



**ANTICORROSIVE HYBRID NANOCOMPOSITE
COATING BY THE SOL-GEL PROCESS**

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Mohammed Jaber Abed -ALOWAIDI

ABSTRACT

M. Sc. Thesis

ANTICORROSIVE HYBRID NANOCOMPOSITE COATING BY SOL-GEL PROCESS

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Corrosion of metallic materials is mostly caused by the corrosive environment, which is especially prevalent in hostile situations such as the sea environment. Corrosion reduces the service life of metal structures, which can lead to structural failure, product loss, and pollution. As a result, it is crucial to adopt approaches for corrosion mitigation. The methods used can be preventive and can be accomplished by adding a barrier layer, such as a coating, which prevents the metallic substrate from coming into contact with the hostile environment. Over the last few decades, the sol-gel synthesis method has become remarkably significant in a variety of application fields. Sol-gel has been used to make organic-inorganic hybrid (OIH) coatings. Sol-gel allows inorganic and organic elements to be mixed in a single phase. OIH coatings have many uses, including reducing corrosion.

In this research, a piece of mild steel rebar made in Ukraine and used in building was cleaned, polished, and washed.

The hybrid coatings made from commercially available tetraethylorthosilicate (TEOS), methyltriethoxysilane (MTES), and (phTMS) in acid catalysis conditions were used just as they were.

The goal of this research is to make and study silane-based organic-inorganic hybrid coatings with special features that can be used to improve the performance of steel structures that are exposed to marine corrosion.

Several tests on specimens made of mild steel, as well as SEM, X-ray diffraction analysis (XRD), polarization tests (tafel), and Fourier transformed infrared (FTIR) analysis were used to characterize the surface and cross-section morphology of coated specimens. FTIR analysis was also used to find out if the coating solutions had different functional groups.

Key Word : Organic-inorganic hybrids coating; sol-gel synthesis; mild steel; corrosion protection.

Science Code : 91510

ÖZET

Yüksek Lisans Tezi

SOL-JEL İŞLEMİ İLE ANTİKOROZİF HİBRİT NANOKOMPOZİT KAPLAMA

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Metalik malzemelerin korozyonuna çoğunlukla, özellikle deniz ortamı gibi düşmanca durumlarda yaygın olan aşındırıcı ortam neden olur. Korozyon, yapısal bozulmaya, ürün kaybına ve kirliliğe yol açabilen metal yapıların hizmet ömrünü azaltır. Sonuç olarak, korozyon azaltma yaklaşımlarının benimsenmesi çok önemlidir. Kullanılan yöntemler önleyici olabilir ve metalik alt tabakanın düşman ortamla temas etmesini önleyen bir kaplama gibi bir bariyer tabakası eklenerek gerçekleştirilebilir. Son birkaç on yılda, sol-jel sentez yöntemi, çeşitli uygulama alanlarında dikkate değer ölçüde önemli hale geldi. Sol-jel, organik-inorganik hibrit (OIH) kaplamalar yapmak için kullanılmıştır. Sol-jel, inorganik ve organik elementlerin tek bir fazda karışmasını sağlar. OIH kaplamaları, korozyonu azaltmak da dahil olmak üzere birçok kullanıma sahiptir.

Bu arařtırmada, Ukrayna'da retilen ve inřaatta kullanılan bir yumuřak elik inřaat demiri temizlendi, parlatıldı ve yıkandı.

Asit kataliz kořullarında ticari olarak temin edilebilen tetraetilortosilikat (TEOS), metiltrietoksisilan (MTES) ve (phTMS)'den yapılan hibrit kaplamalar olduđu gibi kullanıldı.

Bu arařtırmanın amacı, deniz korozyonuna maruz kalan elik yapıların performansını iyileřtirmek iin kullanılabilir zel zelliklere sahip silan bazlı organik-inorganik hibrit kaplamalar yapmak ve incelemektir.

Kaplanmış malzemenin yzeyini ve enine kesit morfolojisini karakterize etmek iin yumuřak elikten yapılan numuneler zerinde eřitli testlerin yanı sıra SEM, X-ıřını kırınım analizi (XRD), polarizasyon testleri (tafel) ve Fourier dnřtrlmř kızıltesi (FTIR) analizi kullanıldı. rnekler. Kaplama solsyonlarının farklı fonksiyonel gruplara sahip olup olmadıđını anlamak iin FTIR analizi de kullanıldı.

Anahtar Kelime : Organik-inorganik melezler kaplama; sol-jel sentezi; hafif elik; korozyon koruması.

Bilim Kodu : 91510

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SYMBOLS AND ABBREVIATIONS INDEX

SYMBOLS

Cl	: Chlorine
Fe	: Ferrous
NaCl	: sodume chloride
Si	: silicon
Ti	: titanume
SiO ₂	: silica
ZrO ₂	: zarconia
TiO ₂	: titania
HCl	: hydrochloric acid

ABBREVIATIONS

TEOS	: Tetraethylorthosilicate
TMOS	: Tetramethylorthosilicate
PhTES	: Phenyltriethoxysilane
PhTMS	: Phenyltrimethoxysilane
FT-IR	: Fourier Transform Infrared Spectroscopy
EtOH	: Ethanol
ormosil	: Organically Modified Silicon
I _{corr}	: Corrosion current
E _{corr}	: Corrosion potential
SEM	: Scanning Electron Microscope
XRD	: X-Ray Diffraction

PART 1

INTRODUCTION

1.1. INTRODUCTION

Damage materials from corrosion, which results due to the metal's decomposition through chemically or electrochemically action, is among the most prevalent issues in the market. Although corrosion cannot be completely stopped, it can be postponed by using a number of approaches like decreasing heat , the elimination of oxygen and other oxides substances, and the modification of the working environment's concentration. Additional inhibitor may be applied to the corrosion environment in small doses to slow the corrosion process. Application of anodic and cathodic protection techniques can increase corrosion resistance [1].

Mild steel is a desirable structural material for a variety of uses. Thanks to its perfect mechanical strength, excellent thermal conductivity, and good machinability, mild steel's rapid rate of oxidation reduces the amount of time it may be used. Many techniques have been designed to enhance mild steel's resistance to corrosion. Surface coating techniques have become popular in recent years as a means of corrosion protection for materials. Ceramic materials are a ideal option for coating materials because they provide defense against high-temperature oxidation, corrosion, and wear [2]. Coatings can be applied on metallic surfaces using a variety of different technologies nowadays. Amorphous or crystalline oxide coatings are created utilizing sol-gel based coatings through chemical processes, and these materials are then heated to transform them into oxides. The substrate surface is better protected by sol-gel coatings. Additionally, because organic groups were present, the coating was flexible and could be cured at the lowest temperatures, which minimized micron cracks [3-5].

Various processes are utilized nowadays to cover metallic materials. Chemical reactions are employed to make amorphous or crystalline oxide coatings utilizing sol-gel based coatings, which are then heated to transform the materials into oxides. The substrate surface is better protected by sol-gel coatings. Additionally, the addition of organic groups made the coating flexible and allowed for their low-temperature curing, which minimizes the appearance of micro cracks [3–5]. Due to their quick hydrolysis characteristics, silicon alkoxides like $\text{Si}(\text{OR}')_4$ and $\text{RnSi}(\text{OR}')_4$, are frequently employed as sources of the monomers. Commonly utilized organically modified silicate (ormosil) compounds include organosilanes containing phenyl, amino, and carboxyl groups [6]. The vitreous, ceramic, and organic inorganic hybrid dense layers can be deposited on various a sample below 500°C using the comparatively straightforward sol-gel procedure [7]. Sol-gel coatings have reportedly been used successfully to increase metals' resistance to corrosion and wear [2,8]. Coating material such as zirconiumoxide, borosilicate, alumina silicate, cerium [9-12] and SiO_2 , [14] have reportedly been shown to prevent rusting. Corrosive substances can more easily enter a material through coating cracks. To avoid fracture formation during the heat treatment, The material to be coated and the coating material's thermal expansion coefficients must be equivalent [15].

