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RESEARCH ARTICLE - CHEMISTRY

Chemical Modification of Silane-Based Coating with Inhibitor for Anticorrosive Application

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Abstract A silane-based coating was prepared by sol–gel method using (3-glycidoxypropyl) trimethoxysilane and tetraethyl orthosilicate as precursor. Aluminium isopropoxide was used as a chemical modifier; the concentration was varied on molar basis as 0.2, 0.4 and 0.6 moles. With the addition of aluminium isopropoxide, hardness properties and anticorrosive properties were observed to be improved. The corrosion inhibitors were added to improve the performance further. Efficiency of the two corrosion inhibitors was compared, i.e. benzotriazole (BT) and 2-mercaptobenzothiazole (MBT), in the system where they get added to the silane backbone through their functional groups. MBT shows better anticorrosive properties over BT, which is evaluated by salt spray and electrochemical impedance spectroscopy. Improvement in hydrophobic nature is also observed with MBT in the system. Mechanical performance of the coating also improves with the addition of MBT as compared to BT. The presence of sulphur linkage in MBT as compared to the BT is the key component for the improvement in the performance.

Keywords 2-Mercaptobenzothiazole · Aluminium isopropoxide · Sol–gel · Anticorrosive coating

1 Introduction

Corrosion is one of the reasons for major destruction of metal. It is a problem faced by many small and large industries [1]. Chromate-based anticorrosive coatings have been the most popular approach for corrosion prevention for many years [2]. Since drawbacks of the chromate-based coatings came into the picture, chromate-based coatings have been banned and replaced on a large scale. Chromate-based coatings are hazardous in nature and carcinogenic, hence not eco-friendly which made their replacement necessary [3]. Various new approaches have been explored such as conductive polymer and its composite [4], graphene and its composites [5], carbon nanotubes [6] and phosphate-based inorganic pigments [7]. Another two approaches could be sol–gel-based coatings and the use of corrosion inhibitors into the system. The sol–gel chemistry is based on simultaneous hydrolysis and condensation of alkoxide precursor [8–11]. The inorganic or hybrid polymers were synthesized most commonly by sol–gel approach. The coating based on such polymers provides excellent adhesion to the surface especially on metal surface on which it is applied. Hence, such coatings are used as pre-treatment to the metal surface. Such coatings provide excellent chemical

Corrosion inhibitor is one of the upcoming technologies in anticorrosive coating [9,15]. Corrosion inhibitors are subdivided into two types: organic corrosion inhibitors, e.g. benzotriazole and 2-mercaptobenzothiazole [16,17], and inorganic corrosion inhibitor, e.g. cerium nitrate [18]. Organic corrosion inhibitors are generally more compatible with the virgin matrix as compared to the inorganic corrosion inhibitors. They are added into the coating in the encapsulated form or in the nanocontainers.

Grafting of corrosion inhibitors to the resin backbone is one of the promising approaches as compared to the above-mentioned techniques. With the encapsulation or in the nanocontainers, corrosion inhibitors just get physically mixed with the resin matrix, whereas with chemical grafting method they get chemically linked to the resin backbone ensuring uniform distribution throughout the system as com-

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pared to physical mixing [16]. The benzotriazole was studied for anticorrosive performance by chemically grafting it with (3-glycidoxypropyl) trimethoxysilane (GPTMS) structure [17].

Metal alkoxides are used in coating as a modifier to improve its specific performance properties; for example, zirconium isopropoxide was used to improve the alkali resistance of the coating [19]. Barrier properties of the coating, hydrophobicity, etc. increased by the addition of tetrabutyl orthotitanate or tetrabutyl orthozirconate [20]. Alumina-based compounds are used in coating to improve its mechanical properties such as wear resistance, scratch hardness and abrasion resistance [21,22].

Here in this study, the performance of two corrosion inhibitors was compared for their anticorrosive properties. Benzotriazole and 2-mercaptobenzothiazole were used as corrosion inhibitors for comparison. Benzotriazole contains –N and –NH linkage in the structure. 2-Mercaptobenzothiazole is another corrosion inhibitor, which has –S and –SH (thiol group) present along with –N groups. Instead of just physical mixing here, inhibitors get chemically linked to the silane structure. Aluminium isopropoxide was added into the study at three different molar concentrations, namely 0.2, 0.4 and 0.6. Aluminium isopropoxide also gets chemically linked to the silane backbone, thus improving the coating performance.

2 Experimental

2.1 Materials

Glycidoxypropyltrimethoxysilane(GPTMS), tetraethylorthosilicate(TEOS), aluminium isopropoxide, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, water, benzotriazole, 2-mercatobenzothiazole and acetic acid are the materials used for sol–gel synthesis. TEOS is obtained from Wacker, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane is obtained from Dow Corning, and all other chemicals were obtained from S.D. Fine Chemicals.

