Journal of Research Updates in Polymer Science, 2013, *2*, 209-231

Sol-Gel Process for Anti-Corrosion Coatings

Saheli Bera[1], G. Udayabhanu[1], Ramanuj Narayan[2] and T.K. Rout[3,*]

[1]*Department of Applied Chemistry, Indian School of Mines, Dhanbad, 826004, India*

[2]*Organic Coatings Department, CSIR-Indian Institute of Chemical Technology, 500 007, India*

[3]*Reserach & Development Department, Tata Steel Ltd, 831007, India*

Abstract: This review paper summarizes the current state of the art of sol-gel technology for formulating anti corrosive protective coating. A brief description of the mechanism of sol-gel reactions, various parameters that influence the property of the final product and the course of the sol-gel reaction has been given. Different types of metal precursors that are extensively used in sol preparation and the advantages and disadvantages have also been mentioned in brief. Surface chemistry of sol-gel matrix and various stabilizing and destabilizing forces that are active on the surface of colloidal particles have also been discussed. Problems related to obtaining good quality product with uniformly distributed concentrations have been outlined. Possible pathways for further improvement of anti-corrosive properties of the coating have been described, such as incorporation of various types of additives into the sol matrix prior to coating. As a whole the present study summarizes the superiority and benefits of organic-inorganic hybrid coatings using sol-gel technique and having good protective and anti-corrosive properties.

Keywords: Corrosion, Sol gel, chrome free, colloid, surface chemistry.

1. INTRODUCTION

Corrosion is the loss of material due to electrochemical interactions with the environment and the electrochemical reactions involving electron transfer. Therefore one of the most effective corrosion control technique is to isolate the cathode from anode [1, 2]. Chromatation is a very efficient coating for aluminum and stainless steel, and is generated from acidic mixtures of soluble hexavalent chromium salts. A continuous layer of chromium compounds having both composition of different ratios of Cr^{+3} to Cr^{+6} are formed by oxidation and reduction reaction with the metal surface. The hexavalent chromium causes hazardous problems for the coating industry because hexavalent chromates are water soluble and have got some toxic features and is carcinogenic [3]. For this reason a number of alternative surface treatments have been established as effective replacements for chromium based conversion coating.

In recent years, researchers found that silane based coatings can protect metals against corrosion. The selection of suitable silane coupling agents based on the structure, molecular functionalities and solvent compatibility for the sol-gel coating process can provide corrosion protection [4, 5]. Over the past 25 years, sol-gel technique has proven to be very successful in a wide range of thin film applications. Organic inorganic hybrid materials such as organically modified silanes (ORMOSIL) have proved to be very efficient in several industrial applications such as anti-corrosive protective coatings, electronic appliances, glass industry and optics for the fabrication of reflective and protective oxide coatings [6]. Organically modified silicates are formed by hydrolysis and condensation of organically modified silanes with traditional alkoxide precursors by sol-gel method [7, 8]. The silica film formed by sol-gel technique has several advantages over chromate conversion coatings, such as, in contrast to the toxic Cr^{+6} the use of the silica film is safer for the workers and the environment, the chemical conditions of the sol-gel process are mild, the hydrolysis and the condensation reactions are catalyzed by an acid or a base, extreme pH conditions can easily be avoided, pH sensitive compounds such as dyes, corrosion inhibitors can be entrapped and still retain their functions [9,10], the hydrophobic property of the silica film prepared by sol-gel process can be varied depending upon the structure of the organo-silica compounds [11,12].

2. CHEMISTRY OF SOL GEL SCIENCE

2.1. Sol-Gel Processing

Sol-gel process always consists in selecting the appropriate precursor molecules, water and a catalyst [13].

Precursor

The precursor molecules lead the reaction towards the formation of the colloid particles. The precursor for synthesizing these colloid particles is composed of a metal or metalloid element surrounded by several

---

*Address correspondence to this author at the Reserach & Development Department, Tata Steel Ltd, 831007, India; Tel: 91-657-6648885, 91-8092088390; E-mail: tkrout5@yahoo.com

E-ISSN: 1929-5995/13 © 2013 Lifescience Global

reactive ligands. The alkoxides are most common reagent because they easily react with water, for example, tetra ethoxy silane (TEOS), tetra methoxy silane (TMOS). Frequently, the inorganic precursor like sodium silicate (Na_2SiO_3) is also used in sol-gel processing.

Water

The complete hydrolysis and polycondensation of the precursor take place in presence of water. Moreover, water is a side product of condensation reaction. Hence excess amount of water in the reaction medium can cause the hydrolysis reaction to proceed in the reverse direction, i.e. hydrolysis of the siloxane bond.

Catalyst

The rate of the hydrolysis reaction is very slow at ambient temperature and often takes several days to reach the completion stage. Hence an acidic or basic catalyst is needed to accelerate the reaction. The amount and type of catalyst used play the key role, which determine the micro structural and physical properties of the final product.

Sol

A sol is a dispersion of colloidal particles and is always in Brownian motion within a fluid matrix. Suspension of particles of linear dimensions within the range of 1nm (10Å) and 1µm (100Å) are called colloids [14]. The particles within this dimension range can be divided into three categories. They can be either composed of subdivided parts of bulk matter (e.g. small particles of alumina), or real macromolecules that are big enough to be colloidal particles (such as proteins), or of small particles that can be treated as both macromolecules and as tiny parts of macroscopic matter (e.g. lacy particles). There are two thermodynamic phases in the subdivided part of the bulk material and the sol is considered as lyophobic, or hydrophobic.

Gel

A gel is a porous interconnected semi-solid network that expands in a stable fashion and three dimensionally throughout a liquid medium. The nature of gels depends on the coexistence between the solid network and the liquid medium. The liquid is present between the solid networks, composing the gel. It does not flow out spontaneously and is in thermodynamic equilibrium with the solid network. Finally, removal of the liquid phase leads to the formation of xerogel or aerogel which depends upon the drying conditions of the gel.

Types of Gel: (a) Colloidal **Gel**

If a system contains colloidal particles within the range of 1-1000 Å and upon aggregation and condensation they are linked into a three-dimensional framework surrounded by a liquid phase, then it may be termed as colloidal gel. *(b)Polymeric gel*: These are considered as suspensions of highly branched macromolecules in which individual particles cannot be distinguished. If the solid network is made up of sub-colloidal chemical units then the gel is polymeric. Polymers are a group of molecules whose structure can be generated through repetition of identical or different monomeric units [15]. The solubility of these macromolecules in a water- alcohol acid medium resists the transformation of these chains into individual particles.

2.2. Hydrolysis

Sols are synthesized by hydrolyzing the monomers, the alkoxy groups (–OR) are converted into hydroxyl groups (–OH) in the presence of an acid or a base as catalyst.

The general hydrolysis reaction can be described as:

$$M(OR)4 + H2O \rightarrow HO - M(OR)3 + ROH \qquad (1)$$

M is a metal atom and R is alkyl group. Products from incomplete hydrolysis can react further in a condensation reaction

$$HO - M(OR)3 + HO - M(OR)3 \rightarrow (OR)3M - O - M(OR)3 + H2O \qquad (2)$$

2.3. Condensation

Condensation reaction follows a two step mechanism where the coordination of the precursor molecule is fully saturated. This takes place *via* nucleophilic substitution with hydroxo group (M--OH), (OH) as nucleophile and H_2O or OH - (OR) molecules are the leaving group (oxolation) depending on acidic and basic catalysis, respectively [4].

$$M1 - OH + M2 - OR \rightarrow M1 - O\ M2 + OR \qquad (3)$$

In the case, when the coordination of the molecular precursor is not saturated both oxolation and olation may occur only *via* addition with (M---OH) and/or (M---O---) as nucleophiles producing chains and cycles:

$$M1 - OH + M2 - OR \rightarrow M1 - O - M2 - OR \quad (4)$$

An increase in the coordination number of M_2 can also be achieved. This depends on the electronic configuration, electronegativity of the metal atom and on water concentration [6].

2.4. Sequential Steps Involved in Sol Gel Technology

Sol-gel method involves following sequences to obtain a final chemistry of materials for various applications. These materials can be used for making thin films over metallic substrates and/or for making nano-particles and/or ceramic cast. The steps are (i) Hydrolysis of the metal precursor by using a suitable catalyst (generally an acid or a base), (ii) Condensation of the hydrolyzed precursors, (iii) Aging of the sol, (iv) Processing or deposition of the coating on metal substrate generally by dip coating or spin coating, (v) Cross linking of film by heat treatment which is known to a) drying and b) densification [16].

3. AQUEOUS AND NON AQUEOUS SOL-GEL PROCESS

Organo-silica compounds are immiscible with water in all proportions. Hence addition of an organic solvent is necessary to achieve the miscibility and to facilitate the hydrolysis reaction. When organo-silica compounds and water are mechanically mixed to promote the hydrolysis reaction, a single phase mixture can be obtained due to hydrolysis. The process is called “water based sol-gel” [17]. This can be achieved for organo-silica compounds with short organic groups. However a problem of miscibility arises when an organo-silica compound with long organic group is mixed with water. In such cases an organic solvent is needed to achieve homogeneity of the sol. Usually alcohols are used as organic solvent and the process is called “alcohol based sol-gel” [18].

3.1. Alcohol-Based Sol-Gel System

Alcohol–based sol-gel process is based on dispersion of organo-silica compound and water in an organic solvent. When alcohol as a solvent and alcohol generated in the hydrolysis step are having similar chemical nature, then a competition between hydrolysis and alcoholysis takes place in the reaction medium. High concentration of ROH in the sol tends to direct the reaction towards alcoholysis. Hence the hydrolysis of the –OR groups by –OH groups in alcohol-based sol does not go to completion [19, 20]. Several studies have been made to understand the effect of organic solvent on the silica coating. Metroke found that the properties of the silica film on aluminum substrate are controlled by the concentration and structure of the alcohol used. The best corrosion protection is achieved when small alcohols are used at low concentrations [20]. In contrast, if the alcohols are used at high concentration, then the hydrolyzed products undergo depolymerization. It can be concluded that appropriate choice of the solvent permits tailoring of the film thickness, coating structure and provides film hydrophobicity.

3.2. Water-Based Sol-Gel System

Using an alcohol as a solvent possesses some major drawbacks in sol-gel films with respect to existing industrial systems. This difficulty arises due to the flammability of the volatile organic compounds (VOC), concerns regarding health, safety issues and cost. Thus researchers are now concentrating on water based sol-gel process. The main advantages of the water-based over the alcohol-based sol systems are [6, 21]: (1) Hydrolysis reaction of the water-based process goes to completion smoothly, whereas hydrolysis of alcohol-based sol reaches equilibrium because of the competition between hydrolysis and alcoholysis reaction. (2) Difference in the thickness and final concentration of the silica sol may be caused due to evaporation of alcohol from sol gel matrix during drying process, water-based sol is free of this problem. (3) Water-based sols are environmental friendly and are non-flammable, while the alcohol-based sols are flammable. (4) The water-based sol-gel process is cost effective as the materials used in this process are cheaper than the materials used in alcohol-based system.

In spite of possessing all these advantages, the aqueous sol-gel chemistry suffers from some serious limitations. The aqueous sol-gel chemistry of transition metal precursors is rather complicated due to very high reactivity of transition metals, and formation of large number of oligomeric species depending on the oxidation state of the metal and pH of the medium. For most of the transition metal precursors, it is almost impossible to control the reaction rate. Due to the presence of vacant d orbitals the transition metal compounds react very fast, resulting in a loss of morphological and also structural control over the final oxide material. Furthermore, the difference in the reactivity of metal alkoxides makes it difficult to control the composition and the homogeneity of complex multi

Table 1: Physical Properties of Solvent

Solvent	Viscosity (cP)	Relative dielectric constant	Boiling point (^{o}C)
Methanol	0.557	32.63	64.7
Ethanol	1.0885	24.55	78.3
n-propanol	1.9365	20.33	97.0
Iso propanol	2.0439	19.92	82.5
n-butanol	2.5875	17.51	117.7
Ethylene glycol	16.265	37.70	I97.3
Acetyl acetone	1.090	25.70	140.0

- metal oxides by the sol-gel process. One useful pathway to decrease and to control the reactivity of the precursors is the use of organic additives like carboxylic acids, β-diketones or functional alcohols that act as chelating ligands and modify the reactivity of the precursors [22, 23]. An alternative strategy involves the slow release of water by chemical or physical processes, allowing control over the local water concentration and thus over the hydrolysis of the metal oxide precursors [24].

In nonaqueous sol-gel chemistry the transformation of the precursor takes place in an organic solvent in absence of water. In comparison to aqueous sol-gel chemistry, the list of potential precursors is longer and in addition to inorganic metal salts and metal alkoxides, metal acetates and metal acetylacetonates can also included.