The study of organic/inorganic hybrid nanocomposite materials created using the sol-gel technique has generated a lot of attention. Due to their homogeneous, high-purity products' homogeneous diphasic structures, which can be produced at room temperature as opposed to the extremely high temperatures required to produce multifunctional materials, inorganic oxide is the predominant component. Numerous studies have concentrated on silica-based gels, Papers that also partially explain the process for non-silicate-based gel cover the physics and chemistry involved in the synthesis [16, 17,18].

In this research, the sol-gel dip coating technique used to cover steel specimens with a hybrid coating. The material's performance and behavior as a wet corrosion barrier in a 3.5 weight percent NaCl solution were then evaluated using low temperature heat treatments (65°C and 160°C). Impedance and electrochemical parameter analysis were utilized to evaluate the corrosion properties. Fourier transformed

infrared (FTIR) functional groups in coating solutions were analyzed, SEM was used to determine coatings' surface and cross-sectional morphology, and X-RAY. It was compared to how well coated and uncoated mild steel resisted corrosion.

Coatings like hybrid mix-up increase the chemical and physical features of metal surfaces with regard to corrosion, friction, and wear performance without changing the substrate's inherent qualities, such as strength and hardness [13]. Hybrid coatings' protective qualities include strong adhesion and resistance to corrosion. According to research, coatings have the ability to prevent corrosion in salt environments.

1.2. GOAL OF THIS WORK

The purpose of this work is to conduct a methodical analysis of an anticorrosion hybrid coating mild steel in a NaCl solution and determine how each component affects corrosive resistance TEOS was condensed and polymerized with MPTS, PhTMS, and trifunctional alkoxy silane to create sol-gel coatings. This was done to make inorganic and organic phases that were covalently bound to each other.

This steel is cheap, easy to make, and strong, so it can be used in a wide range of industrial and consumer products. These coatings are intended to guard steel structures from corrosion in saltwater settings

PART 2

THEORETICAL PART AND LITERATURE REVIEW

2.1. INTRODUCTION

This chapter deals with CORROSION and the types of corrosion, the details of the coating process by means of sol gel and its types for the purpose protection from corrosion. And the method of coating used (dip coating).

2.2. CORROSION

Corrosion is when chemicals or electricity attack metals or alloys in the environment and cause them to break down or disappear.

The presence of salt in the moisture will hasten the production of rust [19].

There are two major categories of metallic substance corrosion:

A: Wet corrosion, also known as electrochemical corrosion, happens when two metals that are not compatible with one another come into contact with a conducting liquid. The distinct anodic and catalytic zones through which current flows The conducting solution is to blame for this corrosion.

B: Dry corrosion (chemical corrosion) is a form of corrosion that mostly results from the direct chemical action of ambient gases such as oxygen and halogens such as H₂, CO₂, N₂, and H₂S [19,20].

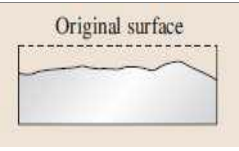
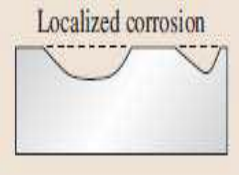
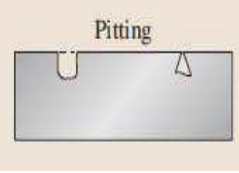
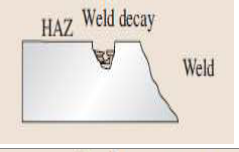
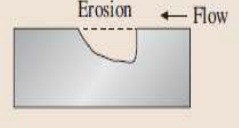

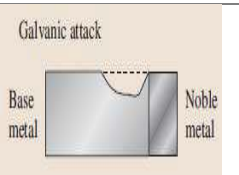
Electrochemical corrosion is caused by anodic-cathodic electron flow. Electrons can move from the negative electrode to the positive electrode when an electrolyte is in contact with it.

In the anodic reaction, metal dissolves to form metallic ions while electrons are released. As a result, corrosion always occurs in the anodic area [21].

2.3. FORMS OF CORROSION

The main types of corrosion that are classified based on the surface after corrosion in table(2.1):

Table 2.1. Types of corrosion.

No.	Type	Characteristic	Image
1	Uniform (General) corrosion [19]	All areas of the metal corrode at the same (or similar) rate.	
2	Localized corrosion [19]	The "heterogeneities" in the metal cause some regions of the metal surface to corrode more quickly than others. either in the surroundings or in the overall geometry of the building. Attacks can be pitting or only slightly localized.	
3	Pitting corrosion [19]	onslaught that was very focused on one location, leaving behind tiny trenches that reached into the metal, which could result in perforation.	
4	Selective dissolution corrosion [19]	Typically, the most active component of an alloy is removed from a material.	
5	Erosion corrosion [19]	localized attack or fracture brought on by the combined effects of corrosion and a mechanical component.	
6	Stress Corrosion Cracking] (SCC)	It is described as the result of the simultaneous occurrence of static tensile strains and corrosion-related crack development. Tensile stresses may be internal stresses brought on by cold working, welding, or heat treatment, or they may result from external loads, centrifugal forces, or temperature variations.	
7	Galvanic Corrosion [2].	This happens when two metals with distinct electrochemical potentials are brought together. are in close proximity inside the same solution.	

2.4. CORROSION PROTECTION AND CONTROL

As corrosion is a natural, spontaneous process that turns metal into a more stable combination, corrosion control is more practical than corrosion avoidance.

2.4.1. Corrosion Inhibitors

Chemical compounds can reduce or control corrosion on metal surfaces. Inhibition is the term used for this type of corrosion control, and compounds are referred to as "inhibitors of corrosion. The inhibitors can impede processes of cathodic reduction, anodic oxidation. The inhibitors produce a protective coating on the metal's surface. It has been suggested that the inhibitors are physically or chemically metal surface-adsorbed [22]. Physical absorption is the electrostatic interaction through the surface of an electrically charged metal with an organic ion. In the process of chemisorption, an inhibitor molecule changes the charge on the surface of a metal to make a "coordinate" connection.

By inhibiting the metal's anodic dissolution reaction, the cathodic evolution of hydrogen, or both, the adsorption inhibitor slows down the pace of corrosion of the surface of the metal [22]. At acidic pH levels ranging from nearly neutral to alkaline, inhibitors can be utilized.

They can be categorized in a variety of ways based on:

- Their chemical composition (organic or inorganic substances)
- The features they exhibit (oxidizing or no oxidizing compounds)
- Pickling, descaling, and acid cleaning are some of their technical applications, such as cooling water systems.

2.4.2. Protective Coatings

With the use of surface modification techniques, it is possible to create new materials for coatings or change the structure or content of a substrate. These can be used to

add one or more properties to the metal substrate, such as increased resistance to wear, scratching, impact, etc., and the ability to act as a barrier. Protective coatings can be created using a variety of techniques, and they can take the form of layers on the metal surface. Additionally, as a result of the large variety of materials produced by each of these methods, three general categories of coatings are metal, polymer, and ceramic [23].

- **Electroplating** is a process in which metals and alloys can be plated on a substrate that conducts electricity and functions as a cathode. Before they can be electroplated, ceramics and plastics need to have a treatment done to them. The metal cations are diminished while they are suspended in the solution. Through the action of an outside current moving through the electrolyte. The rate of deposition is determined by the cation concentration, as well as the temperature and the current density [24].
- The procedure of depositing metal ions from an electrolyte solution onto a substrate is known "electrolysis plating." This approach doesn't require an electric current, and the plating happens as a result of chemical reactions that happen on the substrate's surface [25].
- "Hot dipping" refers to the process of applying a coating by submerging a metal
- substrate in a bath of molten metal, which is often composed of aluminum or zinc. This method is widely used in the metalworking industry. The fact that the coating that was placed was already molten makes the melting process faster. The temperature of the metal coating ought to be kept at a moderate level [26].
- **Physical Vapor Deposition (PVD)** involves vaporizing the coating material in a vacuum, transporting the vapor to the substrate, and then condensing the vapor on the surface of the substrate. The method included goes along atomistic lines and, for the most part, does not entail any chemical interactions [33]. There is a wide range of possibilities the thickness of the deposits, from angstroms to millimeters [34].
- In the process known as chemical vapor deposition (CVD), a coating is created on the surface of a heated sample that has been exposed to a gas

mixture. A result of a chemical reaction or the decomposition of gases present on the substrate material, this coating is created [25].