2.2 Preparation of Sols

The sols were prepared as reported in the previous literature [17]. GPTMS and TEOS used as silane precursor were mixed in the presence of water and stirred at room temperature for 5 h. Dilute solution of acetic acid of 0.05 mol/L concentration was used as a catalyst in the formulation. Aluminium isopropoxide was added at various concentrations at the starting point with GPTMS and TEOS. After completion of 5 h, corrosion inhibitor, i.e. benzotriazole or 2-Mercaptobenzothiazole, was added into the respective system. After the addition of inhibitor, the solution was again stirred at room temperature for 30 min. In case of aminosilane-based systems, the aminosols were prepared separately by the above-mentioned process. After the addition of MBT, the aminosols were mixed with the main sol and stirred together for another half n hour. The formulations for all sols are given in Table 1.

2.3 Application of Coating Film

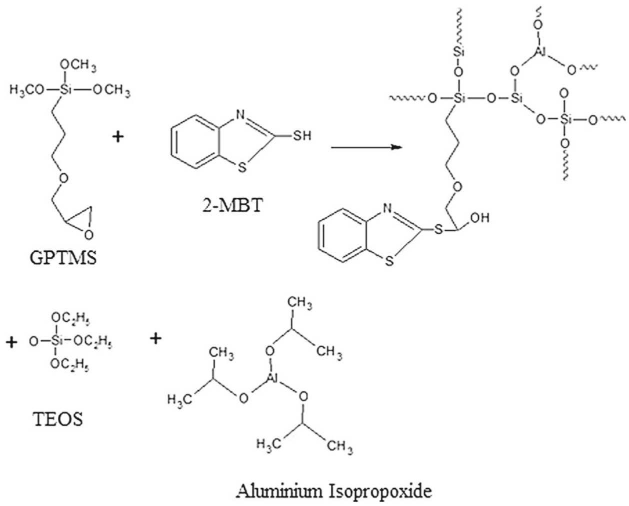
The prepared sols were applied on mild steel panels having dimensions 150 mm × 100 mm × 0.5 mm. The panels were cleaned to remove oil and grease first by washing with detergent powder, followed by deionized water and then dried. The panels were sanded with emery paper of number 800 after that cleaned with solvent. We used 2-propanol for this purpose. Then coating was applied on the panel by dip coating technique. The coating was kept at room temperature for 5 min. Then, it was kept in oven for curing at 90 °C. The reaction occurring in sol–gel formulation is as represented in Scheme 1.

2.4 Characterization

The anticorrosive properties of the coating were evaluated by salt spray and electrochemical impedance spectroscopy (EIS). The corrosion resistance was checked using salt spray with 5 % NaCl solution according to ASTM B117. EIS was done using Versa STAT-3 instrument (AMETEK, Princeton

Table 1 Formulation of the sols

Sr. no	Ingredient (In moles)	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9
1	GPTMS	3	3	3	3	3	3	3	3	3
2	TEOS	1	1	1	1	1	1	1	1	1
3	Water	20	20	20	20	20	20	21.55	21.67	22.77
4	Aluminium isopropoxide	0	0	0.2	0.4	0.6	0.6	0.6	0.6	0.6
5	Benzotriazole	0	3	3	3	3	0	0	0	0
6	MBT	0	0	0	0	0	3	3	3	3
7	Aminosilane	0	0	0	0	0	0	0.111	0.333	0.555



Scheme 1 Reaction scheme for the sol–gel system in the presence of 2-MBT

Applied Research, Oak Ridge, TN). The 3.5 % NaCl solution was used for this purpose. The Tafel plot and Bode plot measured using EIS. In Tafel plot, the corrosion current (I_{corr})and corrosion rate were measured. A saturated calomel electrode is used for the characterization in EIS. The measurements were taken at room temperature, and the exposed area was 3.14 cm^2 in all the coating formulation. The contact angle of water on coating was measured using rame-hart goniometer. FTIR spectroscopy was used to characterize the coating using a Bruker spectrophotometer by ATR method. The flexibility and impact resistance of the coating were measured according to ASTM D522 and ASTM D2794, respectively. The scratch resistance was measured according to ISO 104. Pencil hardness of the coating film was measured according to ASTM D3363. Acid resistance and alkali resistance of the coating were measured according to ASTM D1308. ASTM D 4752 was used to measure the solvent resistance of the coating and MEK, and water is used as solvent.

3 Results and Discussions

Here in this study, silane-based anticorrosive coating was prepared by the incorporation of corrosion inhibitor. The chemical structures of both the inhibitors are shown in Fig. 1.