4. FACTORS AFFECTING SOL-GEL PROCESS

4.1. Effect of Solvent Used

In sol-gel chemistry generally the hydrolysis step is carried out in an aqueous, organic or mixed solvent along with a catalyst (either an acid or a base). The extent of evaporation of the liquid medium imparts important effect on the final structure of the gel products. If the solvent undergoes evaporation too fast, the corresponding products possess cracks, disruption and unequal concentration distribution. Its quantity in the system also affects the intensity of the agglomeration and polymerization processes [25]. Table **1** represents physical properties of some frequently used solvents.

4.2. Influence of pH of the Medium

The rate of hydrolysis of a precursor is dependent on the acidic or basic catalyst. The acidity of the medium has a strong influence on the length of the polymeric chain and on the content of the non-reacting components of the precursor. Hence two different acids can promote two different rates of hydrolysis, even if they are added at the same molar quantity.

Izumi *et al*. [26] has investigated the difference in the hydrolysis rate of methyl triethoxy silane and phenyl triethoxy silane in acidic (HCl) and basic (NH_4OH) medium. In acidic media methyl triethoxy silane undergoes almost 100% hydrolysis in an hour, but the other silane requires almost four hours for achieving the same. On the other hand in alkaline medium the latter undergoes 100% hydrolysis after two hours but the former achieved the same in five hours. The hydrolysis and condensation rate of $Si(OR)_4$ is given schematically in Figure **1**, where it is clear that rates of hydrolysis and condensation decreased in a similar manner up to pH≈6 and thereafter the behaviors changed in opposite manner in alkaline pH. The availability of –OH ion drives condensation reaction significantly.

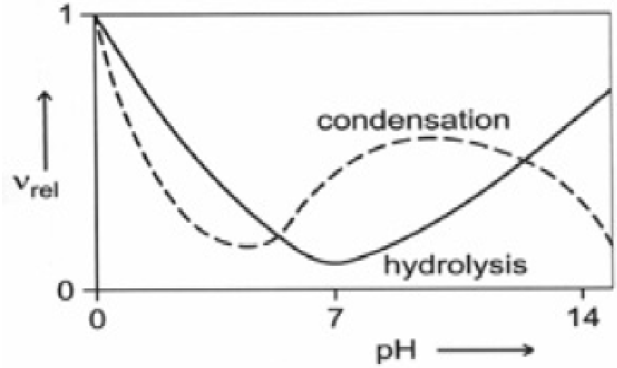


Figure 1: Variation of hydrolysis and condensation rate of $Si(OR)_4$ with pH of the medium [27].

4.3. Effect of Temperature

The temperature plays an important role in determining the rate and mechanism of the sol-gel reaction. The kinetics of a chemical reaction is directly related to temperature. It possesses indirect influence over the evaporation of the part of the solvent present in a system and hence the viscosity of the resulting film is also increased [28].

4.4. Effect of Gaseous Environment

Almost all the sol-gel reactions are carried out in atmospheric pressure which can affect the system in following two ways;

Pressure Over the System

If the atmospheric pressure is very low (as depicted in Figure **2**) it will cause greater evaporation of the liquid medium. As a consequence the pores with bigger sizes will be formed in the resulting film. By contrast higher value of pressure will resist the pore formation process by slowing down the evaporation rate but will accelerate the hydrolysis process abnormally.

Effect of Gaseous Components Present in Atmosphere

As mentioned earlier, transition metal alkoxides are very reactive towards hydrolysis. As a result they can readily react with moisture present in atmosphere and undergo crystalline precipitation. The presence of acidic oxides (CO_2, SO_3, NO_2) and strong oxidants or reductants (CO, H_2) can react with the gel forming system. This leads to change in pH and porosity of the final films. The interference of reacting species in the gel forming reactions can be avoided by using a sealed container or an inert gas atmosphere [29].

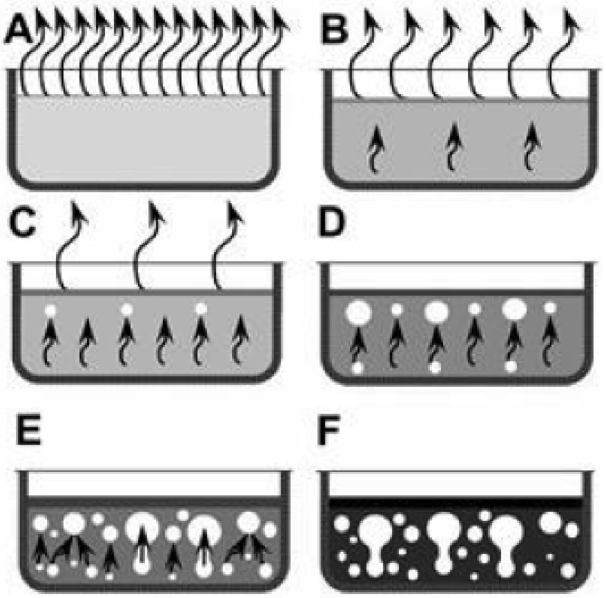


Figure 2: Pore formation in the resulting film [25].

4.5. Particle Size

Particle size has also been found to have a sharp influence on controlling the cracking of the deposited film during drying. It has been observed that with reduction of the particle size, the crack formation in the film is also diminished. Cracks produced in the film from a suspension containing relatively smaller particles are much less than in films deposited from suspension containing larger particles. Hence reduction in particle size certainly improves the morphology of the resulting film [30].

5. SURFACE CHEMISTRY OF SOL-GEL PROCESS

5.1. Methods for Stabilizing Colloidal Sol Particles

Sol-gel synthesis provides a wide range of organic, inorganic and organic-inorganic porous materials that can be synthesized by following a common preparation strategy. Generally the sol-gel process involves evaluation of inorganic network through the formation of colloidal suspension (sol) and gelation of the sol in a continuous liquid phase (gel). Colloidal particles in a dispersion medium possess a continuous Brownian motion and hence collide with each other frequently. The stability of colloids is thus determined by the interaction during collisions. There are two basic types of interactions: one being attractive and the other being repulsive. When attractive force dominates over the repulsive force, the particles will adhere with each other and entire dispersion may coalesce. When repulsion force dominates, the system will be stabilized and remain in a dispersed state [31].

Since there are always strong, long-range attractive forces existing between similar colloidal particles, it is essential to create a long-range repulsion between the particles to provide stability to the system. This repulsion should be strong enough to compensate the attractive force between the colloidal particles. Stability can be achieved by surrounding colloidal particles with an electrical double layer (electrostatic or charge stabilization) or by adsorbed or chemically attached polymeric molecules (steric stabilization) or by a free polymer in the dispersion medium (depletion stabilization) [31].

The first stabilization mechanism is often referred as “Electrosteric Stabilization”, whereas the last two types of stabilization mechanisms are collectively termed as “Polymeric Stabilization” [31].

Polymeric stabilization mechanism holds either in case of long chain precursors as a starting material for the sol-gel system or surface modification of colloidal particle by macromolecular grafting. Thermodynamically metastable dispersion is generated by electrostatic effect, while steric/polymeric stabilizers provide thermodynamically stable sols [31, 32]. Polymers are the most effective stabilizing agents due to their high molecular weight, especially when they contain repeating double units. Repeatable carboxyl and hydroxyl segments with repeating polar and nonpolar units impart high stability to a colloid system [33]. These substances can work in both aqueous and non-aqueous dispersion mediums.

5.2. Point of Zero Charge (PZC)

Stabilization due to electrostatic repulsion originates from the formation of electrical double layer. The surface charge of a particle is determined by the ionic groups covering the surface of the particle. To maintain the electro-neutrality the counter ions will cover the layer on the surface, thereby the particle is shielded from the rest of the solution.

For hydroxides the surface potential is determined by the reaction between the H^+ and OH^- ions and therefore it can be said that the surface potential is pH dependent.

$M\text{-}OH + H+ \rightarrow M\text{-}OH_2^+$

$M\text{-}OH + OH^- \rightarrow M\text{-}O^- + H_2O$

If pH is greater than PZC, then the surface is negatively charged and if pH is smaller than PZC then the surface is positively charged. The pH at which the charge of the surface is zero is called zero point charge. If the particle surface charge is low, particles would coagulate with relatively large inter particle distances leading to porous, sponge like deposits. On the other side, if particle surface charge is very high, particles would repulse each other and particle would occupy position with high packing density [30]. Once PZC of the metal oxides are known in the sol-gel matrix, one can play the trick to select right medium to stabilize sol and control the coating formulation sol-gel matrix for the deposition. Table **2** represents the PZC of different metal oxides [30,34].

Table 2: PZC of Metal Oxides

Metal Oxides	PZC value
Al_2O_3	9.1
ZnO	9.5
FeO	7.0
MnO_2	7.2
SiO_2	2.5
TiO_2	6.0
MgO	12.0
CeO_2	8.1

6. PARAMETERS AFFECTING THE PERFORMANCE OF SOL-GEL FILMS

6.1. Nature of the Precursor

6.1.1. Silica Precursor

Silica coatings obtained by aqueous sol gel route are popular as non-toxic protective coatings. The sol consists of organo silica compounds. Organo-silica materials have the general formula $Si(OR)_4$, where OR is the alkoxy group such as (OCH_3) or (OC_4H_9). For the water-based sol-gel system, OR groups in the organo-silica materials should have a short structure (low hydrophobic) to achieve the sol homogeneity without using VOC. For alcohol-based sol-gel system, alcohols are added to the sol as a solvent, OR groups with long structure can be used. [35]. Therefore, the structure of the organo-silica material controls the type of the sol, alcohol-based or water-based. SiO_2 can improve the oxidation and acidic corrosion resistance of metals under different temperatures due to its high heat resistance as well as chemical resistance [36,37]. Vasconcelos *et al*. formulated SiO_2 coating on AISI 304 stainless steel using tetra ethyl ortho silicate (TEOS) as precursor [37]. Presence of Si, O, and Fe elements was found in the coating and a transition layer was formed between steel substrate and SiO_2 layer. The obtained silica coatings were homogeneous and free of cracks. Samples were investigated in 1 mol/L H_2SO_4 solution and 3.5% NaCl solution. The coating increased corrosion potential and decreased corrosion current density. The advantages of silica matrix are: (a) Besides being nontoxic the silica films possess many other excellent features such as cost-efficiency, thin film formability and the capability to coat materials of various shapes; with the easiness to control the composition of the sol. (b) The silica coating has interesting supplementary features like hydrophobic, self-cleaning, anti-reflection, easy to clean, anti-microbial properties [38-40]. (c) The organosilica compounds of the water-based sol have low hydrophobic properties; the homogeneity of the water-based sol can be achieved by mechanical stirring without using the VOC. Therefore, the choice of the organo- silica compounds is an important aspect to prepare the water-based sol [41].

The disadvantages are: (a) Very slow rate hydrolysis. Hence complete hydrolysis of silica precursors cannot be achieved without a suitable catalyst (either acidic or basic) and moreover it often takes a longer period of time for the completion of the hydrolysis and condensation processes. (b) Some of the traditional silica precursors such as tetra ethyl orthosilicate and tetra methyl orthosilicate have some toxicity.

Roohangiz Zandi Zand and co workers [42] prepared organically modified silica sol by hydrolysis and condensation of 3-glycidoxypropyl-trimethoxy silane (GPTMS) and bisphenol-A (BPA) as crosslinking agent in acid catalyzed medium. They investigated the corrosion performance of the coating on 304L stainless steel and also observed the effect of addition of Cerium ion and BPA as crosslinking agent. The coatings were examined by scanning electron microscope (SEM), FTIR analysis, potentiodynamic polarization, AC impedance and neutral salt spray test (Figure **3**). The photographs clearly show that the silica hybrid coated (sample A) and Ce doped silica hybrid coated sample (sample B) exhibits no sign of blistering, delamination and corrosion. The original shining effect of the surface is retained even after exposure of 2000 hr. But the bare plate and Ce doped silica hybrid coated sample without BPA showed limited resistance towards neutral salt spray test.

