

# Novel Bis-Urethane Bis-silane Precursor Prepared via Non-Isocyanate Route for Hybrid Sol-Gel Coatings

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**Abstract-** Effective pre-treatment of aluminum alloys is very critical for success of protective coating systems for aerospace applications. Sol-gel method is an environmental friendly technique of surface protection and has shown the potential for replacement of toxic pre-treatments and coatings which have traditionally been used for increasing corrosion resistance of metals.

We have successfully developed organic-inorganic hybrid (OIH) coating systems by using suitably tailored organosilane precursors and sol-gel processing conditions. A novel bis-urethane precursor has been developed via non-isocyanate polyurethane (NIPU) route and employed as an organic precursor of OIH systems. Coating formulations with variable proportions of this organic component were prepared and applied on AA 2024-T3 metal substrate. These coatings were evaluated for mechanical, chemical properties, corrosion resistance (Potentiodynamic polarization, salt-spray corrosion test).

**Index Terms**—Sol-gel, pre-treatment, bis-urethane, hybrid, non-isocyanate, coating, corrosion.

## 1 INTRODUCTION

Excellent mechanical properties combined with high strength-to-weight ratio makes aluminium alloys (such as AA2024-T3) as a suitable candidate for number of applications like aerospace, containers, packaging, transportation etc. Besides their uses, all metal alloys are subjected to localized corrosion in aggressive environments. One of the generic way to protect the metals and to improve adhesion of subsequent organic coating is the surface pre-treatment by Chemical conversion coatings which are oxide-based, phosphate-based, or chromate-based thin films that can be used as a base (primer).<sup>[1]</sup> Chromate conversion coatings (CCCs) can provide exceptionally good corrosion resistance, depending upon the base metal (Al, Mg Sn, Cd, Cu, Zn, Ag), the treatment used, and the film thickness. However, due to their carcinogenic nature (Cr<sup>+6</sup>), toxicity hazards, and associated costs, chromium-based compounds pose serious challenges in their usage and are a target for replacement.<sup>[2-3]</sup>

One of the promising approaches for substitution of the CCCs is Sol-Gel derived thin films which can readily be applied to most of the metallic substrates.<sup>[4-5]</sup> These Sol-Gel derived Organic-Inorganic hybrid (OIH) thin films possess number of advantages like room temperature synthesis, chemical inertness, barrier protection and commercially demonstrated scale-up potential and very low health hazard as compared to CCC. Such hybrids are formed by hydrolysis and condensation of organosilanes with traditional alkoxide precursors. It has been found that they provide good corrosion resistance as they combine the mechanical and chemical

characteristics of the comprising organic-inorganic networks.<sup>[6-8]</sup> The present study aims at developing OIH coatings with maximum covalent bonding between sol-gel matrix and metal substrate through Si-O-Al linkages which decides the adhesion and hence the anticorrosion performance of the system.

We have successfully synthesized an organosilane precursor bearing two urethane linkages through non-isocyanate route (Figure 1). Non-isocyanate method of urethane synthesis is an eco-friendly process as it does not involve use of toxic isocyanate compounds.<sup>[9]</sup> It has consistently been observed that bis-silanes, with six hydrolysable alkoxy groups, perform much better in corrosion protection performance than mono-silanes on various metals and alloys.<sup>[3]</sup> Incorporation of urethane (-NH-COO-) moiety onto the bis-silane structure allows for strong intermolecular H-bonding which helps in improving the barrier properties of the films while maintaining good mechanical performance. Furthermore, such groups would also improve adhesion with subsequent coating system through similar interactions.

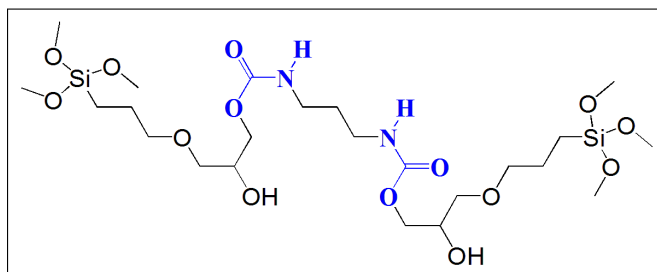


Figure 1. Structure of Bis-urethane Bis-silane precursor

## 2 MATERIALS

(3-Glycidyloxypropyl)trimethoxysilane (GPTMS), M2-Diethoxy silane, Tetraethyl orthosilicate (TEOS) were received

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from Wacker Silicones, Mumbai. Tetrabutylammonium bromide (TBAB), Triethyl amine (TEA), Glacial acetic acid (GAA), Propane diamine were reagent grade chemicals supplied by SD fine Chemicals, Mumbai

### 3 EXPERIMENTAL

#### 3.1 Synthesis of Bis-urethane bis-silane precursor

The first step to prepare urethane precursor is the cyclo-carbonation of GPTMS which was carried out in high pressure autoclave reactor. The reactor was provided with controlled supply of CO<sub>2</sub> gas. Tetrabutyl ammonium bromide (TBAB) was added as a catalyst for the reaction. The reaction was maintained at temperature 120<sup>o</sup> C and pressure of 600 psi for 6 hours. After completion of the reaction, the product was analysed by FTIR spectroscopy to confirm functional group conversion.