Generally, corrosion inhibitors are added in the encapsulated form or in nanocontainers, but in this study, they were chemically linked to the silane structure, hence improving the performance. Benzotriazole contains –NH linkage which readily reacts with oxirane group of GPTMS, whereas 2-mercaptobenzothiazole is linked to the GPTMS by thiol group reaction, i.e. reaction of oxirane groups with –SH group of MBT. These functional groups also help to improve

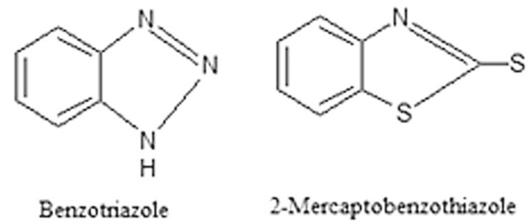


Fig. 1 Structural comparison of benzotriazole and 2-Mercaptobenzothiazole

the adhesion of the coating to the metal surface. Aminosilane was incorporated which also reacts with GPTMS through amine–oxirane reaction. Aluminium isopropoxide gets chemically linked into silane backbone through Si–O–Al linkage. So the additional step of addition of nanoparticles such as Al_2O_3 nanoparticles can be avoided, where such nanoparticles are only physically mixed with the coating system. Here in this study, the metal moiety, i.e. aluminium, gets incorporated into resin backbone through Si–O–Al linkage which helps to improve the hardness and adhesion also.

3.1 FTIR Analysis of Coating

FTIR analysis was done to study the progress of the reaction. The results are shown in Fig. 2. The strong peak at 995–1020 cm^{-1} corresponds to Si–O–Si network. The epoxide ring group observed at 1261 and 900 cm^{-1} is absent in MBT-based system which is proved that MBT gets chemically linked to the epoxide group. A strong single peak appeared at 747 cm^{-1} in MBT structure corresponds to the CH and NH wagging. This is reflected in MBT silane system where broadening and sharpness of the peak increases at the region 747–750 cm^{-1}. The Al–O–Si and Si–O–Si bending modes appear at 686–689 cm^{-1} region. The band at 1130 cm^{-1} corresponds to Al–O bond in aluminium isopropoxide overlapped with the Si–O–Si linkage broad spectrum. The MBT peak corresponds to C–S stretching and appears at 1033–1076 overlapped with Si–O–Si network peak in MBT-based system. The bond appeared at 848 cm^{-1} corresponding to Al–O–C in aluminium isopropoxide is absent in MBT silane-based system which clearly indicates that hydrolysis and condensation of aluminium isopropoxide have taken place. The band appeared at 3585–3610 cm^{-1} is due to the formation of –OH functionality due to the reaction of thiol and oxirane reaction. Hence, this bond is absent in plain GPTMS system and appears in MBT silane system [23,24].

3.2 Mechanical Properties

The results for all mechanical testing are given in Table 2.

The dry film thickness (DFT) of the coating was found to be around 60 ± 05 μm, which was measured by a digi-

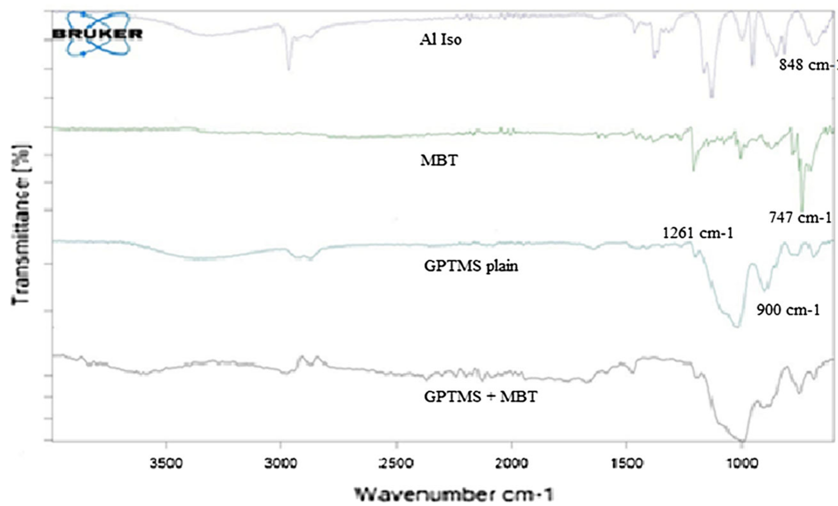


Fig. 2 FTIR analysis of the coating

Table 2 Mechanical properties of the coating

Batch no.	Properties						
	Dry film thickness (DFT) (µm)	Cross-hatch adhesion	Pencil hardness	Scratch hardness (kg)	Impact resistance (kg-cm)		Flexibility (mm)
					F.I	B.I.	
Batch 1	60 ± 5	4B	3H	1.6	61.2	61.2	0
Batch 2	60 ± 5	4B	3H	1.8	74.8	74.8	0
Batch 3	60 ± 5	4B	3H	2.1	81.6	81.6	0
Batch 4	60 ± 5	4B	3H	2.2	81.6	81.6	0
Batch 5	60 ± 5	4B	3H	2.3	81.6	81.6	0
Batch 6	60 ± 5	5B	4H	3	81.6	81.6	0
Batch 7	60 ± 5	5B	4H	3	81.6	81.6	0
Batch 8	60 ± 5	5B	4H	3	81.6	81.6	0
Batch 9	60 ± 5	5B	4H	3	81.6	81.6	0