6.1.2. Aluminum Precursor

Al_2O_3 is a well known insulator and has very low conductivity to transmit electrons, which is required for protective coatings. Masalski *et al*. [43] designed two, four and six layer Al_2O_3 coatings on AISI 316 stainless steel for improving its local anti-corrosion ability. It was found that the cathode current density varied inversely with sintering temperature. It was concluded that at

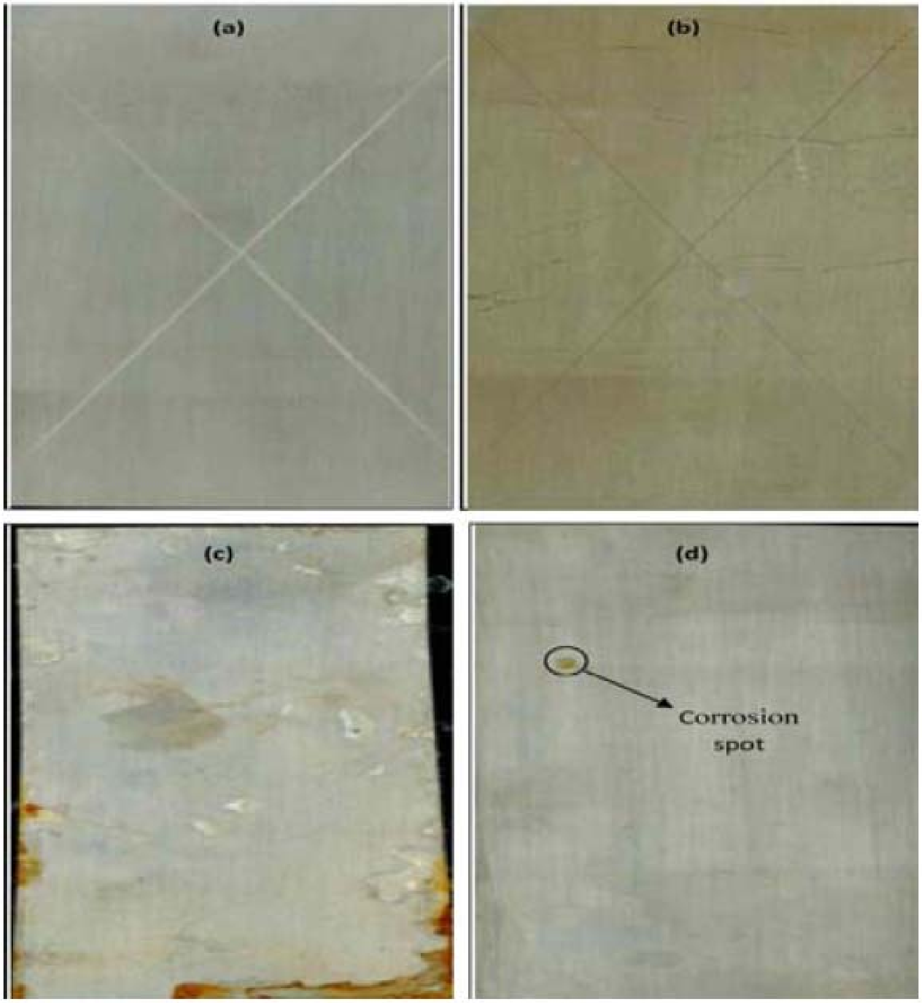


Figure 3: Photographs of **a**) silica hybrid coated, **b**) Ce doped silica hybrid coated, **c**) non BPA Ce doped silica hybrid coated, **d**) bare 304 stainless steel samples after 2000 h exposure of salt spray chamber [42].

higher temperatures, conversion of γ-Al_2O_3(less resistant to aggressive agents) into the α-Al_2O_3 modification (corundum, more resistant to aggressive agents) proceeds readily. However, a marked increase in the anodic branch was observed with the increase in sintering temperature.

6.1.3. Transition Metal Precursors

Due the presence of incomplete d orbitals, the transition elements show more reactivity towards hydrolysis reaction in comparison to the silica precursors. As a consequence no catalyst is needed to facilitate the hydrolysis process. Hence in recent times silicon precursors are replaced by transition metal alkoxides like zirconium, titanium, cerium and vanadium. However zirconium and titanium precursors are used most widely due to their easy availability.

Zirconium Precursors

As a transition element having incomplete d sub-shell (allows multi ligands connections) it is an outstanding precursor for protection of metals from corrosion and temperature damage. ZrO_2 has a high expansion coefficient and hence the formation of cracks during high temperature curing process is significantly reduced [44,45]. ZrO_2 has also good chemical stability and high hardness [46] which makes it a good protective material. Perdomo et.al. [47] synthesized ZrO_2 coating on 304 stainless steel by sol gel method and densified in air in oxygen free (argon or nitrogen) atmospheres. The corrosion behavior of stainless steel was studied by potentiodynamic polarization method and they observed that the zirconium coating extended the lifetime of the material to a significant extent even in aggressive medium, independent of the preparation procedure. In order to increase the adhesion between the organic protective coating and metal substrate, Fedrizzi *et al*. [46] prepared ZrO_2 sol-gel coating on low carbon steel sheets, further polyester organic coating was applied onto the ZrO_2 layer. From the result of adhesion testing it was found that the samples pretreated with ZrO_2 layer showed excellent performance. Li *et al*. [45] also found that ZrO_2 sol-gel films on mild steel heat treated at 400^o and 800^oC were homogeneous, crack free and has good corrosion resistance. Few examples of

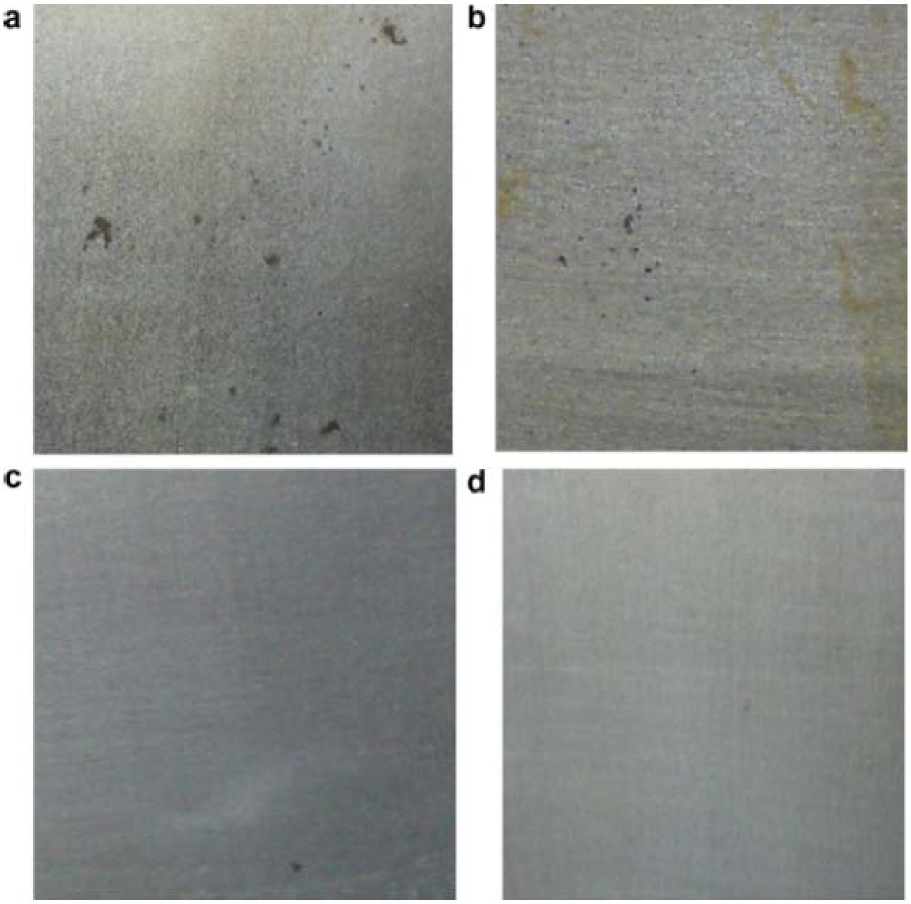


Figure 4: Appearance of epoxy coated specimens containing different concentration of ZrO_2 particles after 2000 h salt spray test, (**a**) without nanoparticles, (**b**) 1wt% ZrO2, (**c**) 2 wt % ZrO_2, (**d**) 3 wt% ZrO_2, [49].

frequently used zirconium precursors are zirconium n-propoxide, zirconium iso-propoxide, zirconium tert-butoxide etc. However the zirconium alkoxides have also got some advantages and disadvantages.

Advantages are: (1) Due to the presence of incomplete d orbitals its reactivity towards hydrolysis is much higher than that of silica precursors. Hence no acidic or basic catalyst is needed. (2) The thermal expansion of this metal is very close to the value of that of titanium and iron. This advantageous property is used to prepare hybrid or individual coating of zirconium on iron or steel against corrosion.

The disadvantages are: (1) Zirconium alkoxides has very high reactivity towards water. Hence the precursors with this metal react quickly with water resulting in crystalline precipitation. To control the hydrolysis rate of zirconium precursor organic chelating agents needs to be used. (2) They are very sensitive to atmospheric moisture. Hence the sol gel reaction for formulating zirconium coating must be carried out in an inert atmosphere or under vacuum. (3) During the heating and cooling processes cracks may appear in the resulting film due to volume expansion. Hence it needs either to be combined with other metal oxides such as cerium, yttrium, magnesium, calcium etc. [48]. (4) In many cases it has been found that the adhesive property of zirconium compound is not very good and to avoid this problem often zirconium precursors are combined with pre-hydrolyzed silica precursors.

Behzadnasab and co workers [49] modified clear epoxy coating by adding various amounts of ZrO_2 nanoparticles. Corrosion performance of epoxy coated mild steel specimens was analyzed by EIS, electrochemical noise (ECN) and salt spray test (Figure **4**). Corrosion of the coated specimen without ZrO_2 nanoparticles was visible to naked eye after 72 hr exposure. Corrosion of the coated sample containing 1 wt% ZrO_2 nanoparticle was visible after 480 hr but the sample containing 2 wt% and 3 wt% ZrO_2 particle did not show any sign of delamination or blistering even after 2000 hr of exposure.

Titanium Precursors

Titanium is also a transition metal and possesses vacant d orbital. As a consequence, its reactivity towards hydrolysis is much higher in comparison to the silica precursors. Guin *et al*. [50] developed titania containing organic-inorganic hybrid sol-gel film using titanium isopropoxide as precursor and methyl hydrogen silicone as coupling agent to improve the adhesion property and hydrophobic nature of the coating. The surface morphology of the coated sample and kinetics of the reaction were studied by SEM and FTIR. Thermal resistance of the coating was analyzed by thermo-gravimetric and differential thermal analysis. The corrosion tests were performed by EIS and salt spray. It was found that the coating obtained was dense, uniform, defect free and showed excellent anti-corrosive performance. Guin *et al*. [51] have also investigated the corrosion resistance of sol-gel derived organic–inorganic nanotitania-silica coating from Ti-isopropoxide and N-phenyl-3-aminopropyl triethoxy silane and applied it on phosphated steel sheets. The surface morphology and properties have been analyzed by SEM, FTIR and thermo gravimetric analysis. The corrosion tests were carried out by EIS and standard salt spray test. The coating was found to prevent corrosion efficiently and film was found to be dense, uniform and defect free.

Poznayak and co workers [52] investigated the salt spray test results (Figure **5**) of chromate conversion coating (CCC) used as reference and the formulated sol-gel coating (Zr1 and Ti2) after 168 and 336 h exposure. No creepage from scratch was obtained on all the studied samples. The chromate conversion coating did not exhibit any defects but showed a slight colouration after 168 hr. On the other hand the sol-gel coating showed some pitting after 168 h and stronger corrosive attack after 336 h exposure.

Photocatalytic Activity

One of the most interest properties of titanium precursors is its photo-catalytic activity. During the past few years, self-cleaning feature of photo catalytic titanium dioxide (especially the anatase crystalline form) has drawn attention both in academic and industrial sectors. If photo catalytic TiO_2 particles are illuminated with an ultra violet light source (e.g. sunlight), electrons are promoted from the valance band to conduction band [53,54], leading to the creation of a region of positive charge (h+) holes in the valance band and free electrons in the conduction band. These charge carriers can either be recombined or be migrated to the surface, while the holes may react with the hydroxyl or adsorbed water molecule on the surface and different radicals such as hydroxyl radicals ($OH^{\cdot}$) and hydroperoxy radicals ($HO_2^{\cdot}$) can be produced. By contrast the electrons are combined with the oxygen and super oxide radicals are produced. These photo- produced radicals are very strong oxidizing species and can cause the destruction of

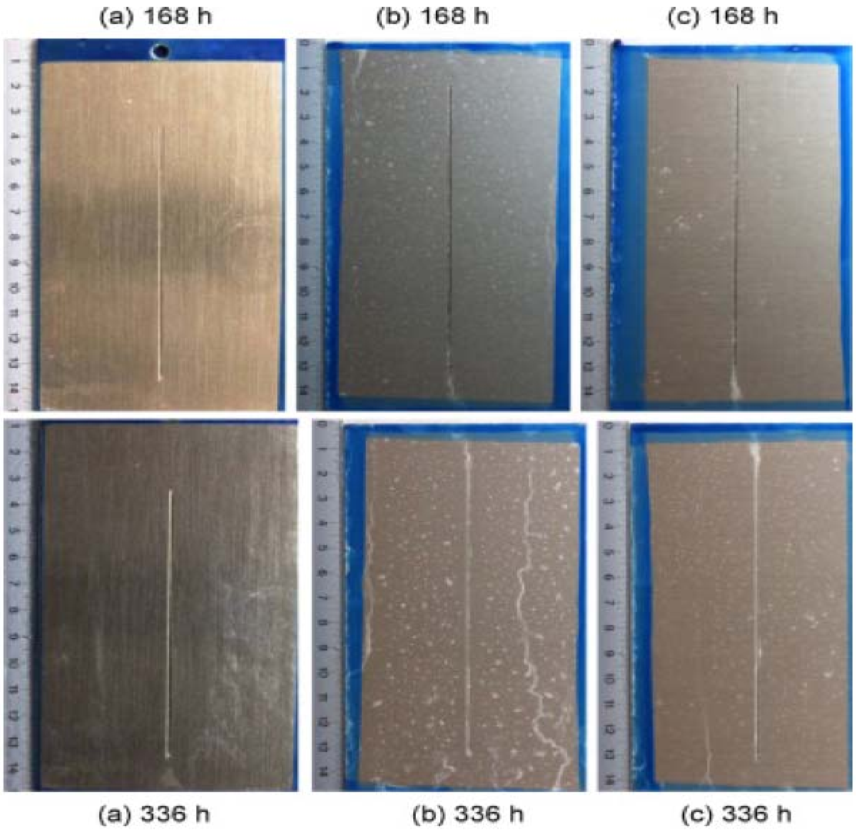


Figure 5: Photographs of AA2024 samples coated with titanium (**a**) Zr1, (**b**) Ti2 (**c**) after168h and 336 h of neutral salt spray test according to ASTM B117 [52].

organic contaminants or microbial pieces on the particle surface [55].