In the second step, cyclocarbonated GPTMS (C-GPTMS) (2moles) product was reacted with propane diamine (1 mole) in presence of triethylamine (TEA) catalyst. The reaction was carried out at 55-60<sup>o</sup> C for 1 hour. After completion of the reaction, the product was dissolved in dry methanol and stored. Figure (2) is a schematic representation of these reactions.

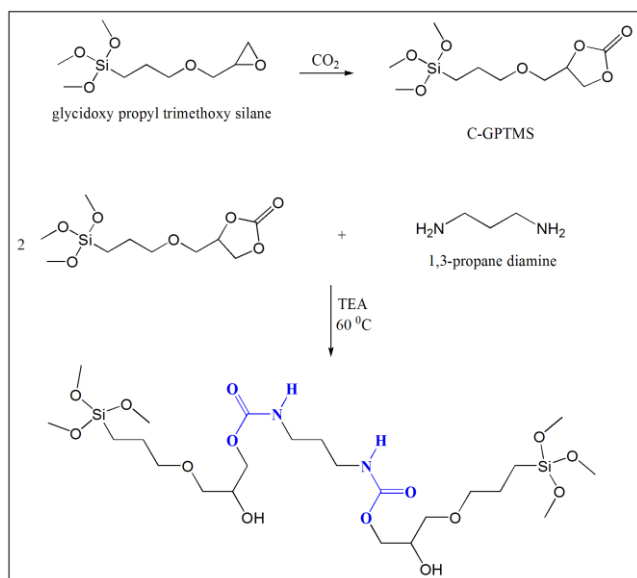


Figure 2. Synthesis of Bis-Urethane Bis-Silane

#### 3.2 Preparation of sol

Mixture of TEOS and M2-Diethoxy silane along with methanol (in a molar ratio of 1:2:2) was allowed to hydrolyze for 12 hours at room temperature (28<sup>o</sup>C) under magnetic stirrer. The pH of the solution was maintained in the range of 3-4 using diluted solution of GAA (glacial acetic acid). After 12 hours of hydrolysis, Bis-Urethane (BU) precursor was added in varying quantity and continued for further 12 hours stirring. For all the formulations, degree of hydrolysis and solid contents was maintained constant.

#### 3.3 Substrate cleaning and coating deposition

AA 2024 T3 panels (2 x 3 square inches) were first hand scrubbed using sand paper followed by acetone washing. These panels were further cleaned by immersion in 5 % KOH solution at 50<sup>o</sup>C for about 15 minutes. After immersion, the substrates were rinsed repeatedly with deionized (DI) water and blow dried.

The films were deposited onto the prepared substrate by dip coating method at room temperature with standard withdrawal speed of 15 cm/min and residence time being 20 second. The coated substrates were allowed to air dry for 10 minutes and were then placed in an air circulating oven at 70<sup>o</sup> C for 1 hr. Typical dry-film thickness of coating was observed to be 8-10 microns.

### 4 METHODS AND MEASUREMENTS

The BU precursor was characterized for functional group using Fourier Transfer Infrared Spectroscopy (FTIR) in the spectra range of 400-4000 cm<sup>-1</sup> on Perkin-Elmer Spectrum 100 Instrument. Applied coatings were tested for mechanical performance as per standard ASTM methods. Coatings were also evaluated for hydrolytic stability (as per ASTM B-1308) using 4-hr boiling water immersion test and observed for detachment of the coating through cross cut adhesion as per standard mentioned above. Completely cured coatings were tested for the Anticorrosive performance was evaluated by Salts Spray method as per ASTM B-117 and tafel analysis, electrochemical impedance spectroscopy.

### 5 RESULTS AND DISCUSSION

#### 5.1 FTIR analysis

FTIR analysis was carried out as described in section 5. Completion of cyclo-carbonation of GPTMS was ensured by the absence of transmission band of 914 cm<sup>-1</sup> for epoxy group and appearance of a new band at 1790 cm<sup>-1</sup> for carboxyl group (-C=O).