In impact Resistance *FI* forward impact, *BI* backward impact
In cross-hatch adhesion, 5B = 0 % of coating area removed, 4B = Less than 5 % of coating area removed, 3B = 5–15 % of coating area removed, 2B = 15–35 % of coating area removed, 1B = 35–65 % of coating area removed, 0B = more than 65 % of coating area removed
In pencil hardness = 6B, 5B. . .4H, 5H, 6H (From left to right softer to harder)

tal electromagnetic thickness gauge. Adhesion of the coating was measured by cross-cut adhesion tool, and it was observed that the addition of MBT into the formulation resulted in significant improvement in adhesion. Addition of any corrosion inhibitor whether it is BT or MBT helps to improve the adhesion of coating. The functional groups present, i.e. –N from BT and –N and –S from MBT, help to form chemisorption linkages with metal panel [17]. Mild steel panels which were used have ferrous as a one of the element, and it has vacant d orbital, whereas the –N and –S elements have lone pair of electrons; as a result, chemisorption takes place which helps to improve the adhesion of the coating to the metal surface. The presence of additional sulphur linkage in MBT helps to improve the adhesion further. With the addition of aluminium isopropoxide, the metallic part of the coating gets chemically linked to the metal surface due to the formation of Si–O–Al–O–Si–O–M linkage. Hence, along with adhesion, hardness of the coating was improved which is proved by improved scratch resistance. The presence of inorganic linkage, i.e. silane and excellent crosslinking density, helps for better hardness and scratch resistance of coating after curing. With the addition of MBT, the adhesion improves further which results in improvement in pencil hardness and scratch resistance properties. Impact resistance of the coating also shows the same trend, where impact resistance increases after the addition of corrosion inhibitor. The improvement of the adhesion could be the key reason for the improvement in impact resistance properties. Due to the presence of organic moiety, all the formulations passed the flexibility test successfully without any crack formation.

3.3 Optical Properties

In optical properties, gloss of the coating was measured on glossmeter at 60° angle and results are reported in Table 3. All the coatings are basically highly transparent coating with glossy finishes.

It is observed that gloss of the coating increases with the addition of aluminium isopropoxide. The 2-MBT system shows highest gloss among all the studied formulation.

3.4 Contact Angle Measurement

The images for contact angle and results are presented in Fig. 3 and Table 4.

It is observed that bare metal shows contact angle of 68°. With increasing concentration of aluminium isopropoxide, contact angle increases, and the addition of MBT makes the surface more hydrophobic. The highest contact angle is observed for the MBT system, i.e. 95°. With the addition of aminosilane, no improvement in contact angle is observed as that of plain MBT system, and as the concentration of aminosilane increases, contact angle starts decreasing. The possible reason could be the presence of unreacted hydrophilic oxirane and amino group, which may be responsible for decrease in contact angle as compared to plain MBT system.

Table 3 Gloss of the coating

Sr. no	Name	Gloss
1.	Batch 1	86.6
2.	Batch 2	86.76
3.	Batch 3	86.98
4.	Batch 4	87.05
5.	Batch 5	90.6
6.	Batch 6	96.825
7.	Batch 7	93.57
8.	Batch 8	90.775
9.	Batch 9	88.45

Table 4 Contact angle measurement for the coating

Sr. no	Name	Contact angle
1.	Bare Metal	68
2.	Batch 1	85
3.	Batch 2	85
4.	Batch 3	85
5.	Batch 4	88
6.	Batch 5	88
7.	Batch 6	95
8.	Batch 7	92
9.	Batch 8	89
10.	Batch 9	88

3.5 Chemical Properties

Chemical resistance of the coating was evaluated by measuring its resistance towards acid, alkali and solvent, and results are given in Table 5.