Hydrophobic Behavior

Another beneficial effect of TiO_2 particles is its super hydrophobic property by virtue of which all the contaminants can be easily washed away with water or rainfall when the coating is applied to the external surface. This effect is known as “water sheathing effect” [56]. Nano TiO_2 coating is also used in anti-UV, anti-bacterial and self-cleaning paints. The self cleaning hydrophobic properties allows water droplets to roll off the fully cured surface (as depicted in Figure **6**) taking the dirt particles and other contaminants along the way.

The addition of silicon oxide to TiO_2 particles increases the self-cleaning property to a significant extent [57].

Disadvantages: (1) The photo catalytic property is not active in dark i.e. in the absence of light. (2) Due to its high reactivity it is very difficult to control the precipitation and particle aggregation. (3) Generally titanium precursors are very costly. (4) The metal expansion is extreme at high temperature and hence often cracks are formed in the resulting film.

Figure 6: Self- cleaning property of titanium [55].

6.1.4. Cerium Precursor

CeO_2 precursors are similar to Ti precursors. Generally the cerium compounds are being widely used in optics, catalyst chemistry, pigments, superconductors and sensors, but in sol-gel chemistry cerium compounds are mostly used as corrosion inhibitors [58,59]. We have presented a summary table for the reference in Table **3**.

Table 3: Properties of Different Precursors Used in Sol-Gel Process [40, 43-45, 48-51, 58-60]

Sl No	Precursors/Mol.wt	Properties	Applications
1	GPTMS (248.39)	Due to the presence of the epoxy ring it provides excellent adhesion to metals Can be used as a coupling agent between the metallic substrate and organic coating. Non-toxic, high thermal resistance & anti-microbial	Anti-corrosive protective coating Optical coating Electronic coating
2	TEOS (208.33)	Excellent barrier properties: Under hydrolysis condition all the Si-OEt bonds are converted to Si-OH bonds and promote the formation of inorganic network. These hydrolyzed bonds interact with the metal substrate and impart a barrier property. Non-toxic Super hydrophobic High thermal resistance & anti-microbial	Same as above
3	Aluminum iso-propoxide& sec-butoxide (204.24)(246.32)	As good insulator due to their very low conductivity. They resist the electron transmission process and corrosion process. Compatible with following solvents: Iso-propanol, n-butanol, tert butanol	Anti-corrosive protective coating As glass coating
4	Titanium-tert-butoxide & iso-propoxide (340.32) (284.22	Due to the photo catalytic activity of titanium it provides excellent self- cleaning property. High hydrophilicity of titanium coatings easily washes away all the contaminants with water or rainfall. Good chemical stability, heat resistance & low electron conductivity Compatible with Tertiary butanol, Iso-propanol, n-propanol ethylene glycol	Optical coating for motor, architecture glasses For bio-medical implantation As electronic coating
5	Zirconium iso-propoxide & tert-butoxide (327.57) (382.16)	Due to high expansion coefficient, crack formation in the final film during high temperature curing is prevented. Good chemical stability High hardness Gives excellent adhesion Compatible with Iso-propanol, propanol, n-propanol, Cyclohexane	Anti-corrosive protective coating for aerospace alloy, steel, aluminum etc
6	Niobium pentoxide (265.81)	Excellent corrosion resistance Thermodynamically stable Compatible with methacrylic acid, acetic acid, acetyl acetone	Anti corrosive protective coating for aerospace alloy, aluminum etc.,
7	Vanadium pentoxide (181.88)	Light weight metal Good resistance to atmospheric condition, moisture and salt water damage High temperature super conductor Compatible with Phosphoric acid	Anti corrosive coating Conductive coating on photographic film

7. METHODS FOR IMPROVEMENT OF THE ANTI-CORROSIVE PROPERTY OF SOL-GEL FILM

7.1. Two and Multiple Coating Systems

The limitations of single component oxide systems can be overcome by using two or multiple component oxide coating. Atik *et al*. [49] reported that 70 SiO_2 - 30 TiO_2 and 75 SiO_2 - 25 Al_2O_3 films showed excellent corrosion protection of 316L stainless steel in aqueous NaCl and acidic media at room temperature. The lifetime of the substrate was increased by a factor of up to 10 in 3% NaCl and 5 in 15% H_2SO_4. The reason of getting high corrosion resistance is due to synergetic effect from both the precursors.

7.2. Organic-Inorganic Hybrid Sol-Gel Coatings

Pure inorganic oxide coatings can provide good protection on metal substrate but they are not free from some major drawbacks from the viewpoint of corrosion resistance: (1) Oxide films are brittle and thicker coating are very difficult to achieve without cracking, (2) Relatively high temperature is often required to achieve good properties [60-62]. To overcome these difficulties much attention has been given on introduction of organic components into the inorganic sol-gel to form the organic-inorganic hybrid sol-gel coating. This turned out to be the most interesting areas of coating science in last decade [63-70]. Hybrid coatings are much more popular than pure inorganic oxide coatings for two basic reasons. First, hybrid coating can produce much thicker coat in micrometer scale without cracks and they can be dried at much lower sintering temperature (generally less than 200^o) in comparison to inorganic oxide layer. Secondly for improvement of the corrosion protection ability a variety of additives such as inhibitors, pigments etc., can be incorporated into the hybrid coating system. Chen *et al*. [71] incorporated nano sized particles (Al_2O_3, ZrO_2, SiO_2) into the sol gel hybrid matrices and applied it on aluminum substrate. The resulting coating was found to be thick, dense, smooth and protected the substrate from corrosion. Sylican *et al*. [65] formulated hybrid sol-gel coatings from alkoxy silane precursors, such as 3-aminopropyl triethoxy silane (APS), 3-(2-Aminoethylamino) propyl dimethoxy methyl silane (AEAPS), 3-glycidoxypropyl methyl diethoxy silane (GPTMS) and 3-Methacryloxy propyl trimethoxy silane (MAPTMS). Coating was sprayed onto aluminum substrate and then cured by UV. Standard ASTM tests proved that coating had very good adhesion and high chemical, mechanical and thermal stability. Boeing Company [72] developed a sol-gel epoxy resin hybrid coating which provided excellent mechanical strength such as hardness and abrasion resistance. Van Ooji and co-workers have been using bis-silane to develop sol-gel protective coating on metal substrates [73-76]. They used BTSTS as a sol-gel precursor and incorporated silica nano particles into the hybrid film and the coating was applied on aluminum substrate [73, 74]. According to their observations, the bis–sulfur silane film was thickened and strengthened by the incorporation of silica nano particles. But extra amount of silica only hardened the surface but not the interfacial layer which may cause film delamination due to pore formation. ZrO_2-TEOS-MAPTMS system was developed by Mehner *et al*., and was applied on aluminum substrate by spin coating technique [77]. The coating thickness was found to be dependent on the spin coating rotational speed. The coating composition influenced the final characteristics as well. Higher ZrO_2 content left an impact on machinability but brittleness of the coating was increased. Wu *et al*. [78] investigated the remarkable influence of the GPTMS/TEOS ratio (R) on the corrosion resistance of TEOS/GPTMS/PDMS sol gel coating. It was concluded that, best result was obtained when R=4. Chou *et al*. [79, 80] prepared hybrid sols by copolymerizing TEOS and MAPTMS with a two-step acid catalyst process. The coating was applied on type 304 stainless steel by dip coating, and annealed at 300^{o}C. The coating was found to be dense, uniform, relatively defect free and showed excellent corrosion protection. The Air Force Research Laboratory of United States have investigated the sol-gel derived anti corrosion coating on magnesium based aircraft components for long time, and has formulated high quality environmentally friendly corrosion protective coating by a sol-gel method [7, 81-89].

7.3. Incorporation of Inhibitor Molecules

The sol-gel derived organic-inorganic hybrid coatings have been demonstrated as promising conversion treatment for long term protection against atmospheric corrosion, but their corrosion protection performance is limited due to presence of pores and cracks in the film. Recently, sol-gel coating chemistry has been re-engineered by incorporating nano-capsules in such a way that the coating can extend protection life over steel, magnesium and aluminum substrates. According to Zheludkevich *et al*. [90] environmentally unfriendly chromate metal surface pre-treatment method can be effectively replaced by sol-gel derived films. Inorganic sol-gel derived films provides excellent adhesion between metals and organic paints, however they cannot offer adequate corrosion protection due to their tendency for crack formation. Incorporation of nano particles into sol-gel hybrid films enhances the corrosion protection ability due to lower porosity and lower cracking potential. Moreover, the incorporation of inorganic nanoparticles might be a way to insert corrosion inhibitors, preparing inhibitor nanoreservoirs for “self-repairing” pre-treatments with controlled release properties.

Organic corrosion inhibitors are promising candidate as they are compatible with the hybrid coating material that can be loaded with inhibitors prior to cross linking and film formation [88]. Depending on solubility, volatility and molecular weight, their percentage may be 1 to 50% by weight. Some examples of organic inhibitors are substituted phenols, hydroquinones and quinone derivative, nitrates, organic acids, salts of organic acids, aliphatic or aromatic amines, amides, triazoles, imidazoles etc [65]. Kharmov *et al*. [91] incorporated inhibitors into hybrid sol-gel system to improve coating’s anti-corrosion ability. TMOS and GPTMS were hydrolyzed under acid catalyzed condition. Later the inhibitors, beta cyclodextrin and cross linkers were added into the sol gel film. Non ionisable heterocyclic inhibitors were chosen to be incorporated such as 2-mercaptobenzothiazole (MBT) and mercaptobenzimidazole (MBI) into the coating as complexes with beta cyclodextrin. Cyclodextrins are cyclic oligosaccharide that possesses a unique molecular cup-shaped structure and are effective complexation agents with the ability to form inclusion complexes with various organic guest molecules within the cavity [92, 93]. It was found that the coating not only had good barrier property but the inhibitors were gently released on the damaged area, imparting a self-healing ability.