- **Thermal spraying** is the process of depositing atomized metal at a high temperature using a gas stream moving at a high velocity to transport the metal to the surface of the substrate [25].
- **Electrophoretic Deposition**, sometimes known as EPD, is a straightforward
- Technique for the production of coating applied to an electrode with the use of a stable solution in direct current field . The EPD method consists of two stages: first, charged particles are suspended in a under the influence of an electric field, the liquid moves closer and closer to an electrode. electrophoresis, in which the particles are allowed to deposit on an electrode, results in the formation of a comparatively dense and even film [27]. The EPD methodology is one of the options available in application of this work, which will be covered in greater detail in the following section [29].
- **Sol Gel:** The production of an integrated network gel can begin either from a solution or from colloidal particles when using the sol gel method, which is a wet-chemical approach for fabricating dies for materials, most often metal oxide [30]. So advantages of using Sol-Gel technologies include availability of a diverse selection of morphologies, such as fine powders, fibers, thin films, xerogels, and aerogels [31].

2.4.3. Cathodic Protection

The application of a direct current (DC) from an anode to the surface to be protected while it is passing through the electrolyte is what is known as cathodic protection. It is common practice to consider this as a means of overcoming the corrosion currents that are present on the structure. That because there is no movement of electrical current (electrons) through the electrolyte, this is not actually what happens. Ionic current does, in fact, pass across the electrolytes; this cannot be denied [32].

The potential discrepancies between the anodes and cathodes on the surface that is corroding are eliminated when cathodic protection is utilized. After this, a potential difference is produced between the cathodic protection anode and the structure in

such a way that the cathodic protection anode can protect the structure from corrosion.

The protective anode has a potential that is more negative than any other place on the surface of the structure. As a result, the structure assumes its role as the cathode in the newly formed corrosion cell shown in fig (2.1). The anode that provides cathodic protection is allowed to erode, but the structure itself does not corrode because it is the cathode [32].

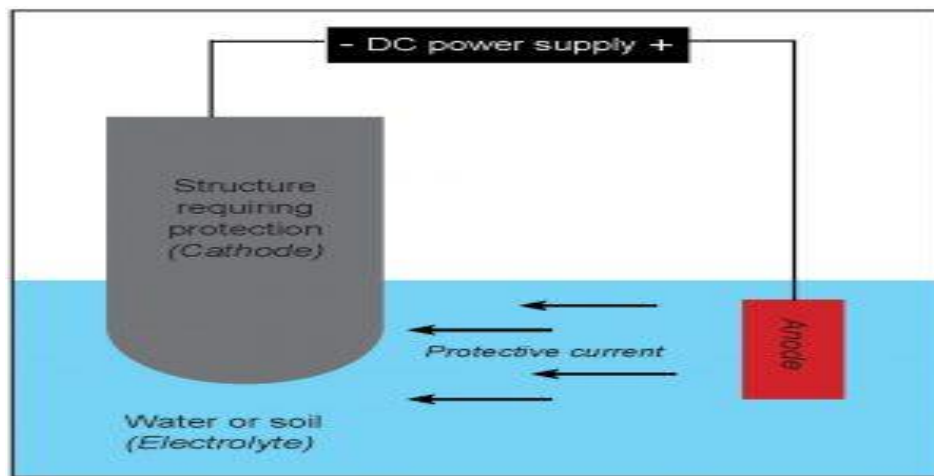


Figure 2.1. Cathode protection cell [32].

2.4.4. Anodic Protection

Anodic protection is potential-control electrochemical technique how effective for preventing the corrosion of a metal in hostile environments such as sulfuric acid. This technology is used to protect metals from corrosion. In this method, the metal that is going to be shielded needs to demonstrate passivity at low current density, making it so that the passive current density is at least an order of magnitude lower than the current density caused by corrosion (i_{corr}). When choosing a material, care needs to be taken to pick one that has a passive potential range that is sufficiently broad. In addition, anodic protection is typically utilized in situations where coatings and cathodic protection technologies do not offer sufficient protection against corrosion [33].

Passivation of the metal to be protected by anodization is required for anodic protection. When an electrical current is passed over the surface of the metal, a film that does not conduct electricity is produced. Once this film has developed, it serves as a barrier that prevents metal from being dissolved, as well as film it is almost completely insoluble in the environment in which it was generated. The process of passivation renders metals extremely non-reactive and, as a result, highly resistant to the effects of corrosion.

2.5. NANOMATERIALS

Nanomaterials are materials that display fascinating electrical, optical, and magnetic properties in addition to high catalytic activity. Nanomaterials are defined as any substance that exhibits features that are unique or innovative as a result of the nanoscale (1-100 nm) structure of the nanomaterial [34]. The structural dimensionality of nanomaterials is an extremely important factor in determining photocatalytic activity. On the other hand, the dimensionality of the structure has a substantial effect on the properties of nanomaterials, as seen in figure (2-2). Spherical nanoparticles with zero dimensionality, for instance, with large specific surface area, which leads to higher rate of photocatalytic breakdown of organic contaminants [35].

One-dimensional fibers or tubes are used to create self-standing nonwoven mats and have benefits including minimal recombination, light scattering qualities, and small distances for charge carrier diffusion. Structures in zero and one dimensions have advanced significantly [36].

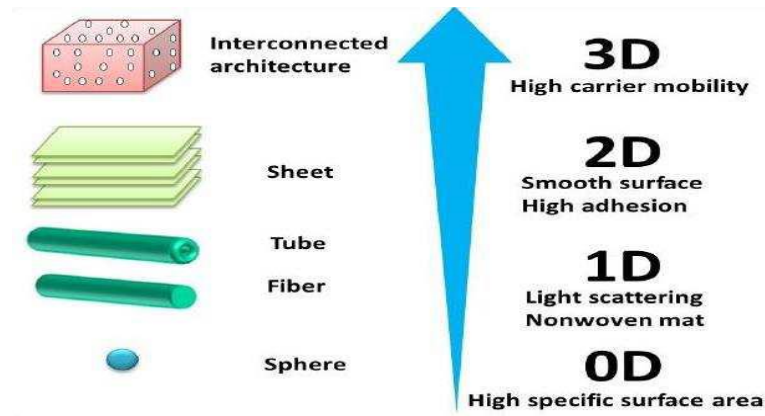


Figure 2.2. Structural dimensionality of nanomaterials with expected properties[34].

Due to their inherent lattice strain, nanomaterials have a larger distortion of surface structure than bulk materials. Therefore, surface alterations of NPs are preferable to bulk particle changes [38]. Due to their small size and high reactivity, these nanomaterials exhibit different toxicity profiles compared to bigger materials throughout the last twelve years. The process of capping involves covering the surface of one semiconductor or metal nanoparticle with a different semiconductor or metal nanomaterial [39].

2.6. FUNDAMENTALS SOL-GEL COATINGS

Since 1846, there has been a sol-gel technique when Ebelmen created silica gels from alkoxides using this straightforward chemical synthesis technique [40]. Sol-Gel is a coating method that can be used to enhance the optical, electrical, chemical, and mechanical properties of surfaces on glass, ceramics, metals, and polymers. Bulk glass, coatings, and fibers are three primary categories into which the manufacture and It is possible to differentiate between the applications of materials produced by the sol-gel technique [41]. The common sol-gel procedure, which aids in the creation of inorganic networks, involves the generation of a colloidal suspension (sol) and the sol's subsequent gelation (gel)[42]. Advantages of using the sol-gel coating technique are outlined below.

- Sol-gel synthesis is a type of low-temperature chemical synthesis that normally takes place at room temperature.

- Since the sol-gel coating technique includes dipping the substrate in liquid sol, coatings can be used on surfaces of any shape.
- Sol-gel coating is an environmentally technique.

2.6.1. The Synthesis Sol-Gel Coatings

A continuous liquid-phase colloidal network is created as a result of the gelation of the inorganic or hybrid sol that is produced as a result of the growth of a colloidal system (gel). Size of the colloidal particles in sols, which are liquid-based dispersions, range from 1 – 100 nm. (Fig 2-3) In the liquid phase, colloidal particles form a 3-dimensional, continuous network known as a gel. In the sol-gel process, molecule is "dissolved" in the liquid so that it can be "reconstituted" as a solid through a series of carefully orchestrated steps [43].

