both

Table 2
Comparison of properties of M-T and Ph-T coatings deposited on as-cleaned, plasma pre-treated and shot blasted surfaces.

Properties	Sol name					
	Ph-T			M-T		
Viscosity of sol (mPa.S) at 24 °C	5.9			6.6		
Water content in sol (%)	9.55			12.48		
	As-cleaned	Plasma-treated	Shot-blasted	As-cleaned	Plasma-treated	Shot-blasted
Pencil scratch hardness	B	*	*	3 H	*	*
WCA (degree)—0 day	82 ± 2	80 ± 2	82 ± 2	89 ± 2	87 ± 2	85 ± 2
WCA (degree)—40 day	61 ± 3	60 ± 6	58 ± 4	58 ± 2	59 ± 2	62 ± 3
Gloss (gloss unit)	152 ± 4	130 ± 3	80 ± 3	135 ± 4	110 ± 5	30 ± 5
Impact strength (Pigmented coating) (lb)	2			6		

hydrolysis and condensation reaction when compared to the bulky phenyl group [7]. The above explanation justifies the better mechanical properties of M-T coatings when compared to Ph-T coatings.

The different methods of surface pre-treatments however did not affect the scratch hardness, since it mostly depended on the nature of the sol. The gloss of the Ph-T coating was found to be more than M-T. Surface treatment also affects the glossiness of surface and a rougher surface shows a lower glossiness [22]. The average surface roughness R_a, for as-cleaned, plasma pre-treated and shot-blasted surfaces are 0.12, 0.13 and 1.35 μm respectively. Accordingly, the gloss values decreased in the order of as-cleaned > plasma pre-treated > shot-blasted surfaces for both Ph-T and M-T coatings. The Ph-T coatings show more reflection due to resonance structure of phenyl group that have π electrons which reflect more light, when compared to methyl groups from M-T and hence, Ph-T coatings appear glossy when compared to M-T coatings.

Wet film thickness was measured after drying at room temperature and dry film thickness after curing at 150 °C for 2 h. A typical thickness shrinkage plot as a function of withdrawal speeds as shown in Fig. 3 for the M-T coating, revealed that the coating was nearly completely dried even at room temperature. The reduction of coating thickness after curing was found to be $\sim$1.7%. This observation indicated that a low temperature of 150 °C was sufficient for nearly a complete densification of the coating, while retaining the organic groups.

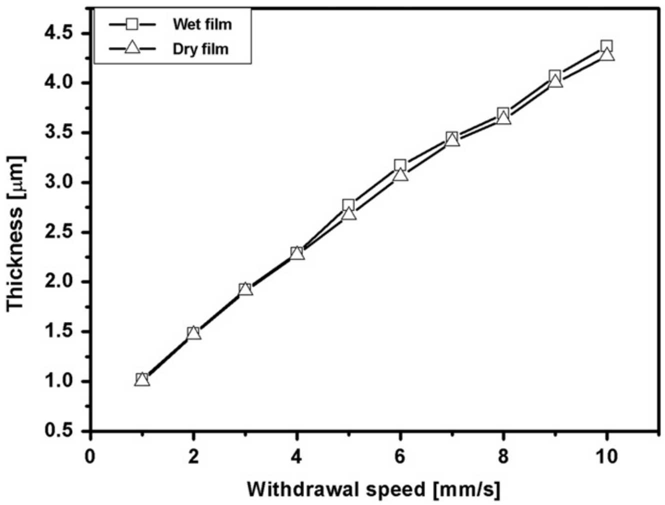

Fig. 3. Comparison of wet film and dried film thickness for M-T coatings generated at different withdrawal speeds.

The WCA on coatings that were deposited after plasma treatment, shot-blasting and as-cleaned substrates and heated at 150 °C for 2 h are presented in Table 2. It can be seen that the different surface pre-treatments do not affect the WCA. This could be expected since WCA depends on the surface free energies that are in turn dependent on the kind of chemical groups present on the surface. Accordingly, there is a difference in WCA between coatings from methyl or phenyl trialkoxysilanes. The M-T coatings are more hydrophobic than Ph-T. Usually, low molecular weight groups on the surface provide more hydrophobicity and hence, M-T coatings where–CH_3 groups reorient on the surface render the surface more hydrophobic. Though the WCA of coatings do not depend on the type of surface pre-treatment, the durability of coatings with respect to hydrophobicity was found to be dependent on the type of surface pre-treatment. The shot blasted surface was mostly found to exhibit higher durability with respect to hydrophobicity and this behavior could be dependent on the critical thickness of coatings. In case of M-T and Ph-T coatings deposited over the shot-blasted surface, a higher critical thickness was exhibited. Though the thicknesses of the coatings deposited on shot-blasted surfaces could not be measured using the Filmetrics F20 equipment, the critical thickness for M-T coatings deposited over plasma pre-treated and as-cleaned surfaces, were 2.5 and 3.2 μm respectively obtained employing withdrawal speed 4 mm/s. In case of coatings deposited over shot blasted surfaces, coatings had not cracked even when deposited at 10 mm/s. The reason for this could be due to an improved adhesion of coatings due to the roughness created on the shot-blasted surface, which in turn improves the durability of coating when immersed in water.