Improved corrosion resistance can also be achieved by preventing the electrolyte reaching the metal surface, by blocking the coating pores with insoluble hydroxide precipitate. This can be obtained by using inorganic inhibitors specially zinc rich primers. Beside this, special attentions have been focused on nitrate, nitrite, vanadate, molybdate, permanganate salt of sodium, magnesium, cerium etc. This salts undergo hydrolysis to form insoluble hydroxide precipitate and block the pores. Varma *et al*., [94] have examined the anti-corrosion properties of Mg (II) nitrate doped sol-gel on aluminum alloy AA2024-T3. From the data it was concluded that, at optimum level of $Mg(NO_3)_2$ concentration the corrosion performance of the sol gel has increased significantly due to the formation of insoluble $Mg(OH)_2$. Mouterlier *et al*., [95] have investigated the effect of incorporation of CrO_3, $Cr(NO_3)_3$, Na_2MoO_4, $KMnO_4$, $CeNO_3$ as inorganic inhibitors in the sol-gel hybrid film which were prepared with tetra methoxy silane, methyl triethoxy silane and gamma-glycidoxy propyl methyl diethoxy silane as a source of hydrolysable silane and tetra propxy zirconium (TPOZ) as a hydrolysable zirconium. From the result it has been concluded that the morphology of the sol-gel and solubility of the additive play an important role in the corrosion protection for a long time. Inhibitors such as molybdate and permanganate ions decrease the sol gel network stability and are too soluble and hence they decrease the corrosion protection efficiency. Ce (III) is also not efficient for long time protection due to its very high solubility. Sol gel films containing Cr (VI) and Cr (III) provide efficient corrosion protection due to sol gel stability and their low solubility. Van Ooji and co-workers [75] added corrosion inhibitors (polytriazole, benzotriazole and inorganic cerium salts) to the sol-gel films and studied their corrosion properties in 0.5 M NaCl solution. It was found that organic inhibitors improved the corrosion resistance significantly but did not impart self-healing effect where as cerium salts showed the property of protecting freshly exposed metal surface. Sugama *et al*., [67] incorporated 20 wt% Ce acetate into 3-aminopropyl trimethoxy silane (APS). The coating extended the lifetime of steel exposed in a salt-fog chamber from ~10 hour to ~40 hours and aluminium panels from ~40 hours to ~1440 hours. Duran and co workers [69] studied cerium loaded hybrid silica sol gel coating and deposited on AISI 304 stainless steel substrate. It was found that cerium doping enhanced the corrosion resistance by the barrier effect, most probably through the formation of $Ce(OH)_3$. Li *et al*. [96] produced Ce ion doped TiO_2 by sol gel method by using tetra-n-butyl titanate as titanium precursor. The sols with different cerium ion content were prepared according to the nominal atomic weight ratio of Ce/Ti such as0.2%, 1.2% and 2.2%. The pure TiO_2 sol was also prepared for comparison. Surface morphology, structure and properties of the resulting coating were analyzed by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscope and energy dispersive X-ray spectroscopy. The anti-corrosive efficiency of the resulting coating was evaluated by EIS in 3.5 wt% NaCl solution in presence and absence of simulated sunlight illumination. The results showed that 1.2% Ce-TiO_2 coating with three layer exhibited excellent photogenerated cathodic protection under illumination. After doping with an appropriate concentration of the cerium ion, the corrosion protection ability of the coating was improved even without irradiation due to self healing effect of cerium ions. Raps *et al*., [97] produced the hybrid sols by controlled hydrolysis of the respective silane sols. Tetraethyl ortho silicate (TEOS), methacryloxy trimethoxy silane (MAPTMS) and phenyl-trimethoxy silane (PTS) were stirred in a magnetic stirrer in an acidic medium (HNO_3 0.1 mol/litre of water). Several corrosion inhibitors such as strontium aluminum phosphate (SAPP, 10 wt % dispersion) and soluble organic inhibitors e.g. BTA were added (3 wt% of the sol-gel formulation) to the resulting sol and at the final stage of the hydrolysis i.e. prior to the deposition by dip-coating 2, 2-azobis (2-methylbutyronitrile) was added (2 wt.% of the sol–gel formulation) for the thermal initiation of the radical polymerization and the formation of the polymer network. The barrier properties and the active corrosion protection of the resulting film were investigated by EIS and scanning electrode technique. Accelerated tests such as neutral salt spray tests confirmed the validity of the electrochemical techniques for the evaluation of the anti corrosive property of hybrid sol gel films. It was concluded that the addition of the inhibitors was favorable to protect the oxide film from the defects. The addition of aluminum phosphate to the sol-gel system caused improvement of the barrier property and long term corrosion protection of the coating. Benztriazole was also incorporated into the sol-gel hybrids as corrosion inhibitor. However the results of neutral salt spray test and pore resistance indicated the negative impact of direct addition of benzotriazole into the sol gel solution and as a consequence the barrier property of the coating was decreased to some extent.

7.4. By Using Chelating Agent or Stabilizing Molecules

To control the hydrolysis rate of transition metal precursors (to avoid precipitation) it is always recommended to add a suitable chelating agent during hydrolysis step. The general mechanism is based on the chelating and bridging properties of the molecules. Hydrolysis or condensation rates can be controlled *via* elimination or substitution of the metal ligand bonds. As a consequence certain sites of the precursor molecules are stabilized and react in a poly-condensation process. Most frequently used chelating agents are carboxyl functional groups like acetic acid and acetone but also hydroxyl, ester, amino and beta di-ketone (ethyl aceto acetate and acetyl acetone are being widely used now a days) groups can also be advantageous [98,99]. Varma *et al*. [100] developed a sol gel coating using 3-(trimethoxysilyl) propyl methacrylate (MAPTMS) as silane precursor and zirconium-n- propoxide under acid catalyzed condition. The performance of the sol gel coating on AA 2024 T3 aluminium sheets were investigated by varying the organic ligands to chelate the zirconium precursors. Three carboxylic acids (acetic acid, methacrylic acid and butyric acid), a beta- di- ketone (AcAc) and bipyridine were used as chelating agents. To evaluate the potential effect of the different chelates the coatings were characterised spectroscopically, electrochemically and calorimetrically. It was concluded that acid ligand modified coating showed the best performance followed by AcAc, whereas the Bipyridine provided the poorest result.

Some organic polymers can also be used as stabilizing molecules such as polystyrene sulfonic acid, hydroxypropyl-, methyl-, carboxymethyl cellulose due to their high molecular weight especially when they contain repeating double units. These organic polymers play the role in two ways – (a) by changing the composite structure, the release of corrosion inhibitors can be delayed, (b) by polymer addition, specially soluble cellulose derivatives, the viscosity of the sols and thus under constant coating conditions the thickness of the coating can be greatly increased, thus making it possible to control the absolute quantity of released corrosion inhibitors within broad limits [91].

Besides the type of stabilizer, its concentration is also important because the stabilizer/precursor ratio determines the number of available reactive sites when more than one stabilizing molecule may aggregate with the precursor particle [91]. Another crucial parameter is the choice of an appropriate solvent because the polar character of the solvent, i.e. its affinity to both stabilizer and precursor molecule can either increase or even reverse the stabilizing effect, resulting in flocculation instead of stabilization [101].

7.5. By Incorporating Dye Molecules

Rout [102] studied anti corrosive property of titania-silica hybrid coating formulated through sol gel process by incorporating dye molecule. The role of dye

Table 4: Different Chelating Agents and their Physical Properties

Chelating agent	Molecular weight (gm/mole)	Appearance	Solubility	Boling Point/ Melting point (^{o}C)
Acetic acid	60.06	Colourless liquid	Ethanol, toluene, other organic solvents	118.50
Acetyl acetone	100.12	Slightly yellowish liquid	Water	140.00
Butyric acid	88.11	Colourless liquid	Ethanol, ether, some other organic solvents	163.50
Ethyl acetoacetate	130.14	Colourless liquid	Water	180.80
Methacrylic acid	86.06	Colourless liquid	Warm water, most organic solvents	161.10
Lactic acid	90.08	Colourless liquid	Water, alcohol	200.00
3,4-diamino-benzoic acid	152.15	Brown powder	Organic solvent	228.00
2,2'-Bipyridine	156.18	White crystalline solid	Methanol, di ethyl ether	273.00

Table 5: Different Stabilizing Agents and their Physical Properties

Stabilizing agent	Appearance	Solubility	Melting point (°C)
Methyl cellulose	White powder	Cold water, glacial acetic acid	290-350
Carboxy methyl cellulose	Solid	Water, polar organic solvent	270-275
Hydroxypropyl cellulose	White powder	Polar organic solvent	100-150
Hydroxyl propyl methyl cellulose	Granular solid	Polar organic solvent	150-156

Table 6: Different Metal - Complexed Dyes and their Properties [103]

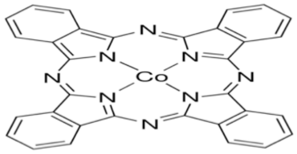
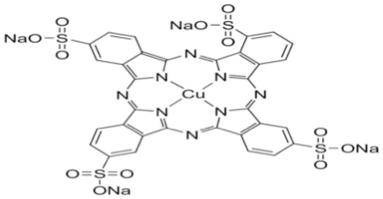
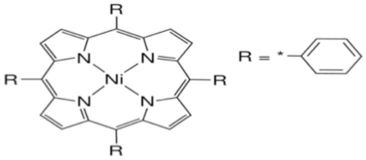
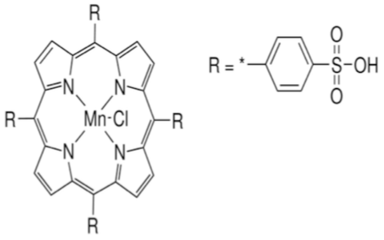
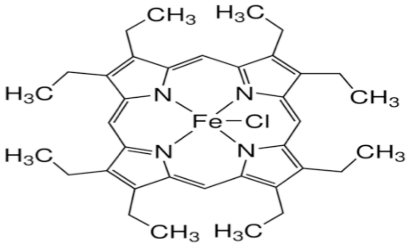
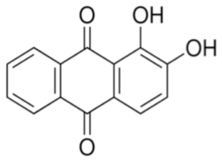
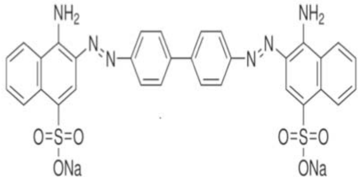
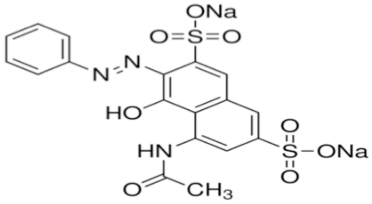
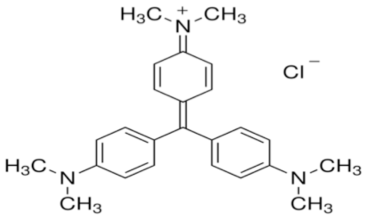
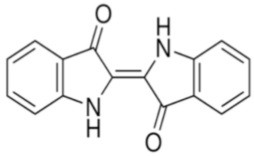
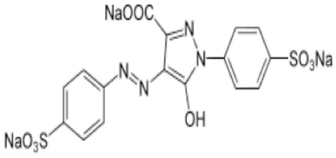
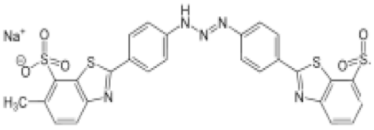
Dye	Molecular weight (g/mole)	Appearance	UV absorption maxima (nm)	Molecular structure
Cobalt (II) phthalocyanine	571.46	Dark purple powder	Not available	
Copper phthalocyanine - 3,4’,4’’,4’’’-tetra sulfonic acid	984.25	Dark purple powder	657 (1st) 630 (2nd)	
5,10,15,20-Tetraphenyl-21H,23H-Porphine nickel (II)	671.41	Crystalline powder	525	
2,3,7,8,12,13,17,18-octaethyl-21H,23H Porphine zinc (II)	598.15	Red Powder	400	
5,10,15,20-tetrakis(4 sulphonato phenyl)-21H,23H-Porphine manganese (II) chloride	1023.56	Powder	466	
2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine iron (II) chloride	624.06	Solid	382	

Table 7: Different Organic Dyes and their Properties [103]

Dye	Molecular weight g/mole	Solubility	Melting point (^{o}C)	Appearance	Molecular structure
Alizerine	240.21	Sparingly soluble n water	279-283	Orange red crystal	
Congo red	696.66	Water Ethanol	>360	Solid	
Azophloxin	509.42	Water Ethanol	No sharp melting point detected	Dark red powder	
Crystal violet	407.98	Water	204-206	Dark green powder	
Indigo blue	262.27	Water	390-392	Dark blue crystalline powder	
Tetrazine	534.3	Water	>300	Lemon yellow powder	
Clayton yellow	350.89	Water	109-111	Brownish green	

molecules is particularly important for increasing the anti corrosive property of the coating. Generally dye molecules consist of large aromatic as well as heterocyclic ring and also contain a hetero atom like oxygen, nitrogen, sulfur etc. All this properties make the dye molecules good corrosion inhibitors. The results of corrosion tests indicated that the reaction is cathodically controlled in presence of dye molecule and EIS results provided a charge transfer resistance of dye of 419 ohms cm^2, which was higher than that of similar coating without dye (360 ohms cm^2), indicating excellent corrosion protection.

7.6. By Incorporating Conducting Polymer

Conducting polymer such as polyaniline (PANI) and polypyrolle (PA) have been established as potential candidates for anti-corrosion coatings for many years [104]. Akid *et al*. [105] incorporated a conducting polymer into a sol-gel coating and resulting hybrid coating had good flexibility and adhesion property as well as it showed a good anti corrosion performance (Figure **7**). This type of coating provides a number of benefits such as the ability of forming a passive layer and the ability to transfer charge within the coating. However in some cases these coatings suffer from limitations like lack of flexibility and adhesion to the substrate. Akit *et al*. [44] developed hybrid coating of poly methyl methacrylate and ZrO_2 and investigated its anti corrosion behavior on 316L stainless steel. The tests were carried out in 0.5 M H_2SO_4 solution through potentiodynamic polarization at room temperature. The coating protected the substrate from the corrosive medium by geometry blocking and increased the life time of the substrate by a factor up to 30. Messaddeq *et al*., [64] analyzed the microstructure of ZrO_2-PMMA coating with the help of SEM and AFM and it was found that the zirconium concentrated domains are surrounded by a secondary phase of PMMA. Maximum corrosion resistance was achieved with the coating containing 17 vol % PMMA. Higher PMMA volume tended to a single phase structure resulting in breakdown and peeling of the coating during electrochemical analysis.