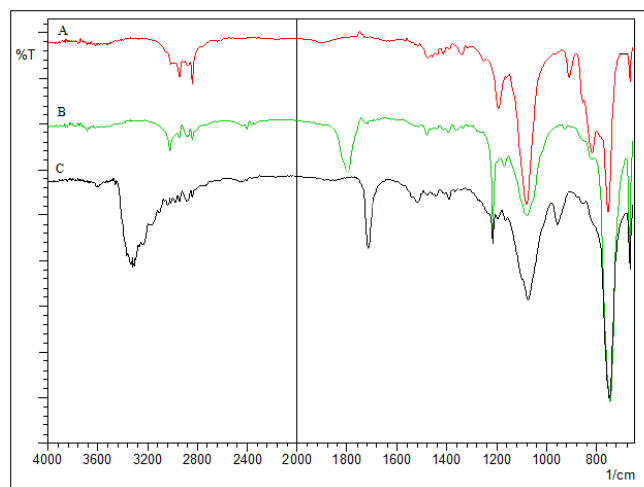


Figure 3. FTIR spectrum for A) GPTMS, B) C-GPTMS, C) BU precursor

BU precursor synthesis was also characterized by FTIR analysis for presence of strong transmission band at 3340  $\text{cm}^{-1}$  confirming generation of hydroxyl groups. Transmission band at 1705  $\text{cm}^{-1}$  indicates conversion of carboxyl  $\text{-C=O}$  group to urethane  $\text{-C=O}$ . Transmission bands at 1080  $\text{cm}^{-1}$  confirmed the presence of silicone methoxide (Si-OMe) groups in the compound. Figure-3 shows detailed FTIR spectra for GPTMS, C-GPTMS and BU precursor.

### 5.2 Mechanical Properties

The coated films were evaluated for mechanical properties including tape adhesion, taber abrasion, scratch hardness, pencil hardness, impact resistance and flexibility (Table 1). Dry crosshatch tape adhesion was observed to be excellent which can be attributed to the covalent bonding of the coated film with the substrate and its unique chemical structure.

Table 1. Mechanical Properties

Coating with BU (%)	Dry Tape Adhesion	Pencil Hardness	Scratch Hardness (kg)
2	5B	2H	1.1
4	5B	3H	1.3
6	5B	3H	1.7
8	5B	4H	2.2

Coating with BU (%)	Impact (Kg-Inch)	Taber Abrasion (Wt. Loss in mg)	Flexibility (mm)
2	26.7	Film Re-moved	0
4	26.7	2.9	0
6	26.7	2.2	0
8	26.7	1.0	0

Scratch hardness and pencil hardness showed an increase with increasing percentage of urethane precursor in the coating. Presence of urethane linkages and hydroxyl groups in the polymer backbone would result in greater chances of inter and intra molecular hydrogen bonding. This was reflected in the increasing trend of hardness properties with increase in the content of urethane precursor in the system and subsequently to a stronger polymeric network. Inter and Intra- molecular hydrogen bonding also helps in improving the barrier properties of the films while maintaining good mechanical performance.

Coated panels were evaluated for flexibility by Conical Mandrel Bend method. It was observed that these coating possessed excellent flexibility which could be due to combined effect of long chain BU precursor and M2-Diethoxy silane resulting in reduced crosslinking density of for overall film maintaining its integrity. Impact resistance was determined using falling ball impact tester for both intrusion and extrusion. Tested panels were observed for any visible cracks. All the films showed no crack development during the impact test. It was confirmed that the excellent impact resistance and

flexibility could be a result of balance between high cross-link density and presence of longer soft polymeric segments which could uniformly distribute the energy incurred due to these mechanical distractions.

### 5.3 Scanning Electron Microscopy

Cured coating were analysed for surface morphology by scanning electron microscope. Uniform distribution of silica particles is observed throughout the surface as shown in figure 5(A). Similarly, presence of softer polymeric segments due to organic urethane precursor can also be confirmed from figure 5(B).

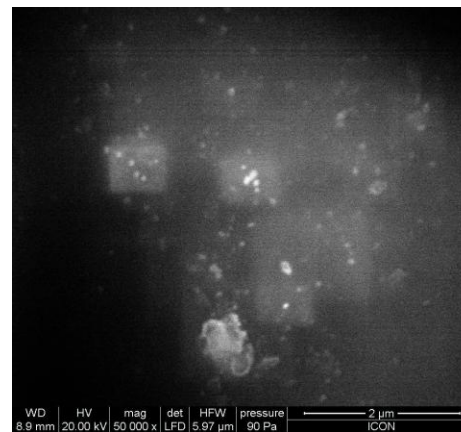


Figure 5 (A) SEM image of cured coating showing distribution of silica particle

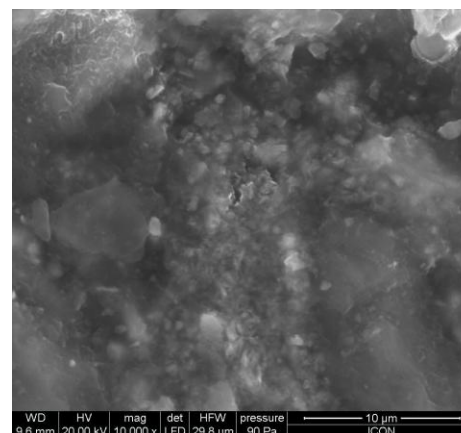


Figure 5(B) SEM image of cured coatings showing presence of softer polymeric segments