In order to study the impact resistance of the coatings, pigmented coatings were used, since it was difficult to conclude on the impact strength when transparent coatings were tested. It was found that, pigmented M-T coatings could bear more loads when compared to Ph-T coatings, as seen from Table 2. The M-T coating did not fail up to 6 lb from 100 cm height while in case of Ph-T coating, the coating failed slightly at 2 lb load but totally failed at 4 lb load, as shown in Fig. 4. The adhesion test carried out using cross hatch cutter showed that the coatings were highly adherent with the substrate and the adhesion strength could be ranked as 5 B for all coatings.

3.5. Corrosion test

The results of the potentiodyamic polarization measurements after 1 h and 24 h exposure to 3.5% NaCl are shown in Fig. 5 and the parameters determined after Rp fitting are given in Table 3. It could be seen that both M-T and Ph-T coatings provided a good barrier protection to the SS 316 substrate, since corrosion current density i_{corr} was lower (nearly one order) for both coatings when compared to that for the bare SS 316 substrate for 1 h and 24 h exposure to the electrolyte solution. The passive region ΔE is well defined for both the types of coatings when compared to that of the bare substrate (600 mV), where M-T coatings show higher ΔE (900 mV) than Ph-T coatings (700 mV) and the breakdown potentials are also higher for M-T coatings. The corrosion potentials were lower for both M-T and Ph-T coatings when compared to that for the bare SS 316 substrate; with corrosion potential of M-T coatings much lower than that of Ph-T coatings. The reduction in the open circuit potential (OCP) could be attributed to the effective suppression of the cathodic reaction due the reason that SiO_2 having a low isoelectric point (IEP = 1.7–3.5) leads to a negative surface charge at pH > 2. Since the coatings are exposed to the electrolyte solution 3.5% NaCl that has a pH of 6.5–7, which is higher than the IEP, the coated substrates showed a lowering of the corrosion potential. Though the coatings had lower corrosion potentials than bare SS 316, they provided a

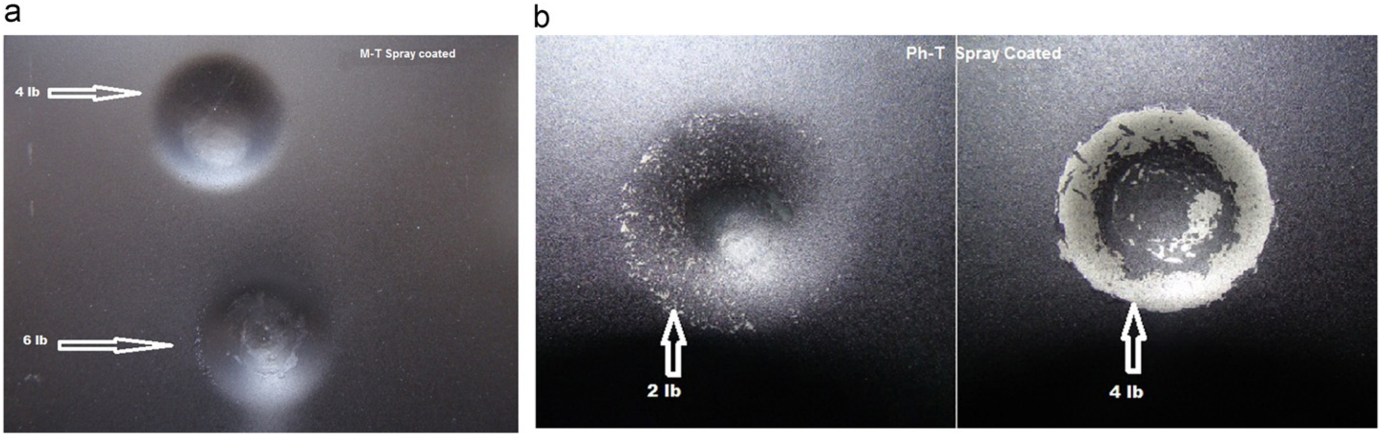

Fig. 4. Results of impact testing on pigmented (a) M-T and (b) Ph-T coatings.