Figure **7** represents the salt spray test results for a comparison study of sol-gel only and the combined sol-gel/CP coating in 5% NaCl at 35^o C. It is clear from the picture that the sol-gel coating alone exhibits poor corrosion resistance and extreme pitting and delamination were observed. However negligible corrosion was observed in the case of solgel/CP coating.

7.7. By Encapsulating a Bio-Active Component

Depending on the type of environment and nutrients, microorganisms can rapidly colonize a surface which is immersed in an aqueous medium. The attachment of micro/macro fouling has enormous economic consequences for many applications such as marine shipping, oil pipeline structures, heat exchangers etc. Furthermore, the development of a bio-film can lead to subsequent colonization of bacterial types that ultimately generate aggressive environments, notably sulphate reducing bacteria (SRB). Here the formation of sulfide and hydrogen sulfide can lead to rapid localized corrosion, especially in ferrous-based materials.

As stated, a primary benefit of the hybrid sol-gel system is that it allows a variety of additives to be incorporated into the matrix, therein enhancing the functionality of the coating system. Incorporation of a bioactive component can prevent biofouling and microbially induced corrosion. Following a “proof of concept” study, it can be concluded that endospores and vegetative cells can be incorporated into the sol-gel matrix to prevent corrosion efficiently [105]. Microorganisms can slow down the corrosion process by different mechanisms, such as (i) microbial consumption of cathodic reactant (e.g. Oxygen consumption by respiratory activity), (ii) forming or stabilizing the protective film on the metal surface (e.g. biofilm exopolymers with metal binding capacity), iii) decreasing aggressiveness of the medium in the

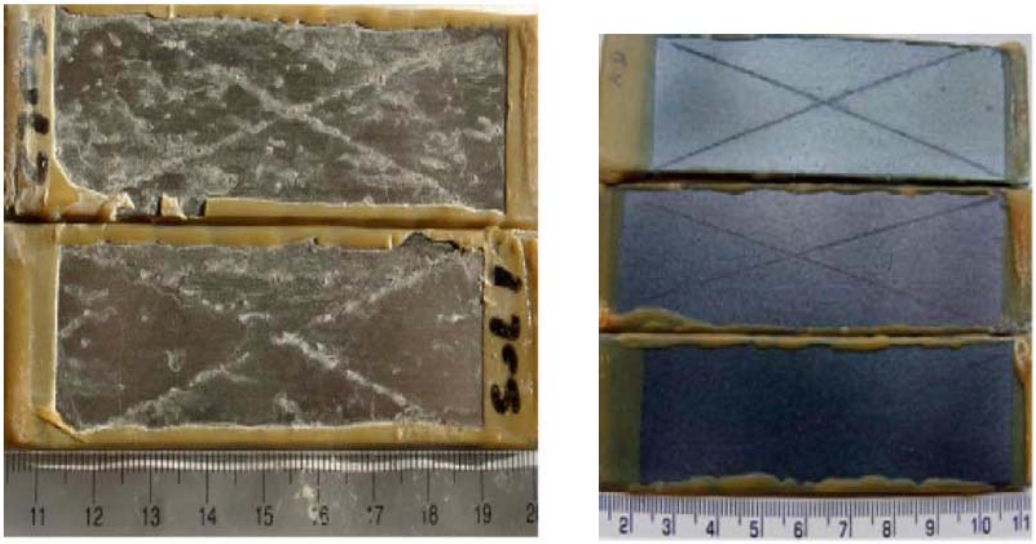


Figure 7: Salt spray test results on AA2024 **a**) sol gel only (168 hrs) and **b**) sol gel/PA (500 hrs) [105].

restricted areas of metal/solution interface (e.g. by neutralizing acidity).

7.8. By the Addition of Plasticizer

Sometime the variation of the coating thickness is needed to achieve the best possible barrier property. This can be done by increasing the number of layers but not beyond a certain limit due to delamination problem. The viscosity of the sol can also be increased by temperature modification but this may cause certain changes in intrinsic properties of the gel first and then coating. Certhoux *et al*. [106] formulated a sol from starting precursor tetra ethyl ortho silicate (TEOS) and 3 (trimethoxysilyl) propyl methacrylate (MAPTMS). They have investigated the effect of addition of PEG (polyethyleneglycol). PEG has been used as plasticizer and both physical and chemical properties of the synthesized hybrid film have been investigated. The concentration of PEG 35000 has been varied as 0, 20, 40, 60, 80 g L^{-1}. The result showed that with the increase in concentration of PEG the sol of the viscosity was also increased. With a concentration of PEG 35000 60 gL^{-1} the viscosity of the sol was increased by a factor of 6, the initial viscosity of the TEOS-MAP sol without plasiticizer. This value was found to be the threshold one, which was not suitable to exceed to avoid some undesirable problems. The mass gain and the thickness of the deposit were significantly increased and improved the barrier property. The anti corrosion property of the hybrid sol gel coated stainless steel was investigated by potentiodynamic polarization curves and impedance spectroscopy. Potentiodynamic polarization curves indicated that the hybrid sol prepared from TEOS/MAP/PEG provided the best anti corrosion property and its excellent barrier effect increased the total impedance and reduced the current densities significantly.

7.9. By the Addition of Red Mud Suspension

Collazo *et al*. [107] studied the effect of addition of 5 wt% red mud into the sol gel film prepared from tetra-n-propoxyzirconium (TPOZ) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) and applied it on AA2024-T3 aluminum alloy. During the caustic digestion of bauxite (for obtaining alumina by Bayer process) red mud is left as an insoluble residue. The composition of red mud is strongly dependent on the origin of bauxite but generally red mud consists of hematite (Fe_2O_3), goethite (FeOOH), titanium oxide, complex of sodium aluminum silicate and sometime boehmite (AlOOH) [108,109]. Recently several studies have been carried out to evaluate steel corrosion inhibition using red mud suspension. According to the results obtained, red mud has been found to be a potential corrosion inhibitor. The red mud particles were characterized by XRD, TGA, and DSC. The anti corrosion property was investigated by salt spray test and EIS. From both results it was evident that the sol-gel films doped with calcined red mud particles has excellent protection property and good anti corrosive property.

7.10. By the Addition of Clay Particles

The clay particles belong to the semicite group having a layered structure with a cation in the interlayer space. Swelling of nanoclay particles in water medium is caused from hydration of the cations in the interlayer space [110]. Because of this swelling phenomenon, the clay particles exhibit a specific viscosity, termed as thixotropy. This particular property imparts a blocking effect towards the dissolved ion in water inside the cavity. Due to this unique property, the clay particles are being used in coating to protect the substrate, even when the film is damaged by cracks or pinholes [110].

Hikasa *et al*. [111] deposited clay and silica multilayer coating (using synthesized hictorite clay and TEOS) on glass substrate by spin coating. The coating was analyzed by SEM, EPMA, AFM and laser microscope. It was concluded that the coating possesses outstanding self healing ability and automatically repaired the damaged part by physical and chemical reaction. Keyoonwong *et al*. [112] obtained high degree of clay exfoliation by three dispersion methods such as normal mixing, shear mixing and high speed mixing. They studied the corrosion behavior of epoxy / organo-clay nanocomposite by conducting weight change, immersion test and penetration behavior. The epoxy composite was bisphenol-A type and montmorillonite was used to produce the nano clay particles. Montmorillonite is one of the most common inorganic filler with an alumino-silicate structure. It consists of two tetrahedral layers sandwiching an octahedral layer containing Na+ or Ca2+ ion. Several polymer-layered silicate nanocomposites have been successfully prepared by using MMT with polyamide [113-118]. These nanoclay particles can reinforce the polymer in the manufacturing of high performance nanocomposite coating. Among the three mixing methods, the high speed mixing method gave the wider interlayer distance, smaller clay agglomerate and best anti-corrosive performance.

8. FUTURE CHALLENGES OF ANTI-CORROSIVE SOL-GEL COATINGS

It can be concluded that the structure, composition and form of the final product is entirely pre-decided by the methods of preparation and condition of their preparations. Like any other process the sol-gel process also has some advantages and disadvantages. Sol-gel process allows the synthesis of hybrid system having high purity because organometallic alkoxy precursors can be purified by distillation and recrystallization. High degree of homogeneity can be achieved by mixing the reagents at molecular level. The pore size, film thickness and particle size of the final film can be controlled according to requirement by appropriate solvent evaporation rate, firing time and heat treatment. As already mentioned previously, the sol-gel system allows encapsulation of several additives, therefore the anti-corrosive property of a sol-gel coating can be improved extensively. Beside this mild chemical condition, uncomplicated instrumental set up have made this process very popular. This process also suffers from some limitations such as, high cost of the metal alkoxide precursors, sensitivity of the precursor complex towards environment, long processing time, development of shrinkage and stresses in the coating leading to cracks and fragmentations. Current synthesis route of sol-gel coating requires long time processing flow, e.g. sol aging often may require several hours to few days which restricts its application in large scale industrial production. During curing process and heat treatment often phase separation occurs, especially in the case of hybrid coating system. So as a countermeasure, invention of new synthesis route and design of new gelation and heat treatment method is needed [62]. The traditional sol-gel precursor such as, TEOS or TMOS are very costly and toxic to some extent. So, new types of eco-friendly precursors or industrial colloid particles can be used to replace the traditional precursors [62].

On the basis of the data available concerning the sol-gel technology, one can say easily the choice of appropriate precursors, the solvent used, the quantitative ratio of alkoxide/solvent, the kind of catalyst used, temperature, pH of the medium, component concentration of the initial mixtures etc., play a very vital role in a successful synthesis of a hybrid coating with desirable features. The chemical reactivity of the metal alkoxide depends on the type of functional groups, the degree of oxidation of the metal ions, ionic radius and coordination number with respect to the anion. Hence heterometal alkoxides are often more appropriate because at a molecular level strong chemical bonds are formed. It also recommends detailed understanding and knowledge about the behavior of the liquid system and their compounds. The moment of the addition of a given substance, its nature and its concentration also has such a significant importance that it is the key factor for obtaining a product with desirable property. In addition to all aspects mentioned in this review, it should be noted that sol-gel chemistry is still in its infancy and a better understanding in basic inorganic and organic polymerization has still to be developed before achieving mastery on this process.

9. CONCLUSION

Along with the demand of new technologies and new processing technique, sol gel science and technology has drawn the attention of researchers. From several studies it can be concluded that the hybrid organic-inorganic coating, formulated by sol-gel route can protect metal and alloy surfaces in various corrosive medium. There are many ways by which modification of the sol gel film can be done to achieve improved corrosion resistance as well as several interesting and beneficial properties such as water resistance, abrasion, self-cleaning; toughness, mechanical strength etc into the resulting film. With further studies, the sol gel technology will have wider and broader application in future.

REFERENCES

[1] Jones DA. Principles and Preservation of Corrosion, 2nd ed., Prentice-Hall, New Jersey 1996.

[2] Shreie LL, Jarman RA, Burstein GT. Corrosion, 3rd ed., Butterworth-Heinemann, Oxford 1994.

[3] Metroke TL, Parkhil R, Knobbe ET. Proceedings of the Material Society Symposium 1999; 576: 203.

[4] Kharmov AN, Balbyshev VN, Voevodin NN, Donley MS. Nanostructured Sol–Gel derived conversion coatings based on epoxy- and amino-silanes. Prog Org Coat 2003; 47: 207-13. http://dx.doi.org/10.1016/S0300-9440(03)00140-1

[5] Metroke TL, Kachurina O, Knobbe ET. Passivation of metal alloys using sol–gel-derived materials-a review. Prog Org Coat 2001; 41: 233-38. http://dx.doi.org/10.1016/S0300-9440(01)00134-5

[6] Livage J, Henry M, Sanchez C. Sol Gel chemistry of trasition metal oxide. Prog Solid St Chem 1988; 18: 259-42. http://dx.doi.org/10.1016/0079-6786(88)90005-2

[7] Parkhil R, Knobbe ET, Donley MS. Application and evaluation of environmentally compliant spray coated ormosil films as corrosion resistant treatment for aluminum 2024-T3. Prog Org Coat 2001; 41: 261-65. http://dx.doi.org/10.1016/S0300-9440(01)00138-2

[8] Kasemann R, Schmidt H. Coating for mechanical and chemical protection based on organic-inorganic sol-gel nanocomposites, France, 8-10 November 1993; 171.

[9] Palanivel V. Modified silane thin films as an alternative to chromates for corrosion protection of AA2024-T3 alloy. University of Cincinnati, MS.c Thesis 2003; 75-88.