Sol-gel stages include:

- Hydrolysis
- Monomers are condensation and polymerized to create chains and particles.
- Nanoparticles growth

When polymer is in the liquid phase, it forms a continuous network. Then, when the polymer structure comes together, it forms a gel. For Si, Zr, Ti, and Al, corrosion-resistant sol-gel coatings are typically prepared using their respective alkoxides. Silicon alkoxides contact with water during the hydrolysis step, Alkoxide groups (-OR) become hydroxyl groups (-OH). During condensation, two OH groups or OR group and OH group condense, forming a network of Si-O-Si links, water, and alcohol. Once hydrolysis begins, condensation and hydrolysis occur simultaneously.

The following some significant influences on the sol-gel process:

- Initial pH and temperature.
- the reactants' molar ratio.
- Solvent composition structure

The rate of the sol-gel reactions is significantly influenced by the type of mutual solvent[44]. Because metal alkoxide and water are not compatible, a mutual solvent, such as alcohol, to achieve homogeneity, must be added to the reaction mixture. By extension, The thickness of the produced sol-gel coating on the metal substrate and, consequently, its corrosion resistance are significantly influenced by the solvent's concentration [45].

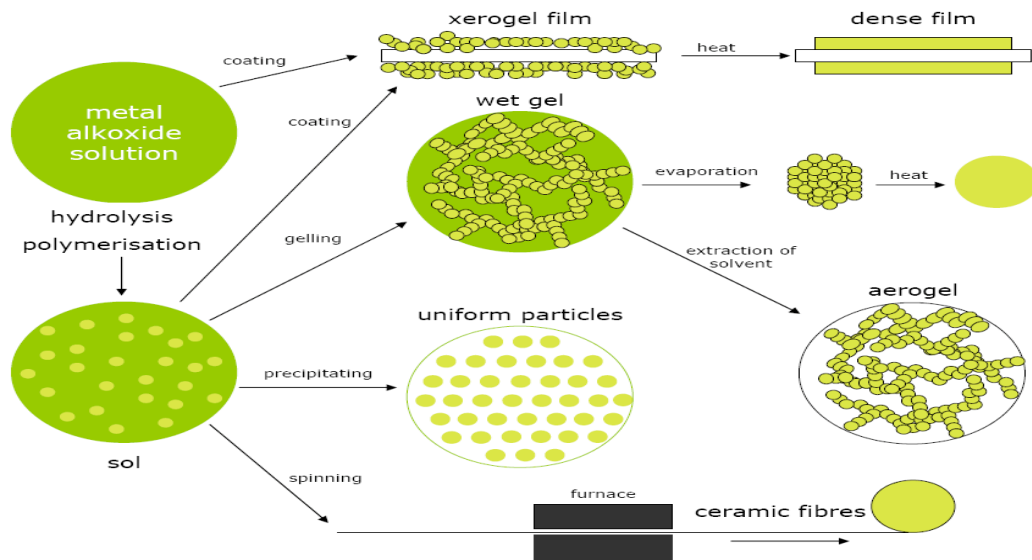


Figure 2.3. Sol-gel processing options [43].

2.6.2. Hydrolysis Reaction and Condensation

In the sol-gel process, very first chemical reaction that takes place is called the hydrolysis reaction. The moment that the hydrolysis reaction begins, the hydrolysis reaction and the condensation reaction both begin at the same time and continue simultaneously. Metal alkoxides are common precursors used into sol-gel reactions or silicon alkoxides because they react with water easily. When stoichiometric water is present, the hydrolysis reaction takes place. As in the following reaction, this reaction creates a hydroxyl group (-OH) bound to the metal atom (M).



Repeat until all alkoxide groups become hydroxyl groups. A sample of a separate step in the hydrolysis reaction that produces silicon tetra alkoxide is shown in Figure (2.4).

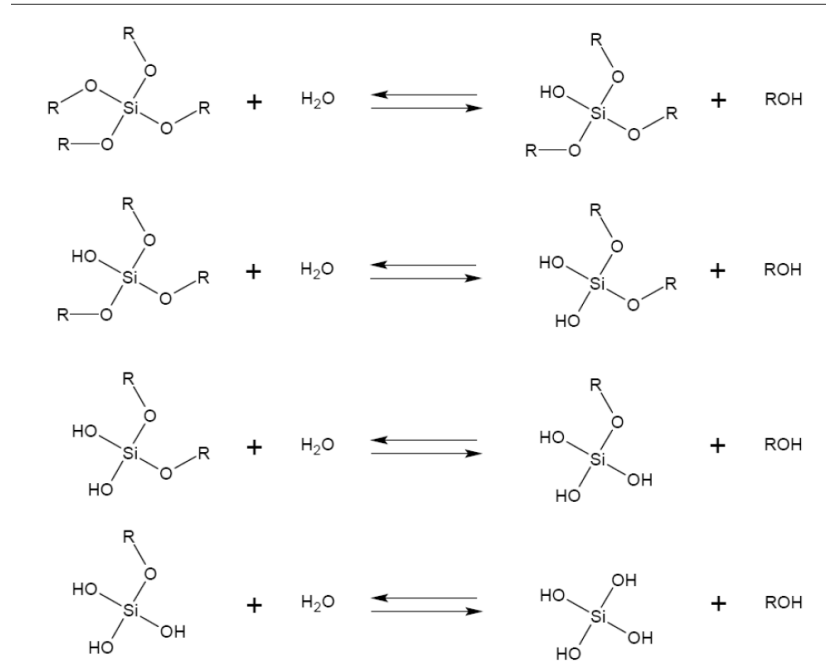
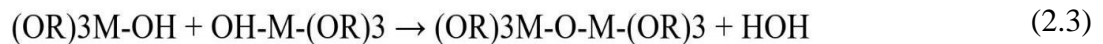


Figure 2.4. Reaction of hydrolysis involved in silicon tetraalkoxide [41].

After hydrolysis, an event called condensation occurs in which two partially hydrolyzed species join forces to form a three-dimensional network by getting rid of a tiny molecule of either alcohol or water.



Typically, the hydrolysis stage ends before the condensation process begins. Through the process of polymerization, this kind of reaction can carry on to create molecules that include silicon or metals that are ever larger [41].

The speed of the hydrolysis and condensation processes has a considerable impact on stability and coating qualities. It is necessary to emphasize that a variety of factors, including molar ratios, pH, solution type, catalysts, aging process, and alkoxide

nature, can affect how quickly hydrolysis and condensation reactions occur. A variety of coating structures with desired attributes could be obtained by adjusting these variables [41].

- **Ageing** : The process of allowing the sol to continue the hydrolysis and condensation processes after components have been combined is known as ageing. Even after the gel-point, chemical processes can occasionally persist. There are some benefits to aging. The aging process for sols used to create monoliths differs from that for sols used to deposit thin films. Aging's primary role in coating sols is to speed up the cross-linking of polymers, which increases the solution's viscosity and makes dip-coating practicable.
- **Gelation** : The solution undergoes two processes: condensation and hydrolysis. Polymerization is the process by which the gel is made. Conditions at the start of the hydrolysis and condensation reactions, such as temperature, concentration of precursors, reaction medium, and type of catalyst, affect how the gel forms. The initial circumstances of the reactions affect gel formation.
- **Drying** : Before the first gel can be converted into a more robust network, the mixture of alcohol and water must be removed. The linkages, which were initially relatively weak, will get stronger as a result. The act of drying does this, Most of the water and alcohol that were lodged in the pores are removed as a result. The resultant substance is referred to as a xerogel [46]. Depending on its purpose, the sol-gel process can be changed for make powders, fibers, coatings, monoliths, or pores. Because gels are so flexible, all of this is possible. Fig (2.5).