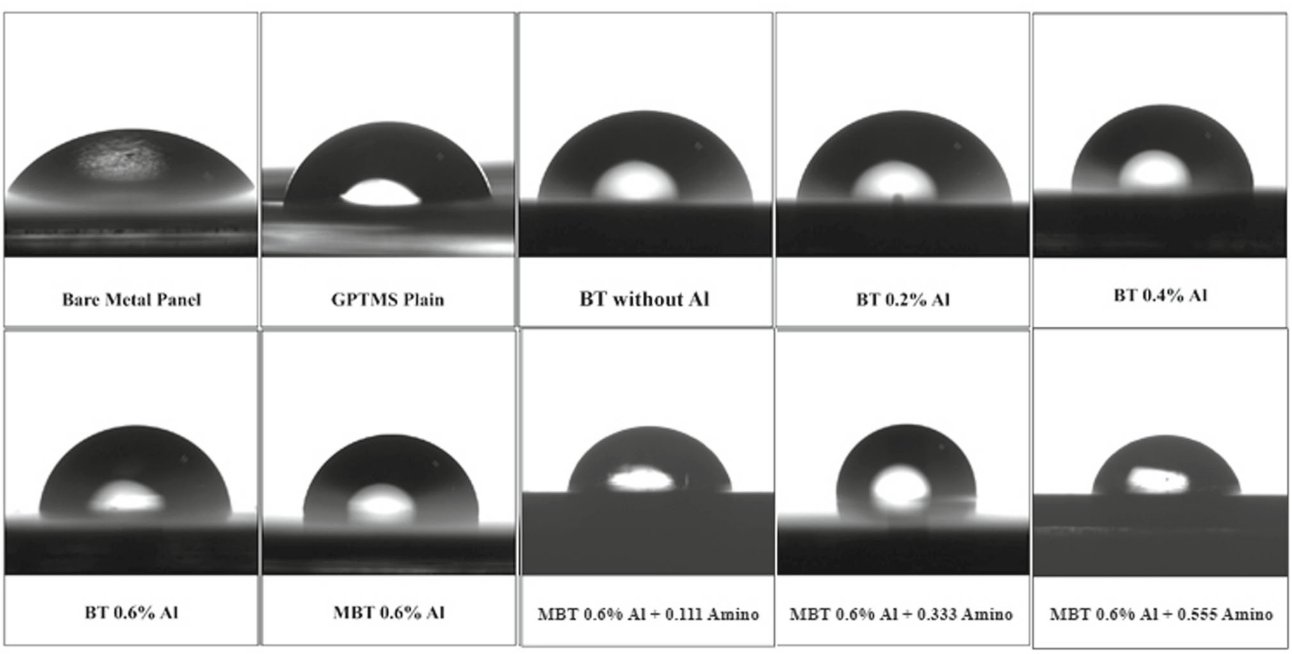


Fig. 3 Contact angle measurement

Table 5 Chemical resistance of the coating

Properties	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9
Acid	D	C	C	C	C	C	C	C	C
Alkali	B	B	B	B	B	B	B	B	B
Solvent	A	A	A	A	A	A	A	A	A

A, Film remains unaffected; B, Loss of gloss; C, softening of the film; D, loss of adhesion of the film from metal