[10] Ciriminna R, Carà P, Sciortino M, Pagliaro M. Catalysis with doped Sol-Gel silicates. Adv Synth Catal 2001; 353: 677-87. http://dx.doi.org/10.1002/adsc.201000731

[11] Wittmar A, Caparrotti H, Veith V. Surf Interface Anal 2011. http://dx.doi.org/10.1002/sia.3771

[12] Tavandashti, Sanjabi N, Shahrabi ST. Evolution of corrosion protection performance of hybrid silica based sol– gel nanocoatings by doping inorganic inhibitor. Mater Corrosion 2011; 62: 411-15. http://dx.doi.org/10.1002/maco.200905529

[13] Introduction to colloid and sol-gel chemistry, Chapter 1. Available from http://www.shodhganga.inflibnet.ac.in

[14] Shaw DJ. Introduction to colloid and surface chemistry, Butterworth, 4th ed.,1992.

[15] Flory JP. "Principles of polymer chemistry" Disc. Faraday Soc 1974; 57: 7. http://dx.doi.org/10.1039/dc9745700007

[16] http://www.gitam.edu

[17] Hamdy A, Butt D. Environmentally compliant silica conversion coatings prepared by Sol-Gel method for aluminum alloys. Surf Coat Technol 2006; 201: 401-407. http://dx.doi.org/10.1016/j.surfcoat.2005.11.142

[18] Metroke T, Apblett A. Effect of solvent dilution on corrosion protective properties of Ormosil coatings on 2024-T3 aluminum alloy. Prog Org Coat 2004; 51: 36-46. http://dx.doi.org/10.1016/j.porgcoat.2004.06.002

[19] Roussia E, Tsetsekou A. Novel hybrid organo-silicate corrosion resistant coatings based on hyperbranched polymers. Surf Coat Technol 2011; 205: 3235-44. http://dx.doi.org/10.1016/j.surfcoat.2010.11.037

[20] Liu D, Troczynski T. Water-based Sol-Gel synthesis of hydroxyapatite: Process Development. Biomaterials 2001; 22: 1721-30. http://dx.doi.org/10.1016/S0142-9612(00)00332-X

[21] Hench L, Ulrich R. John Wiley & Sons Inc 1984; ISBN 0471896691, pp. 320-355.

[22] Brinker C. Materials Research Society 1986; ISBN 0931837391, pp. 55-69.

[23] Hubert-Pfalzgraf LG. Coordination. Chemistry. Review. 178-180, 967-997 (198).

[24] Corriu RJP, Leclercq D, Lefevre P, Mutin PH, Vioux A. Preparation of monolithic metal oxide gels by silicon halides by non-hydrolytic sol-gel rocess. J Non Cryst Solids 1992; 146: 301-303. http://dx.doi.org/10.1016/S0022-3093(05)80505-8

[25] Kozhukharov S. Journal of the University of Chemical Technology and Metallurgy 2009; 44(2): 143-50.

[26] Izumi K, Tanaka H, Uchida Y, Tonge N, Minami T. J Mat Sci Lett 1993; 12: 723-27. http://dx.doi.org/10.1007/BF00626699

[27] http//www.uio.no

[28] Del Coro Serrano M, Kozhukharov S. Applicationof sol-gel techniques for obtaining of new multi- functional materials, Development - Future Perspectives and Innovations in the science, Proc., Sofia 2006; 84-93.

[29] Dislish H. Sol-Gel 1984 → 2004 (?). J Non-Cryst Sol 1985; 73: 599-12.

[30] Besra L, Liu M. A review on fundamentals and applications of electrophoretic deposition (EPD). Prog Mater Sci 2007; 52: 1-61. http://dx.doi.org/10.1016/j.pmatsci.2006.07.001

[31] Shi J. CISM; Steric stabilization, Literature Review, Ohio State University, 06502, 2002. Available from http://www.matsceng.ohio-state.edu/ims/LR_Stericstablization.pdf

[32] Brinker CJ, Scherer GW. Sol-gel science: The physic and chemistry of sol-gel processing, Academy Press, San Diego, USA 1990.

[33] Napper DH. Polymeric Stabilization of Colloidal Dispersions, Academic Press, New York, USA 1983.

[34] Sarkar P, Nicholson PS. Electrophoretic Deposition (EPD): Mechanisms, Kinetics, and Applications to Ceramics. J Am Ceram Soc 1996; 79(8): 1987-2002. http://dx.doi.org/10.1111/j.1151-2916.1996.tb08929.x

[35] Weng W, Chen H, Tsai S, Wu J. Thermal property of epoxy/SiO_2 hybrid material synthesized by the sol–gel process. J Appl Polym Sci 2004; 91: 532-37. http://dx.doi.org/10.1002/app.13217

[36] Galliano P, Damborenea JJD, Pascual MJ, Duran A. Sol-Gel Coatings on 316L Steel for clinical application. J Sol–Gel Sci Technol 1998; 13: 723-27. http://dx.doi.org/10.1023/A:1008653208083

[37] Vasconcelos DCL, Carvalho JAN, Mantel M, Vasconcelos WL. Corrosion resistance of stainless steel with sol-gel silica. J Non-Cryst 2000; 273: 135-39. http://dx.doi.org/10.1016/S0022-3093(00)00155-1

[38] Li D, Huang F. Sol-gel preparation and characterization of nonporous ZnO/SiO2 with broadband anti reflective properties. Appl Surf Sci 2011; 257: 9752-56. http://dx.doi.org/10.1016/j.apsusc.2011.05.126

[39] Belleville P. Functional coatings: The sol-gel approach. Comptes Rendus Chimie 2010; 13: 97-105. http://dx.doi.org/10.1016/j.crci.2009.12.005

[40] Yasuda Y, Nishikawa K, Furukawa S. Structural colors from TiO2/SiO2 multilayer flakes prepared by sol-gel process. Dyes Pigm 2011; 92: 122-1125.

[41] Antonio Ugas Carrión R. Investigation of stabilizing agents in thin sol-gel zirconium oxide anti-corrosion coatings on iron materials, Vom Fachbereich Chemie der Technischen Universität Darmstadt, PhD Thesis.

[42] Zanda RZ, Verbekenb K, Adriaensa A. Corrosion resistance performance of cerium doped silica sol-gel coatings on 304L stainless steel. Prog Org Coat 2012; 75: 463-73. http://dx.doi.org/10.1016/j.porgcoat.2012.06.008

[43] Masalski J, Gluszek J, Zabrzeski J, Nitsch K, Gluszek P. Improvement in corrosion resistance of the 316l stainless steel by means of Al_2O_3 coatings deposited by the sol-gel method Thin Solid Films 1999; 349: 186-90. http://dx.doi.org/10.1016/S0040-6090(99)00230-8

[44] Atik M, Neto P, Avaka LA, Aegreter MA. Sol-gel thin films for corrosion protection" Ceram Int 1995; 21: 403-406. http://dx.doi.org/10.1016/0272-8842(95)94466-N

[45] Li H, Liang K, Mei L, Gu S, Wang S. Corrosion protection of mild steel by zirconia sol-gel coating. J Mater Sci Lett 2001; 20: 1081-83. http://dx.doi.org/10.1023/A:1010918224936

[46] Fedrizzi L, Rodriguez FJ, Rossi S, Deflorian F, Maggio RD. The use of electrochemical techniques to study the corrosion behaviour of organic coatings on steel pretreated with sol–gel zirconia films. Electrchim Acta 2001; 46: 3715-24. http://dx.doi.org/10.1016/S0013-4686(01)00653-3

[47] Perdomo F, Lima PD, Aegreter MA, Avaka L. Sol-Gel deposition of ZrO2 films in air and in oxygen-free atmospheres for chemical protection of 304 Stainless Steel: A comparative corrosion Study. J Sol-Gel Sci Technol 1999; 15: 87-91. http://dx.doi.org/10.1023/A:1008769231899

[48] Parralejoa A, Orti A. Effect of type of solvent alcohol and its molar proportion on the drying critical thickness of ZrO 2–3

mol% Y2O3 films prepared by the sol–gel method. Surf Coat Technol 2011; 205: 3540-45.
http://dx.doi.org/10.1016/j.surfcoat.2010.12.037

[49] Behzadnasaba M, Mirabedin SM, Kabiri K, Jamali S. Corrosion performance of epoxy coatings containing silane treated ZrO_2 nanoparticles on mild steel in 3.5% NaCl solution. Corr Sci 2011; 53: 89-98.
http://dx.doi.org/10.1016/j.corsci.2010.09.026

[50] Guin AK, Nayak S, Rout TK, Bandyopadhyay N, Sengupta DK. Corrosion resistant nano hybrid sol-gel coating on steel sheet. ISIJ Int 2011; 51: 435-40.
http://dx.doi.org/10.2355/isijinternational.51.435

[51] Guin AK, Nayak S, Rout TK, Bandyopadhyay N, Sengupta DK. Corrosion behavior of nanohybridtitania/silica composite coating on phosphated steel sheet. J Coat Technol Res 2012; 9: 97-106.
http://dx.doi.org/10.1007/s11998-011-9321-6

[52] Poznyak SK, Zheludkevich ML, Raps D, Gammel F, Yasakau KA, Ferreira MGS. Preparation and corrosion protective properties of nanostructured titania-containing hybrid sol–gel coatings on AA2024. Prog Org Coat 2008; 62: 226-35.
http://dx.doi.org/10.1016/j.porgcoat.2007.12.004

[53] Fujishima A, Hashimoto K, Watanabe T. TiO2 photocatalysis, Fundamental and Applications. BKC, Tokyo 1999; p. 66.

[54] Watanabe T, Bull; Super hydrophilic TiO2 photocatalyst and its application. Ceram Soc Japan 1996; 31: 837-40.

[55] Mathiazhagan A, Joseph R. Nanotechnology-A new prospective in organic coating –review. Int J Chem Eng Appl 2011; 2: 225-37.
http://dx.doi.org/10.7763/IJCEA.2011.V2.108

[56] Fujishima A, Rao TA, Tyrk DA. Titanium dioxide photocatalysis. J Photochem Photobiol C: Photochem Rev 2000; 1: 1-21.
http://dx.doi.org/10.1016/S1389-5567(00)00002-2

[57] Kumar GS. Functional coatings and microencapsulation: A general perspective.Available from http://www.Johnwiley.com

[58] Sugama T. Cerium acetate-modified aminopropylsilanetriol: A precursor of corrosion-preventing coating for aluminum-finned condensers. J Coat Technol Res 2005; 2: 649-59.
http://dx.doi.org/10.1007/BF02774594

[59] Pepe A, Apericio M, Duran A, Cere S. Cerium hybrid silica coatings on stainless steel AISI 304 substrate. J Sol- Gel Sci Technol 2006; 39: 131-38.
http://dx.doi.org/10.1007/s10971-006-9173-1

[60] Rabinovich EM. Sol-Gel technology for thin films, fibers, performs, electronics and speciality shapes, L.C Klein, New Jersey, USA 1988.

[61] Wen J, Wilkes GL. Chem Organic/Inorganic hybrid network materials by the sol−gel approach Mater 1996; 8: 1667-81.

[62] Wang D, Bierwagen GP. Sol-gel coatings on metal for corrosion protection. Prog Org Coat 2009; 64: 327-38.
http://dx.doi.org/10.1016/j.porgcoat.2008.08.010

[63] Castro Y, Ferrari B, Moreno R, Duran A. Silica sol-gel coatings on metals produced by EPD. J Sol-Gel Sci Technol 2003; 26: 735-39.
http://dx.doi.org/10.1023/A:1020750222322

[64] Messadeq SH, Pulcinelli SH, Santellii CV, Guastaldi AC, Messadeq Y. Microstructure and corrosion resistance of inorganic–organic (ZrO_2–PMMA) hybrid coating on stainless steel. J Non Cryst Solids 1999; 247: 164-70.
http://dx.doi.org/10.1016/S0022-3093(99)00058-7

[65] Sylikan H, Senar S, Senar E, Sulu M. The sol-gel synthesis and application of some anticorrosive coating materials. Mater Sci 2003; 39: 733-39.
http://dx.doi.org/10.1023/B:MASC.0000023514.74970.73

[66] Sugama T, Gawlik K, Jung D. Polyaminopropylsiloxane coatings for geothermal air-cooled condensers. Recent Res Devel Mat Sci 2003; 4: 695.