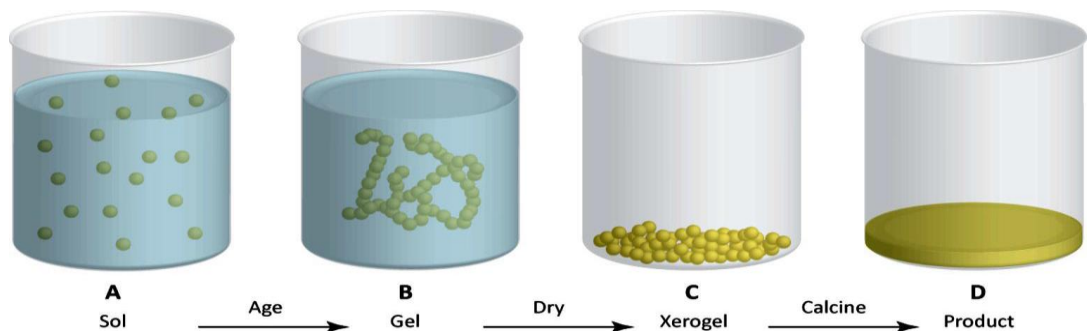


Figure 2.5. Representation of the Sol-Gel process[46].

- **Calcination** : The xerogel in question lacks crystalline structure, and as a result, its mechanical strength is subpar. When heated to a high temperature, often in the vicinity of 500 degrees Celsius, the xerogel transforms into a substance that is viscous and, in some cases, crystalline. This is done so that the material can be strengthened and densified, as shown in Figure [46]. Instead of producing a thin film, the sol-gel technique described above results in a solid powder. When using sol-gel to make a thin film coating, the procedure must be altered so, the aged sol may be deposited onto a substrate that is appropriate for the coating. The liquid sol can be deposited onto a spinning substrate either by "dip coating," . After being coated, the substrates are subjected to calcination, which results in the formation of thick and crystalline thin layers. Figure (2.6) [46]. provides a visual representation of this procedure.

2.6.3. Thin Film Sol-Gel Deposition

Sol-gel approach employs hydrolysis, condensation, and metal organic precursors in a low-temperature process [47, 48]. Sol-gel processes require a metal alkoxide precursor, water, solvent, and catalyst. These fundamental components are completely combined to attain molecular homogeneity. Condensation and hydrolysis reactions are responsible for the formation of viscous gels. A viscous gel is an amorphous porous solid that contains a liquid solvent within the pores. The densified form is produced by employing this gel to create thin films that are either porous or densified. The porous form is created by curing a thin sol-gel-derived coating at low temperatures (100 °C). In light of this, it appears that the sol-gel process is highly flexible and suited for a variety of applications.

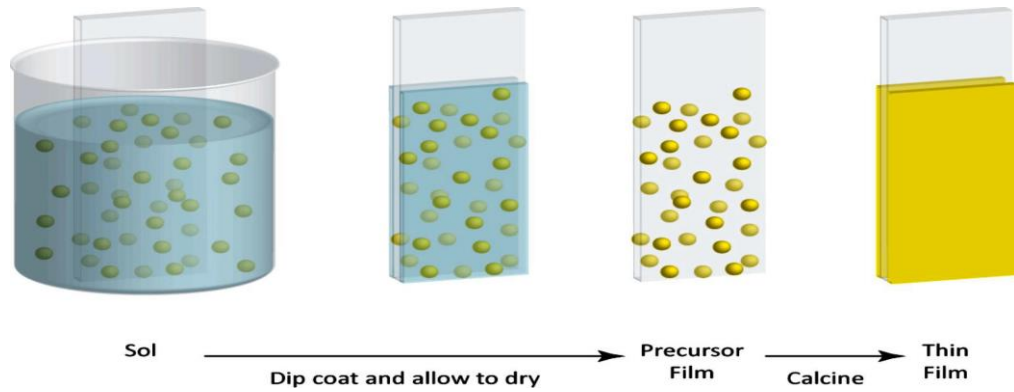


Figure 2.6. Schematic representation Sol-Gel method to producing thin films by dip coating [47].

2.7. SOL-GEL COATING TYPES

2.7.1. Inorganic Sol-Gel Coatings

The first form of coatings developed from sol-gel that was used to shield metallic substrates from corrosion was known as inorganic sol-gel coatings, also known as metal oxide coatings. SiO_2 , ZrO_2 , TiO_2 , etc. are the most prevalent kind of metal oxide coatings that are applied on top of various kinds of metallic substrates. In most cases, the corrosion protection performance of a coating made from sol-gel generated metal oxide is equivalent to, or on par with, that of a chromate conversion layer and phosphate pretreatment as it would often appear. protective layers made of inorganic materials made from sol-gel did not, however, offer enough corrosion resistance when such covered panels were subjected to corrosive conditions [49].

Sol-gel produced metal oxide coatings have a number of problems, the most significant of which are the creation of porosity when increasing the thickness of the coatings and the breaking down of the coating layer at isolated spots. The thin layer of sol-gel film that is developed on metallic substrates typically results in the formation of cracks or pores during the curing process when the temperature is raised to high levels. This is because the metal oxide layer created by sol-gel and the underlying metal surface have different thermal expansion coefficients [50]. Properties such as resilience to high temperatures and chemicals make sol-gel silica films an appropriate coating for enhancing oxidation and corrosion resistance in

acidic environments at varied temperatures. This is made possible by the films' high temperature resistance and chemical resistance [51, 52]. Sintering at high temperatures causes silica coatings to become less porous because of the enormous expansion coefficients that occur throughout the process [53]. Between the organic coatings and the metallic substrate is a layer of adhesion that is provided by inorganic protective films made of sol-gel [54, 55, 56].

2.7.2. OIH Sol-Gel Coatings

Sol-gel-derived inorganic coatings could provide effective corrosion protection for metallic substrates, they have two significant drawbacks, which are listed below.

- It is challenging to create thicker coatings ($> 1 \text{ m}$) without any thermally induced cracking because metal oxide sol-gel films are breakable.
- Sintering at high temperatures is frequently necessary to achieve good, ideal characteristics [57, 58].

Adding organic moieties to the coating matrix makes pure inorganically generated sol-gel coatings less brittle and eliminates the need for high temperature sintering. The qualities of both organic polymeric and inorganic ceramic materials are imparted via hybrid coatings. The inorganic portion of the hybrid system enhances scratch resistance, durability, and adhesion to metallic substrates, and organic functional groups help in the formation of thick, crack-free hydrophobic surfaces. The compatibility and adherence of thin protective hybrid sol-gel coatings to common organic paint systems are also improved by the organic functionality [50]. There are three basic methods for creating hybrid sol-gel films, varies according to the inorganic and organic components and chemical relationship [57] (Fig 2.7).

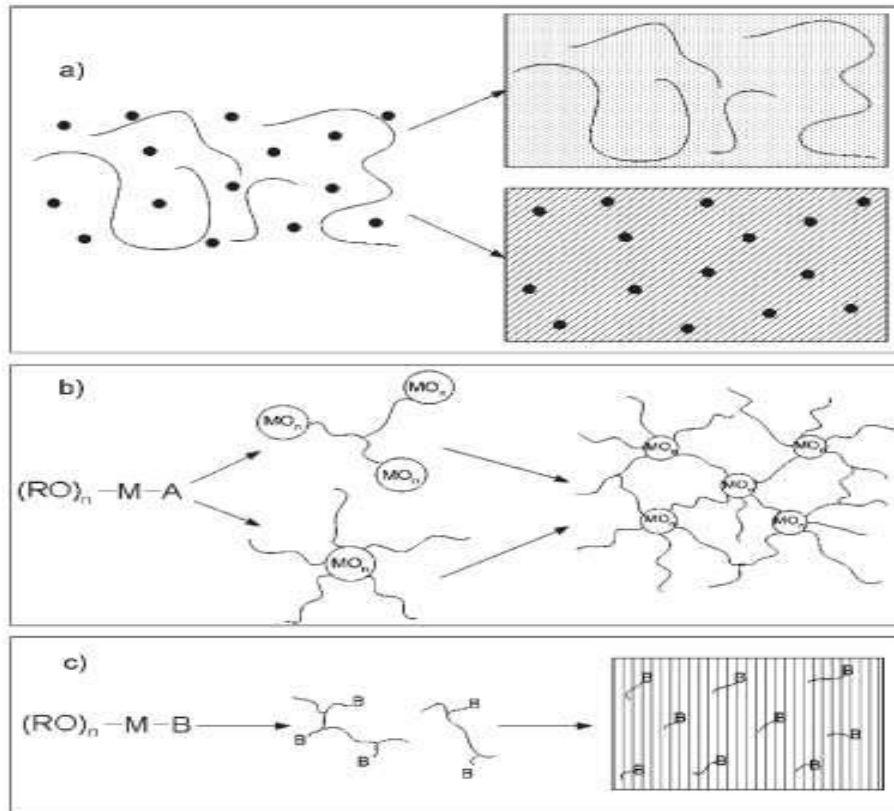


Figure 2.7. Schematic of sol-gel hybrid materials[57].