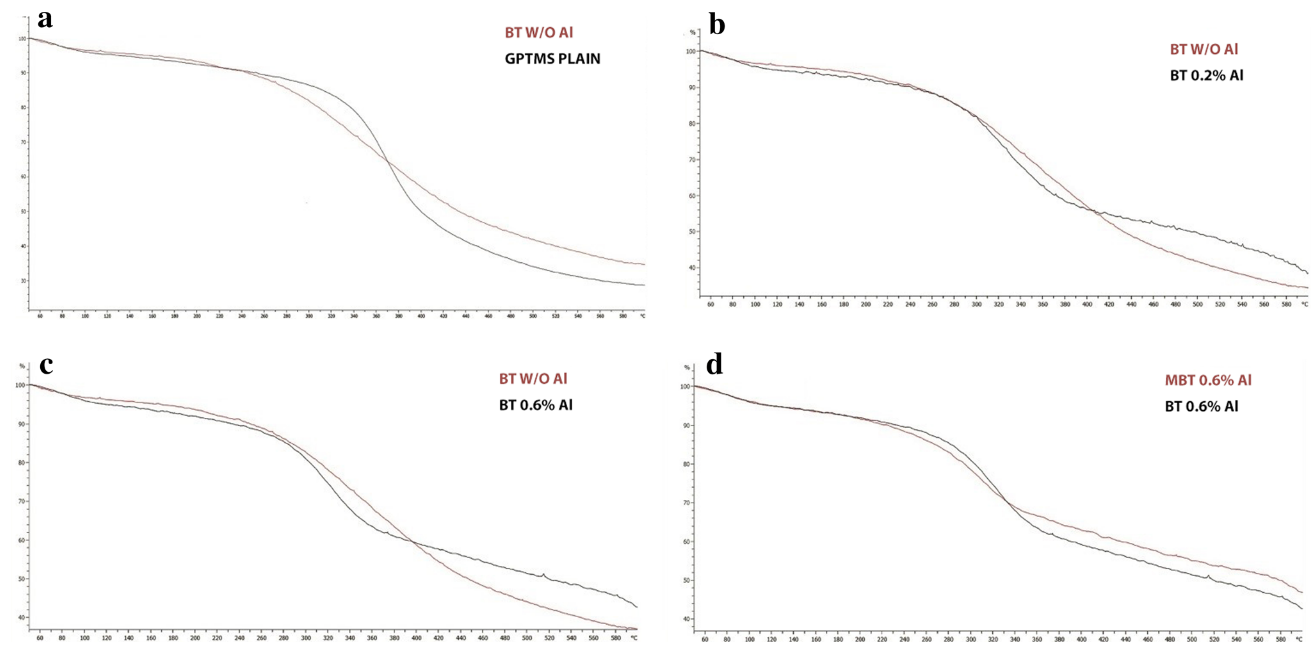


Fig. 4 TGA analysis of the coating

The plain GPTMS formulation shows least resistance to acid with the loss of adhesion of the coating from the substrate. All other formulations show slightly better resistance to acid as compared to the plain GPTMS system by maintaining their adhesion to the substrate; however, softening of the film is observed. Loss of gloss was observed in case of alkalis. However, for all the formulations alkali resistance was observed to be better as compared to the acid resistance. Excellent solvent resistance was shown by all the formulations.

3.6 Thermal Analysis Results

As shown in Fig. 4, GPTMS virgin system starts degrading quite late as compared to the system with corrosion inhibitor. The presence of organic part is higher in the inhibitor system since inhibitor is organic in nature. Hence, degradation of inhibitor- based system starts early as compared to the virgin GPTMS system. With the addition of aluminium isopropoxide, as such, degradation temperature is not affected, but the residue remains is higher. This is because, with the addition of the metal component, the inorganic content increases and the residue is higher. Both corrosion inhibitors almost show the same starting degradation temperature, but the percentage of residue remain is higher with MBT compared to BT-based system.

3.7 Anticorrosive Properties

3.7.1 Salt Spray

The results for salt spray are represented in Fig. 5. The results were evaluated for 0, 12, 24, 72 and 100 h, respectively.

As shown in Fig. 5, improvement in anticorrosive properties was observed after the addition of corrosion inhibitor, i.e. benzotriaole as compared to the virgin GPTMS system. With the addition of aluminium isopropoxide, further improvement in the performance was observed. As the concentration of aluminium isopropoxide increased, its corrosion resistance also improved. If the results were compared for 48 or 72 h, it is clearly seen that the formulation with BT with 0.6 % Al shows better anticorrosive properties as compared to the BT