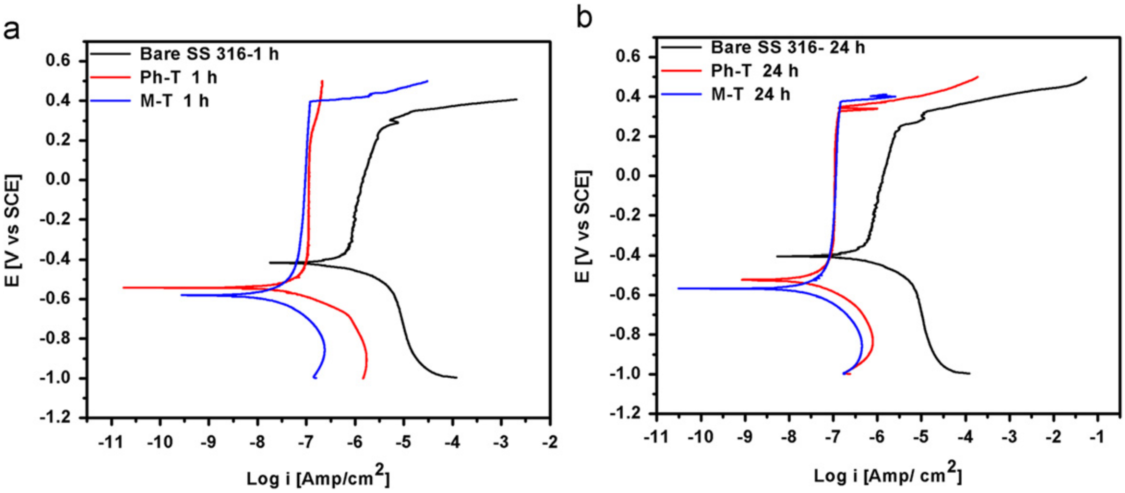

Fig. 5. Comparison of polarization data for M-T and Ph-T coatings with bare SS 316 for (a) 1 h exposure and (b) 24 h exposure to 3.5% NaCl solution.

Table 3
Results of the potentiodyamic polarization measurements for Ph-T and M-T coatings after 1 h and 24 h exposure to 3.5% NaCl, after Rp fitting.

Sample name	Thickness (μm)	Exposure time (hours)	Corrosion potential E_o (V)	Corrosion current density i_{corr} (A/cm^2)	R_p (Ω.cm^2)
Bare SS 316		1	−0.411	5.388E^{-7}	4.8417E^4
		24	−0.402	4.476E^{-7}	5.8278E^4
Ph-T—3 mm/s	3.08	1	−0.540	4.36E^{-8}	5.984E^5
		24	−0.523	3.378E^{-8}	7.726E^5
M-T—3 mm/s	1.83	1	−0.58	1.743E^{-8}	1.497E^6
		24	−0.566	2.552E^{-8}	1.022E^6

good barrier effect and reduced the corrosion currents. Since the M-T coatings were much denser (due to very good network formation evidenced by high hydrolysis and condensation rates) than Ph-T and due to the higher hydrophobicity of M-T coatings than that of Ph-T coatings, the barrier properties of M-T coatings were superior than that of Ph-T coatings.

It could be found from the present investigations that organic–inorganic hybrid coatings derived from methyl substituted organically modified silane could exhibit superior mechanical and barrier properties when compared to those obtained from phenyl substituted trialkoxysilane, though the gloss of coatings from the latter was higher than that from the former. Hence, if a glossy coating having very good mechanical and barrier properties is required, a bilayer coating configuration can be generated with the layer adjacent to the substrate being M-T and top layer being Ph-T.

4. Conclusion

The effect of different organic groups, namely methyl and phenyl groups on coatings derived from methyl and phenyl modified trialkoxysilane on SS 316 was systematically studied. The effect of different surface pre-treatments prior to coating deposition viz, plasma pre-treatment and shot blasting were also studied on the hydrophobicity, adhesion and durability of coatings. Organic–inorganic hybrid coatings derived from methyl substituted organically modified silane could exhibit superior mechanical and barrier properties when compared to those obtained from phenyl substituted trialkoxysilane. The coating deposited on a shot-blasted surface was found to be more adherent to the substrate and durable. The higher rate of hydrolysis and condensation reaction in case of methyl substituted organically modified silane that allowed formation of a denser silica network was found to be the reason for improved properties of coatings derived from methyltriethoxysilane when compared to phenyltrimethoxysilane.

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