- There is no chemical bond between the organic and inorganic groups;
- The inorganic group is bonded to the organic group that can be polymerized;
- Inorganic phase is bonded to organic groups that can't be turned into polymer.

The three various methods are as follows:

- Using the mixture of organic and inorganic sol-gel systems directly; The final material is a simple combination with no organic-inorganic chemical connection.
- forming an organic-inorganic chemical bond by reacting an existing functional group inside a polymeric or oligomeric molecule with an inorganic precursor solution that has been hydrolyzed.
- The sol or one of the precursors of the sol-gel reaction is alkoxy silane, and the alkyl group is an organic group that can be polymerized in a second stage. This is usually done by photochemical or thermal curing after the sol-gel reaction [57].

Figure 2.8 provides structural models for various hybrid sol-gel coating types. The first type of hybrid sol-gel system consists of, organic and inorganic groups are not chemically connected, but there are slight dispersion forces like van-der Waals contacts between them. Strong chemical linkages between the organic moiety and the hydrolyzed inorganic phase exist in the second and third types of hybrid materials. Common precursor solutions for obtaining organic and inorganic sol-gel systems, respectively, include organic alkoxy silanes and metal alkoxides. The two types of organically modified sol-gel systems can be distinguished based on the type of organic alkoxy silanes employed to insert organic groups on them;

- Nonfunctional organic alkoxy silanes;
- Organic functional alkoxy silanes [50, 54].

The structures of several of the most popular alkoxy silanes are shown in Figure 2.6. Alkoxy silanes with methyl groups are frequently employed to create hybrid sol-gel coatings with non-functional components [59, 60, 61–62]. organic silanes Epoxy, meth acrylic, acrylic, allyl, alkyd, phenyl, or vinyl functional are often utilized organ functional precursors [63–65]. Further polymerization of organ functional groups including epoxy, vinyl, and meth acrylic will increase cross-linking and improve mechanical characteristics [64, 66]. The barrier quality of coatings is improved by the extra polymerization of these organ functional groups during coating preparation.

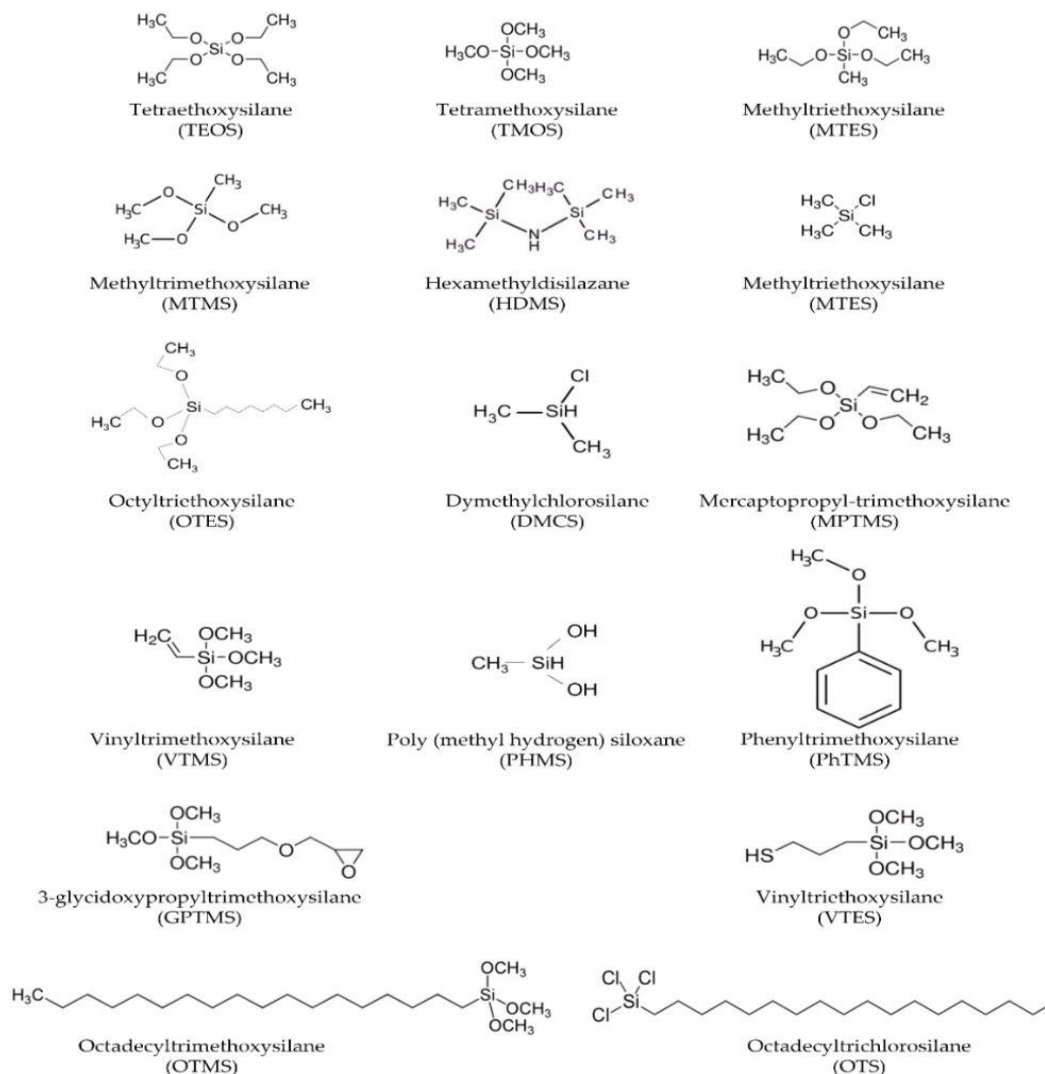


Figure 2.8. Chemical structures of oih silicon alkoxide precursors[50].

2.8. PHASE SEPARATION: PHENOMENA AND KINETICS

In order to generate hybrid materials with a consistent mixture throughout, the degree of phase separation must be carefully managed. It is necessary to have a robust interface between the organic and inorganic domains in order to exert control over this. The rivalry that takes place between phase separation and gelation determines the morphologies of the gels that are formed. When the gelation process is quicker than the phase separation process, it is possible to generate homogeneous hybrids. When phase separation occurs more quickly, the end product is either heterogeneous hybrids or sedimentation. In general, the nature of the precursors, the volume fraction of the organic group, its size, shape, and orientation, the composition of the solvent,

the processing conditions, and the degree of adhesion between the two phases all affect how phase separation behaves in sol-gel systems. Employing a coupling agent, functionalizing oligomer or polymer ends, picking polymers with the proper backbone structures, or using copolymers with functional groups that may interact with the forming inorganic oxide network solved this challenge[67].The ternary system of TEOS, ethanol, and water has been studied to find out how the reactions affect the phase separation that happens when silanol (Si-OH) groups are made through hydrolysis and siloxane (Si-O-Si) bridges are made through condensation [68]. These reactions are responsible for the formation of siloxane (Si-O-Si) bridges. Polymerization is chemically similar to continuous physical cooling in terms of chemical interaction (mutual solubility) and solute mobility.

That is to say, the polymerizing system that ends up producing a sol-gel transition can be compared to a system that is continually cooled and ends up producing a glass transition. Alkoxysilanes typically hydrolyze into polycondensable compounds in an acidic environment, the molecular weight distribution of the polymerizing oligomers is given. Due to the basically irreversible polycondensation reactions that take place between the monomers and oligomers, the molecular weight of the polymerizing species in a solution will rise as the reaction time progresses.

According to the laws of thermodynamics governing solutions, the mutual solubility of the polymerizing species is required to decrease as the average molecular weight of the solutions increases. The primary cause of this is the entropy loss that occurs during the mixing of the components. Polymerization is responsible for the decrease in mutual solubility, which leads to an increase in the free energy of mixing.takes place when the sign of the free energy of mixing of the system changes to become positive. This has been shown to be the case in a number of other systems that comprise polyacrylic acid [69] and formamide [70].