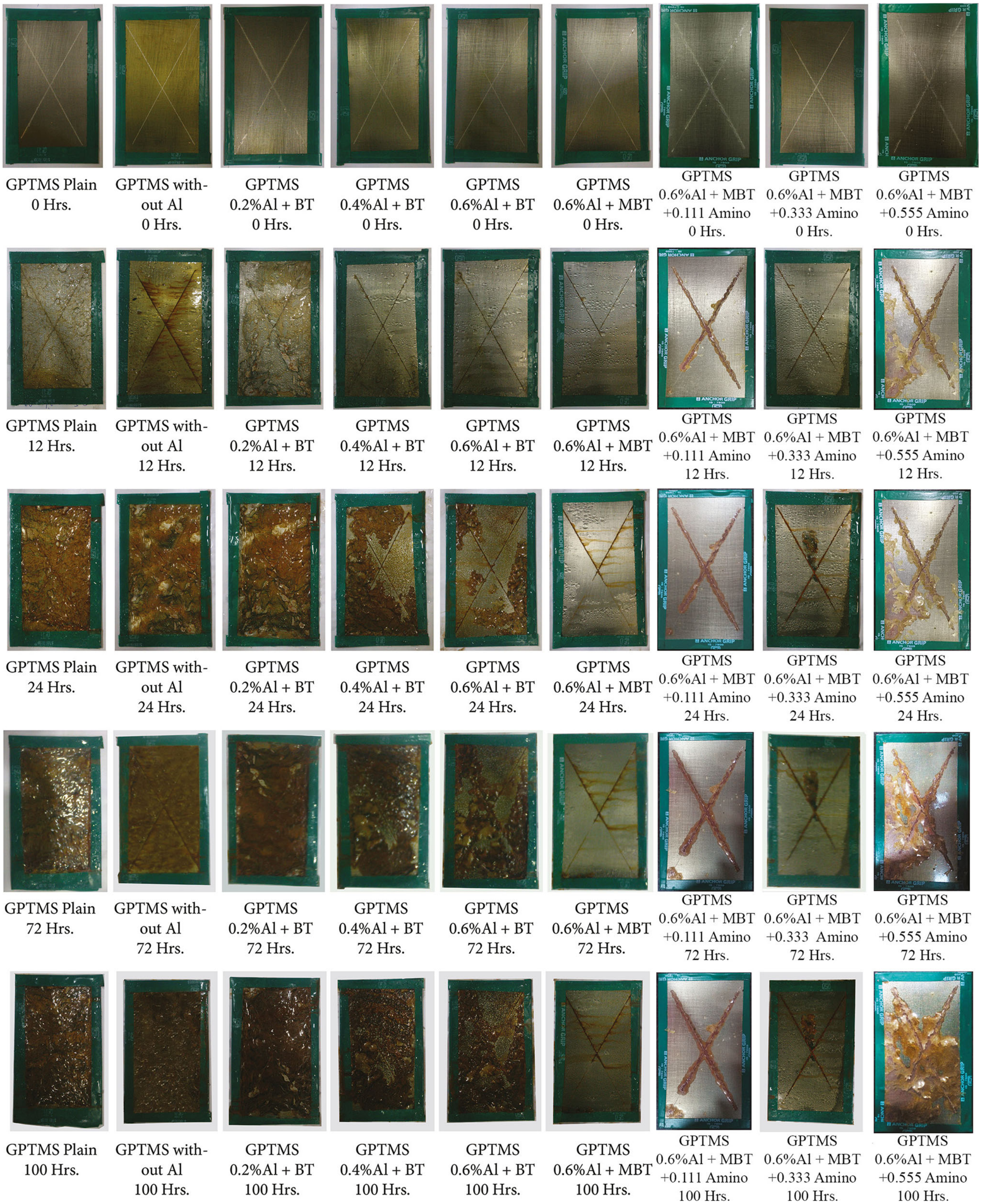


Fig. 5 Salt spray analysis of the coating

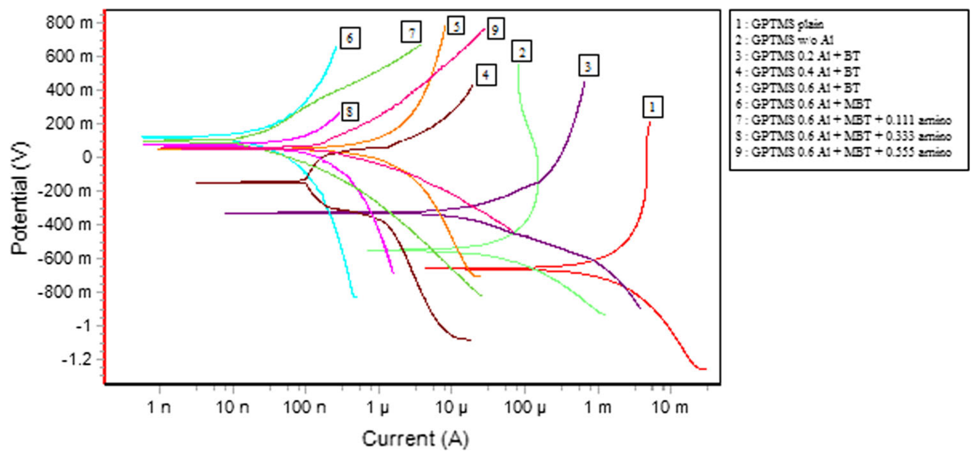


Fig. 6 Tafel plot for the coating

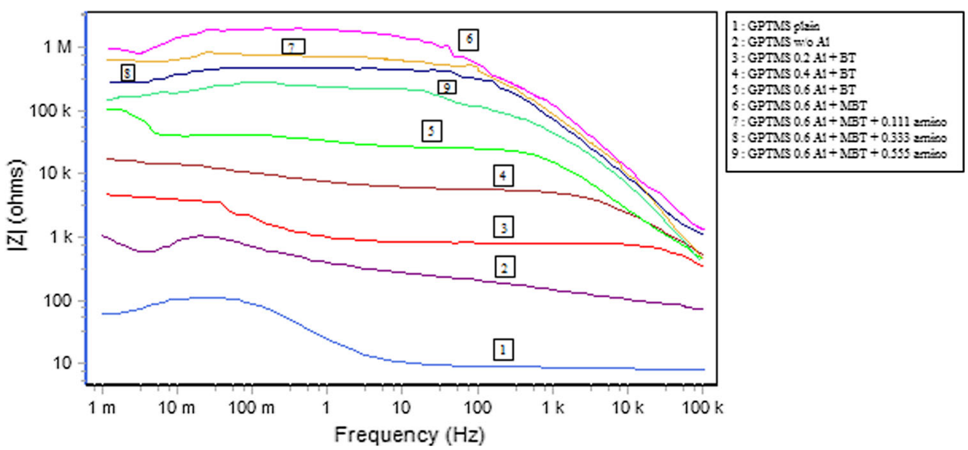


Fig. 7 Potentiostatic EIS of the coating

with 0.4 % Al. MBT with 0.6 % Al shows highest corrosion resistance followed by MBT amino system. As the concentration of aminosilane increases, anticorrosive properties start decreasing at the concentration of 0.555 moles of aminosilane, the properties affected drastically, and least corrosion resistance is observed as compared to other aminosilane-based systems. When all other formulations failed at 100 h with drastic corrosion, the MBT with 0.6 % Al system sustained with good anticorrosive strength as shown in Fig. 5.

3.7.2 *Electrochemical Impedance Spectroscopy*

The results for electrochemical impedance spectroscopy are shown in Figs. 6, 7 and Table 6.