### 5.4 Chemical Resistance

#### 5.4.1 Acid Resistance

Acid resistance of the coated film was found to improve with the increasing percentage of BU precursor. Films with 2 and 4 % BU precursor showed blister formation after 12 hours of exposure whereas coatings containing 6 and 8 % BU precursor showed acid resistance up to 22 and 26 hours respectively. The observations could be related to increasing cross-link density with increasing proportion of precursor which in other way helps in improving the barrier properties. The effect of

acid susceptible free hydroxyl groups is thus balanced by improved barrier properties.

### 5.4.2 Hydrolytic Stability

The boiling water stability test was carried out to study the hydrolytic stability and permeability of films to water. In this test, the coated films were kept in boiling water for 4 h and were observed for subsequently any damage and secondary adhesion. The tested panels were unaffected and no discoloration was observed. The crosshatch tape adhesion was also unaffected which confirms minimum permeability of water through the coated films.

### 5.5 Corrosion Resistance Performance

The cured coatings were evaluated for corrosion resistance using Tafel Analysis (Figure 6) and Bode plot (Figure 7). All electrochemical measurements were carried out at room temperature in 3.5% NaCl solution. Test system consisted of three electrode cell, in which Ag/AgCl electrode, a platinum electrode and a coated panel as reference, counter and working electrode respectively. The exposed area of the coated panels to the NaCl solution was 3.14 cm<sup>2</sup> in all the cases. The corrosion rate was observed to decrease with increasing precursor content and hence better corrosion resistance at higher concentration. The corrosion potential also moved in anodic direction in the same order. The corrosion current density  $I_{corr}$  values were found to be very low in comparison to bare metal. In general, lower  $I_{corr}$  values for all sol-gel coatings compared to bare substrate indicate that sol-gel coatings indeed can provide a physical barrier for blocking the electrochemical process. When compared to chromate based primer, the performance was slightly inferior but it was proved that the sol-gel coatings were efficient enough to provide adequate corrosion protection

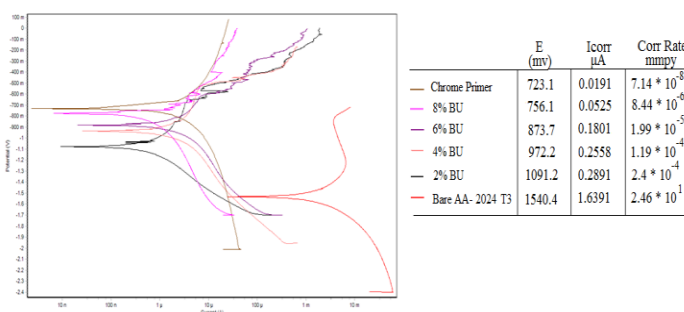


Figure 6. Tafel analysis for coated substrates

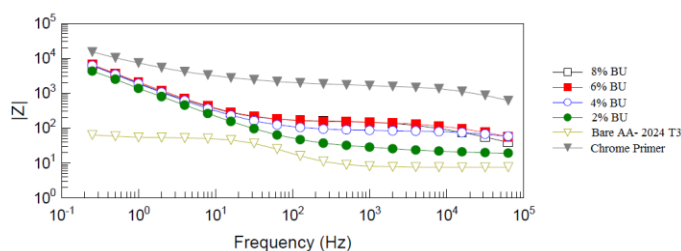


Figure 7. Bode plots evaluated by electrochemical impedance spectroscopy.

Similar trend was reflected in salt spray resistance. Coatings with 2, 4, 6, and 8 % urethane precursor could withstand 280, 305, 370 and 450 hours of salt spray exposure respectively. Chromate primer showed salt spray resistance for more than 500 hours.

## 6. CONCLUSION

The bis-urethane precursor synthesized via non-isocyanate route was used as organic precursor in preparation of sol-gel based organic-inorganic hybrid (OIH) coatings for AA2024-T3 substrate. The OIH coatings showed improvement in overall performance as the percentage of bis-urethane precursor was increased. Corrosion study reveals that the performance is controlled by proportion of urethane precursor in OIH coating. At higher precursor content, the overall properties could be adversely affected hence optimization is necessary. Optimization of hydrolysis time and chain length of urethane precursor for overall balanced performance properties is under study. The use of this precursor further extends to the versatile chemistry of sol-gel processing in even more environmental friendly way as a possible replacement of currently available conversion coatings for metal pre-treatments.

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