2.9. HYBRID SOL-GEL ADDITIVES PROTECTIVE COATINGS

Sol-gel systems have organic components, but they also have additives like nanoparticles and inhibitors added to them to the corrosion resistance of the coating

system should be increased. This is done in addition to the organic components. Although the addition of organic components encourages the production of thicker films that are free of cracks, this benefit comes at the expense of a reduction in the wear resistance as well as other mechanical properties of the sol-gel films[76]. Inorganic nanoparticles can be dispersed into the coating matrix to give the hybrid sol-gel films more tensile properties. Since inorganic particles smaller than 500 NM may be uniformly disseminated on sol-gel matrix to produce coatings, they are typically utilized [58]. As a result of the increased thickness and decreased permeability of such coating systems, the inclusion of nanoparticles improves the corrosion resistance of metallic substrates [77–78].

There are two methods for adding nanoparticles to the hybrid coating matrix: (1) adding nano powder directly on the sol-gel system [58, 74]; and (2) directly synthesizing oxide nanoparticles while the sol-gel process is underway [85, 77, 80]. Direct production of nanoparticles using the sol-gel technique is preferable to the mechanical nanoparticle introduction. Inhibitors are a different class of beneficial additives that improve coatings' ability to resist corrosion. Inhibitors prevent or reduce corrosion by altering anodic or cathodic corrosion [81].

2.10. APPLICATIONS OF OIH COMPOSITES

Sol–gel-produced organic–inorganic hybrid materials have led to novel industrial uses. Without a shadow of a doubt, these newly developed The fields of optics, electronics, energy, the environment, membranes and separation devices, smart coatings, fuel and solar cells, catalysts, and sensors could all use hybrid materials. [71].

The primary reason for people's fascination with hybrid materials is that these materials have properties that are comparable to those of inorganic glasses or ceramics, but they are also capable of being functionalized and processed in the same manner as organic carbon-based polymers, and they can do so without the utilization of pricey processing technology, such as vacuum methods. Temperatures in the range

of 1000-1400 degrees Celsius are necessary for the transformation of ordinary gels into nonporous glasses, ceramics, and inorganic–inorganic micro composites.

To generate materials that are not porous, heat treatment of organic–inorganic hybrids must be carried out at temperatures no higher than 200 degrees Celsius [72]. Current and potential uses for the sol gel process are detailed in a number of books [72,73]. and articles [74-75]. Coatings, due to their transparency, their high adherence to many substrates, and the fact that they may be applied to a wide variety of surfaces, are one of the most attractive fields of application.

chemical inertness or stability. Coating applications that take place at low temperatures are very significant, especially when the coatings in question are able to give resistance to abrasion and corrosion [75]. The use of thin film coating is essential to the operation of a great number of technologically advanced products, such as solar cells, vision lenses, smart phones, and a variety of other applications: [74].

- Protective transparent coatings.
- Photovoltaic cell application
- impediment systems.
- Dental applications.
- Microelectronics.
- Batteries.
- Additional uses include cable insulation, water-repellent coatings,
- Cosmetics, adhesives, and cosmetic products.

2.11. SILICA DIOXIDE (SiO₂)

On this planet, silica is the oxide that is most abundant. It can be produced in a variety of shapes, including cylindrical pellets [82] and fibers [83]. Silica offers excellent thermal and mechanical stability. It can be found in various polymorphs, each of which has different structural traits as well as chemical and physical features. Each silicon atom in SiO₄ tetrahedral is joined to two silica and four oxygen atoms

to form the compound SiO₂. Fig 2.9 Siloxane groups (Si-O-Si) and sialon groups are two different forms of functional groups that exist on the surface of silica (Si – O – H). Any surface-based process takes place at the sialon groups as its sites of influence, whereas the siloxane sites are thought to be nonreactive [84].

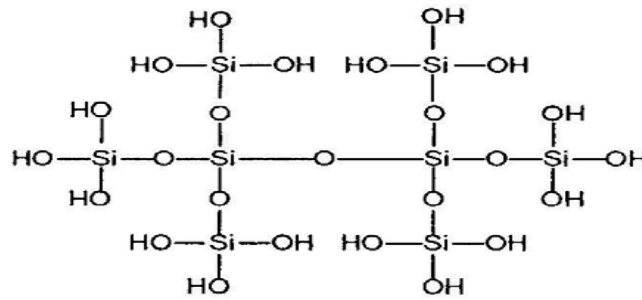


Figure 2.9. Linkages of SiO₂ tetrahedral[84].

2.11.1. Interesting (SiO₂) Hybrid Material

MPTS and TEOS are two alkoxides utilized in the sol-gel method [86]. These compounds aren't miscible with water, thus a solvent (usually methyl or ethyl alcohol) must be added to make a homogenous liquid. Under certain settings, TMOS's quick hydrolysis is beneficial, but the poisonous methanol generated can harm the eyes and lungs. TEOS yields less hazardous ethanol but hydrolyzes slowly. [82]. Hydrolysis and polycondensation can be sped up or slowed down with the use of an appropriate acid or base catalyst. These tasks are generally incomplete and are performed simultaneously, as was already explained. Depending on how much water is around, the rate of hydrolysis may slow down or keep going until the metal is completely broken down.

2.11.2. Sol-gel Synthesis of SiO₂

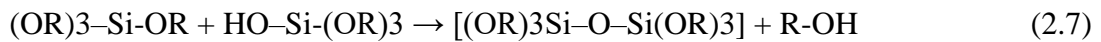
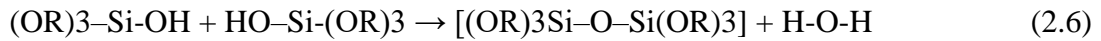
Si(OC₂H₅)₄ or Si(OR)₄ is the chemical formula for TEOS. Alkoxides react well with water, making them good sol-gel precursors. Hydrolysis occurs when the hydroxyl ion binds to silicon.



Depending on the quantity of water and catalyst present, hydrolysis may continue until all OR groups are replaced by OH groups as in the following examples:



Any intermediate ((OR)₂-Si-(OH)₂) or ((OR)₃-Si-(OH)) species would be regarded as the outcome of partial hydrolysis. Additionally, a condensation reaction can result in the formation of a siloxane [Si-O-Si] bond between two partially hydrolyzed molecules:



Thus, siloxane (Si - O - Si) bonds create a 1, 2, or 3-dimensional network during polymerization, along with the generation of (H-O-H) and (R-O-H) species. [86-87].

2.12. APPLICATION METHODS FOR SOL-GEL ON SUBSTRATES

The early applications of sol-gel technology were in the production of coatings and films. The capacity to apply sol-gel coatings to surfaces can be achieved using a variety of processes, including as spraying, electrodeposition, dip coating, and spin coating, among others [88].

These include the two most widely used coating methods, spin coating as well as dip coating, both of which are relatively simple. Due to the usage of extremely basic equipment, the dip coating method was used in this research and offers numerous important advantages over alternative deposition procedures. The sol-gel dipping method is used to make layers that are transparent to light. This is done by submerging the substrate in a liquid and then pulling it out at a certain rate while keeping the temperature and air pressure the same [89].

2.13. DEPOSITION AND CURING OF SOL-GEL COATINGS

Dip coating, spin coating, spray coating, and electrodeposition are the principal techniques for applying sol-gel coatings on metal surfaces [90-91]. The main methods for putting sol-gel coatings on metal surfaces include dip coating, spin coating, spray coating, and electrodeposition [91-92]. The deposited sol-gel layer must next be sintered, which is another crucial step. During the process of drying the sol-gel coating, there will be a significant decrease in volume in addition to an accumulation of internal tension. This is because the coating will lose both its solvents and its water content [95, 94]. In a dried sol-gel coating, it is very common to find cracks and pores. This is because the coating generates internal tension, which causes the cracks and pores. In most cases, the corrosion resistance of a sol-gel coating will lessen as the sintering temperature rises. This is because fractures caused by thermal stresses will make the coating more likely to break [93-98].

Normally, there are two methods for drying sol-gel films that have been formed on metallic substrates. These methods are referred to as high temperature sintering and low temperature sintering [94]. Sintering at high temperatures results in the creation of porosity, which lowers the corrosion resistance of the generated coatings while simultaneously increasing the mechanical properties of the coatings [99].