The EIS results also show the same trend as that of salt spray. The virgin GPTMS system without any inhibitor shows the least corrosion resistance. Hence, highest corrosion current and corrosion rate are observed among all the studied formulation in Tafel plot as shown in Table 6. The impedance value is also least for this formulation as seen from potentiostatic EIS graph. As the corrosion inhibitor, i.e. benzotriazole, is added, it shows some improvement in the corrosion resistance. As explained earlier, benzotriazole gets chemically adsorbed on the metal panel; hence, adhesion of the coating increases and corrosion resistance improved [17]. With the addition of aluminium isopropoxide, corrosion resistance further improved. As the concentration of aluminium isopropoxide is increased in the formulation, the corrosion rate and corrosion current decrease as shown in Table 6. The impedance value also increases as the concentration of aluminium isopropoxide increases which proves its

Table 6 Tafel results of the coating

Sr. no.	Name	Ecorr (mV)	Icorr (μA)	Corrosion rate (mmpy)
1.	Batch 1	−663.58	2570.4	4.2718
2.	Batch 2	−559.26	1311.7	2.1799
3.	Batch 3	−331.37	2.4831	0.0041266
4.	Batch 4	−125.92	0.9891	0.00029422
5.	Batch 5	9.754	0.03986	1.05890e-04
6.	Batch 6	91.801	0.00069182	1.1497e-06
7.	Batch 7	65.21	0.006618	0.6671e-05
8.	Batch 8	53.53	0.014151	2.3518e-05
9.	Batch 9	39.49	0.028973	1.7492e-04

better resistance to corrosion. The probable reason could be that aluminium isopropoxide forms chemical bond with the metal surface through Al–O–Si–O–M linkage, and hence, adhesion improves further. With the addition of MBT, highest corrosion resistance is observed among all the studied formulations with least corrosion current and corrosion rate. The addition of aminosilane does not show any improvement in anticorrosion properties, and its corrosion resistance is lower as that of plain MBT system. The probable reason could be that, with the addition of aminosilane, some epoxy groups react with amino groups of the silane and some with the thiol group of MBT. Hence, in this case some of the MBT molecules remain as such in the coating without getting chemically linked, whereas some of the amino groups also remain free in the system and this phenomenon could lead to decrease in corrosion resistance of the system. Hence, as the concentration of aminosilane increases in the system, the number of free amino groups increases in the system, and hence, corrosion resistance decreases. And as shown in salt spray results also at the concentration of 0.555 moles of aminosilane, the corrosion resistance falls drastically because at this concentration the number of free amine groups in the system increases in large numbers and they are hydrophilic in nature also so the coating after exposure to aqueous salty environment in case of both salt spray and EIS; this formulation could not succeed as successfully as that of other aminosilane-based system. Its anticorrosive properties fall in the same range as that of BT-based system even though MBT present in it.

The MBT-based system shows the highest adhesion to the metal panel which is proved by cross-hatch adhesion test. The presence of sulphur linkage provides the better adhesion to the metal surface which is absent in the benzotriazole which is one of the reasons to improve the corrosion resistance [10]. Another reason could be the hydrophobicity of the coating, which is proved by contact angle measurement. As the aluminium isopropoxide is added into the system, its hydrophobic nature increases which helps to increase the corrosion resistance. Among all the studied formulation, MBT with 0.6 % Al isopropoxide shows the highest hydrophobicity. The increase in hydrophobic nature helps to decrease the attack of water and other hydrophilic species. Due to decrease in attack of water obviously, it is going to show the better anticorrosive property which is proved by both EIS and salt spray measurements. The results for all other formulation lie in-between the plain GPTMS-based system and MBT-based system even for Tafel plot also and potentiostatic EIS.

As shown in Fig. 7, the impedance value for plain GPTMS system is ($\leq$100 ohms) and for MBT-based system ($\geq$1 Megaohms). With such a wide difference in impedance value, it clearly indicates that MBT-based systems show tremendous improvement in anticorrosive properties as compared to the plain GPTMS system without addition of any corrosion inhibitor.

4 Conclusion

Silane-based anticorrosive coating was successfully synthesized by sol–gel method. The performance of two corrosion inhibitors, i.e. benzotriazole and 2-mercaptobenzothiazole was compared, and it was observed that 2-mercaptobenzothiazole gives better anticorrosive performance. The two key components are the presence of sulphur in MBT which provides better adhesion to the metal surface and the hydrophobic nature of the MBT-based coatings which provide better resistance to corrosion. Aluminium isopropoxide was added into the system at various concentrations, and it was chemically linked to the silane backbone. Improvement in mechanical and anticorrosive properties was observed along with increase in hydrophobic nature as the concentration of aluminium isopropoxide increased in the formulation. With the addition of metal moiety in the silane backbone, additional step of addition of encapsulated inhibitors and then physical mixing of nanoparticles for the improvement in properties could be eliminated.

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