[67] Ono S, Tsuge H, Nishi Y, Hirano S. Improvement of corrosion resistance of metals by an environmentally friendly silica coating method. J Sol-Gel Sci Technol 2004; 29: 147-53.
http://dx.doi.org/10.1023/B:JSST.0000023849.33761.86

[68] Jianguo T, Gaoping G, Chuanwei Y. EIS study of corrosion behaviour of organic coating/Dacromet composite systems. Electrochim Acta 2005; 50: 3320-32.
http://dx.doi.org/10.1016/j.electacta.2004.12.010

[69] Menning M, Schelle C, Duran A, Demborenea JJ, Guglielmi M, Brusatin G. Investigation of glass-like sol-gel coatings for corrosion protection of stainless steel against liquid and gaseous attack. J Sol-Gel Sci Technol 1998; 13: 712-22.
http://dx.doi.org/10.1023/A:1008601224013

[70] Sasaki T, Kamitani K. Preparation of thick and hard coating films *via* sol–gel process with a low temperature treatment. J Sol-Gel Sci Technol 2008; 46: 180-89.
http://dx.doi.org/10.1007/s10971-008-1685-4

[71] Chen Y, Jin L, Xie Y. Sol-Gel processing of organic-inorganic nanocomposite protective coatings. J Sol-Gel Sci Technol 1998; 13: 735-38.
http://dx.doi.org/10.1023/A:1008657408992

[72] Joshua Y, Du, Damron M, Tang G, Zheng Prog H. Inorganic/organic hybrid coatings for aircraft aluminum alloy substrates. Prog Org Coat 2001; 41: 226-32.
http://dx.doi.org/10.1016/S0300-9440(01)00133-3

[73] Palanivel V, Jhu D, Van Ooji WJ. Nanoparticle-filled silane films as chromate replacements for aluminum alloys. Prog Org Coat 2003; 47: 384-92.
http://dx.doi.org/10.1016/j.porgcoat.2003.08.015

[74] Jhu D, Van Ooji WJ. Corrosion protection of AA 2024-T3 by bis-[3-(triethoxysilyl)propyl]tetrasulfide in sodium chloride solution: Part 2: mechanism for corrosion protection. Corr Sci 2003; 45: 2177-97.

[75] Jhu D, Van Ooji WJ. Corrosion protection of AA 2024-T3 by bis-[3-(triethoxysilyl)propyl]tetrasulfide in neutral sodium chloride solution. Part 1: corrosion of AA 2024-T3. Corr Sci 2003; 45: 2163-75.
http://dx.doi.org/10.1016/S0010-938X(03)00060-X

[76] Jhu D, Van Ooji WJ. Corrosion protection of metals by water-based silane mixtures of bis-[trimethoxysilylpropyl]amine and vinyltriacetoxysilane. Prog Org Coat 2004; 49: 42-53.
http://dx.doi.org/10.1016/j.porgcoat.2003.08.009

[77] Mehner A, Datchary W, Bleil N, Zoch HW, Klopfstein MJ, Lucca DA. The influence of processing on crack formation, microstructure, density and hardness of sol- gel derived zirconia films. J Sol-Gel Sci Technol 2005; 36: 25-32.
http://dx.doi.org/10.1007/s10971-005-4792-5

[78] Wu KH, Chao CM, Yeh TF. Thermal stability and corrosion resistance of polysiloxane coatings on 2024-T3 and 6061-T6 aluminum alloy. Surf Coat Technol 2007; 201: 5782-88.
http://dx.doi.org/10.1016/j.surfcoat.2006.10.024

[79] Chou TP, Chandrasekaran C, Limmer SJ, Cao GZ. Organic–inorganichybrid coatings for corrosion protection. J Non Cryst Solids 2001; 290: 153-62.
http://dx.doi.org/10.1016/S0022-3093(01)00818-3

[80] Chou TP, Chandrasekaran C, Cao GZ. Sol-Gel-derived hybrid coatings for corrosion protection. J Sol–Gel Sci Technol 2003; 26: 321-27.
http://dx.doi.org/10.1023/A:1020736107842

[81] Voevodin NN, Grebasch NT, Soto WS, Kasten LS, Grant JT, Arnold FE. An organically modified zirconate film as a corrosion-resistant treatment for aluminum 2024-T3 Prog Org Coat 2001; 41: 287-93.
http://dx.doi.org/10.1016/S0300-9440(01)00156-4

[82] Voevodin N, Jeffcoate C, Simon L, Khobaib M, Donley M. Characterization of pitting corrosion in bare and sol–gel coated aluminum 2024-T3 alloy. Surf Coat Technol 2001; 140: 29-34.
http://dx.doi.org/10.1016/S0257-8972(01)01000-3

[83] Kasten LS, Grant JT, Grebasch N, Voevodin N, Arnold FE, Donley MS. An XPS study of cerium dopants in sol–gel coatings for aluminum 2024-T3. Surf Coat Technol 2001; 140: 11-15. http://dx.doi.org/10.1016/S0257-8972(01)01004-0

[84] Voevodin NN, Grebasch NT, Arnold FE, Donley MS. Potentiodynamic evaluation of sol–gel coatings with inorganic inhibitors. Surf Coat Technol 2001; 140: 24-28. http://dx.doi.org/10.1016/S0257-8972(01)00999-9

[85] Santiago A, González, Iruin JJ, Fernández-Berridi MJ, Irusta L. Preparation of superhydrophobic silica nanoparticles by microwave assisted sol–gel process. J Sol–Gel Sci Technol 2012; 61: 8-13. http://dx.doi.org/10.1007/s10971-011-2583-8

[86] Voevodin NN, Balbyshev VN, Khobaib M, Donley MS. Nanostructured coatings approach for corrosion protection. Prog Org Coat 2003; 47: 416-23. http://dx.doi.org/10.1016/S0300-9440(03)00131-0

[87] Tan ALK, Soutar AM, Annergren IF, Liu YN. Multilayer sol–gel coatings for corrosion protection of magnesium. Surf Coat Technol 2005; 198: 478-82. http://dx.doi.org/10.1016/j.surfcoat.2004.10.066

[88] Khramov AN, Voevodin NN, Balbyshev VN, Donley MS. Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors. Thin Solid Films 2004; 447: 549-57. http://dx.doi.org/10.1016/j.tsf.2003.07.016

[89] Khramov AN, Voevodin NN, Balbyshev VN, Mantz RA. Sol–gel-derived corrosion-protective coatings with controllable release of incorporated organic corrosion inhibitors. Thin Solid Films 2005; 483: 191-96. http://dx.doi.org/10.1016/j.tsf.2004.12.021

[90] Zheludkevich ML, Miranda I, Salvado, Ferreira MGS. Sol–gel coatings for corrosion protection of metals. J Mater Chem 2005; 15: 5099-11. http://dx.doi.org/10.1039/b419153f

[91] Chung YJ, Jeanjaquet SL, Kendig MW. The Boeing Company, Corrosion inhibiting sol gel coatings for metal alloys US Patent 6579472.

[92] Rekharsky MV, Inoue Y. Complexation Thermodynamics of Cyclodextrins. Chem Rev 1998; 98: 1875-15. http://dx.doi.org/10.1021/cr970015o

[93] Connors KA. The stability of cyclodextrin complexes in solutions. Chem Rev 1997; 97: 1325-57. http://dx.doi.org/10.1021/cr960371r

[94] Varma PCR, Duffy B, Cassidy J. Influence of magnesium nitrate on the corrosion performance of sol–gel coated AA2024-T3 aluminium alloy. Surf Coat Technol 2009; 204: 277-84. http://dx.doi.org/10.1016/j.surfcoat.2009.07.024

[95] Mouterlier V, Neveu B, Gigandet MP. Evolution of corrosion protection for sol gel coating doped with inorganic inhibitors. Surf Coat Technol 2008; 202: 2052-58. http://dx.doi.org/10.1016/j.surfcoat.2007.08.040

[96] Li S, Wang Q, Chen T, Zhou Z, Wang Y, Fu J. Nanoscale Research Letters 2012; 7: 227. doi:10.1186/1556-276X-7-227. http://dx.doi.org/10.1186/1556-276X-7-227

[97] Raps D, Hack T, Weh J, Zheludkevic HML, Bastos AC, Ferreira MGS, Nuyken O. Electrochemical study of inhibitor-containing organic–inorganic hybrid coatings on AA2024. Corrosion Science 2009; 51: 1012-21. http://dx.doi.org/10.1016/j.corsci.2009.02.018

[98] Woudenberg FCM. Nanostructured oxide coatings *via* emulsion precipitation. Thesis, University of Twente, Enschede, Netherlands 2001.

[99] Chemie VF. Investigation of stabilizing agents in thin sol-gel zirconium oxide anti-corrosion coatings on iron materials, Zur Erlangung des akademischen Grades eines, PhD thesis.

[100] Varmaa PCR, Colreavya J, Cassidy JB, Oubahac M, Duffya B. McDonaghc, Effect of organic chelates on the performance of hybrid sol–gel coated AA 2024-T3 aluminum alloys. Prog Org Coat 2009; 66: 406-11. http://dx.doi.org/10.1016/j.porgcoat.2009.09.004

[101] Nazeri A, Qadri SB. Alumina-stabilized zirconia coatings for high-temperature protection of turbine blades. Surf Coat Technol 1996; 86: 166-69.

[102] Rout TK. Anti-Corrosion Methods and Materials, research, development and technology,Tata Steel Ltd (Europe), Ijmuiden, The Netherlands. Available from http://www.emeraldinsight.com

[103] http://www.sigmaaldrich.com

[104] Akid R, Wang HM, Smith TJ, Greenfield D, Earthman JC. Biological functionalization of a sol–gel coating for the mitigation of microbial-induced corrosion. Adv Funct Mater 2008; 18: 203-11. http://dx.doi.org/10.1002/adfm.200600493

[105] Akid 1, Wang H, Gobara M, Smith TJ, Gittens J. Green Coatings for Industrial ApplicationsR Materials and Engineering Research Institute, Biomedical Research Centre, Sheffield Hallam University. Available from http://www.shu.ac.uk

[106] Certhouxa E, Ansarta F, Turqa V, Boninoa JP, Sobrinob JM, Garciab J, Rebyc J. New sol–gel formulations to increase the barrier effect of a protective coating against the corrosion of steels**.** Prog Org Coat 2013; 76: 165-72. http://dx.doi.org/10.1016/j.porgcoat.2012.09.002

[107] Collazo A, Covelo A, Nóvoa XR, Pérez C, Corrosion protection performance of sol–gel coatings doped with red mud applied on AA2024-T3. Prog Org Coat 2012; 74: 334-42. http://dx.doi.org/10.1016/j.porgcoat.2011.10.001

[108] Chevdov D, Ostap S, Le T. Surface properties of red mud particles from potentiometric titration. Colloids Surf 2001; 182: 131. http://dx.doi.org/10.1016/S0927-7757(00)00814-1

[109] Pascual J, Corpas FA, Lopez-Beceiro J, Benítez-Guerrero M, Artiaga R. Thermal characterization of a spanish red mud. J Therm Anal Cal 2009; 96: 407-18. http://dx.doi.org/10.1007/s10973-008-9230-9

[110] Egloffstein TA. Natural bentonites—influence of the ion exchange and partial desiccation on permeability and self-healing capacity of bentonites used in GCLs. Geotextiles and Geomembrances 2001; 19: 427-44. http://dx.doi.org/10.1016/S0266-1144(01)00017-6

[111] Hikasa A, Sekino T, Hayashi Y, Rajagopalan R, Niihara K. Preparation and corrosion studies of self-healing multi-layered nano Coatings of silica and swelling Clay. Mat Res Innovat 2004; 8.2, 84-88. 1432-8917.

[112] Keyoonwong W, Guo Y, Kubouchi M, Aoki S, Sakai T. International Journal of corrosion 2012; 2012. Article ID 924283, 10 pages doi:10.1155/2012/924283. Available from http://dx.doi.org/10.1155/2012/924283

[113] Curtu O, Motoc DL. Theoretical - experimental comparisons of multi-phase composite materials elastic coefficients retrieved from tensile, compressive and bending tests. Influencing Factors. Material Plastice 2008; 45: 366-71.

[114] Esfandiari A, Nazokdast H, Rashidi A-S, Yazdanshenas M-E. Review of polymer-organoclaynanocomposites. J Appl Sci 2008; 8: 545-61.

[115] Esfandiari A. The statistical investigation of mechanical properties of PP/natural fibers composites. Fibers Polymers 2008; 9: 48-54. http://dx.doi.org/10.1007/s12221-008-0008-2

[116] Shan C, Zheng G, Wang L, Peiyao L, Guojun S, Zhenbin G, Xiaoyu Y. Preparation, Characterization, and application of NR/SBR/organoclay nanocomposites in the tire industry. J Appl Polymer Sci 2011; 119: 1185-94. http://dx.doi.org/10.1002/app.32773

[117] Sterky K, Jacobsen H, Jakubowicz I, Yarahmadi N, Hjertberg T, Influence of processing technique on morphology and mechanical properties of PVC nanocomposites. Eur Polym J, 2010; 46: 1203-209. http://dx.doi.org/10.1016/j.eurpolymj.2010.03.021

[118] Sterky K, Hjertberg T, Jacobsen H. Effect of montmorillonite treatment on the thermal stability of poly(vinyl chloride) nanocomposites. Polymer Degradation Stability 2009; 94: 1564-70.

Received on 25-08-2013 Accepted on 05-10-2013 Published on 13-01-2014

DOI: http://dx.doi.org/10.6000/1929-5995.2013.02.04.4