High-temperature sintered sol-gel coatings are typically utilized as wear-resistant layers or barriers against extremely hot oxidation of metallic substrates [96,100-102]. Due to the wide pores present, these coatings are typically not employed to prevent wet corrosion [96, 97]. Sol-gel films are dried at a temperature of less than 200 °C in low temperature sintering. Solvents and water evaporate during drying at this temperature, further solidifying the gel that has formed. To create a hybrid organically modified sol-gel coating with a crack-free compact film, low temperature curing is typically used [103,104]. Sol-gel coatings that are cured at a low sintering temperature can resist wet corrosion better than coatings that are cured at a high sintering temperature.

2.14. “SMART” COATINGS FOR ACTIVE CORROSION PROTECTION

By forming a barrier or physical layer to keep water and other corrosive species from coming into contact with the metallic substrates, the hybrid sol-gel coating can only provide passive protection. However, unbroken and free of any mechanical flaws sol-gel coatings can only provide acceptable protection. To provide active protection, it is therefore required to incorporate certain active agents. Corrosion inhibitors are included into protective barrier layers in active corrosion prevention systems, which reduces the rate of corrosion when the passive barrier layer begins to deteriorate. The two primary strategies now employed to prevent corrosion are active and passive prevention [106]. By adding inhibitors to the coating system, metallic substrates can be actively protected from corrosion.

The corrosion inhibitors can be added to the pretreatment, priming, or topcoat layers of the coating system. Traditionally, lead, hexavalent (chromates), or trivalent chromium (dichromate)-containing materials are utilized as corrosion-inhibiting additives and can be found in pretreatment layers. But strict environmental laws and regulations have made it necessary to search for an alternative to these dangerous inhibitory chemicals. Therefore, it is imperative that ecologically acceptable corrosion inhibitors be developed for protective coatings. Organic corrosion inhibitors are particularly effective at preventing corrosion while not harming the environment. The correct range of solubility in the corrosive media is necessary for the inhibitors to effectively control corrosion. Because inhibitors have a very low solubility, there aren't enough inhibitive species to diffuse or migrate to the metal surface and protect it.

However, because the active drugs will be leached out, very high solubility of inhibitors may only provide enough protection for a limited time. Additionally, a coating's physical and mechanical qualities may be harmed by a higher concentration of inhibitors in the coating, which could also result in blistering and delamination of the coating [105,106]. To get around this, the inhibitive species can be contained in certain containers, which stops them from directly interacting with the coating matrix.

2.15. FACTORS OVER THE SOL-GEL SYSTEMS

The synthesis circumstances affect the products' structure and qualities, just like they do in all the other chemical technologies. The following are some of the most crucial variables in the production of sol gels:

- **Composition and nature of precursors:** The precursor must be liquid-soluble and system-reactive. The gel's qualities rely on the precursor employed, its concentration, and the sol's reactions. Alkyl radicals are critical for composition, structure, and characteristics of the sol and the resulting film, as is the metal ion in the alkoxides utilized [107]. have studied the following four tetraalkyl silanes: tetrabutylloxysilane (TMOS), tetrapropylloxysilane (TPOS), and tetramethoxysilane (TMOS) (TBOS). By using in-situ chromatographic techniques, they were able to prove that each tetraalkoxysilane had a unique distribution of chains with a variable rate of polymerization in each gel-forming system under the same conditions. Similar studies were conducted by other writers [108]. They created a protective covering using $C_3H_7-Si(OCH_3)_3$, $C_8H_{17}-Si(OCH_3)_3$, $C_{18}H_{37}-Si(OCH_3)_3$, and $(CH_3O)_3Si-C_2H_4-Si(OCH_3)_3$. The endurance and protective capacity of the coatings made from these sols are significantly influenced by the length of the aliphatic chain, according to the authors' research. The characteristics of the films as well as the intermolecular interactions among the related organic chains are influenced by the length of the alkyl chain and the type of functional group. For instance, the literary [109]. Reports on the synthesis of materials made of 3-glycidoxypropyl trimethoxysilane (GPTMS), a crosslinking agent, and metal alkoxide (TEOS), could also be found in the literature. For the purpose of obtaining corrosion-protective coatings, that system has been modified [110,111].
- **Solvent.** Alcohols, water, and catalysts are typically used to depict the liquid medium of reacting systems. The hydrolysis is typically catalyzed in an acidic environment, but there are accounts in the literature of sol being produced with an alkali catalyst[112]. The structure of the gel products is significantly influenced by the management of evaporation intensity. The associated products (xerogel, powder, etc.) will exhibit fractures, disruptions, cracks, and

differences in the density distribution if the evaporation rate is too high. Additionally, the intensity of particle agglomeration and condensation processes is influenced by the rate of evaporation.

- **Influence of pH of the medium.** The rate of hydrolysis is affected by the pH of the sol solution and is also dependent on the kind of precursor, the length of the alkyl chain, and the amount of unreacted monomer residues present in the sol. Even if two acids are added in the same molar amount, they may cause distinct rates of hydrolysis. The differential in the oxidation activity of the respective anions is what caused that event. As is common knowledge, the synthesis of silica sol occurs in alkaline conditions, producing a highly branched cluster (e.i. spherical nanoparticles). In contrast, the synthesis in an acidic environment produces mostly linear or randomly branched polymers [116]. have examined the variations in the rates of silane hydrolysis in acidic (HCl) and alkaline (NH₄OH) environments for methyl-triethoxysilane (CH₃Si(C₂H₅O)₃) and phenyl-triethoxysilane (C₆H₅Si(C₂H₅O)₃). As a result, the hydrolysis rate is dependent on the type of precursor even though the medium employed to hydrolyze it has the same property. The CH₃Si(C₂H₅O)₃ precursor has already hydrolyzed (100%) in an acidic environment after one hour, but the (C₆H₅Si(C₂H₅O)₃) precursor exhibits total hydrolysis after four hours. Compared to hydrolysis catalyzed by HCl, the reaction is slower in an alkaline media. The first precursor, (C₆H₅Si(C₂H₅O)₃), hydrolyzes at the second hour, but the second one takes five hours. The pH of the medium is also impacted by the addition of salts. The dissociation equilibrium of the acid should go closer to the neutral point when a buffer (weak acid and its salt) is used. The salts might be used to modify various organic hydroxyl derivatives. Salts' effects are influenced by their chemical composition, amount, and adding time [113][114].
- **Temperature.** The temperature has a considerable impact on the characteristics of the synthesized sol, just like it does in all other types of synthesis. The rate, mechanism, and interaction of condensation and hydrolysis reactions are all influenced by temperature. It is obvious that it directly affects the kinetics of chemical reactions. The temperature of the synthesis is also

significant since it affects the solvent's evaporation and, in turn, the concentration of the constituents in the sols [115].

- **Surfactants.** The solubility of the precursor in the solvent is affected by the action of the surfactant. At the same time, they cause flocculation, which means that they are likely to have a reduced availability in solution. The formation of a cover on the surface of the particle is the process upon which the activity of the surfactant is based. Therefore, as a result of the existence of these films, there is depicted to be a separation between the particle and the liquid medium. Because of their actions, the surfactants in the system change the surface tension between the various components. Therefore, they have the potential to play the role of a particle stabilizer in the sol, which would significantly slow down the sedimentation process. It is feasible to build homogeneous films using this method, as well as adjust the porosity and flexibility of the films that are realized on the surface.

2.16. DIP COATING TECHNIQUE DEFINITION

The technique known as "dip coating" refers to the process of coating a solid substance with another material by dipping things in suspension. This procedure results in the coating of the solid substance. This method is frequently employed because it is an effective approach to generate thin films that have a high optical quality and are homogeneous. The term "sol" is frequently used to describe the suspension of colloidal particles [117]. The method comprises immersing the substrate in the dip-coating solution in phases and gradually removing it from the solution at a steady rate in order to form a film. The solvent evaporates once the substrate has been removed from the mixture [118].

2.16.1. Dip Coating Process

A clean substrate is dipped in the liquid and withdrawn at a precise pace under controlled temperatures and humidity. Temperature and humidity are two examples of environmental elements that have an impact on coating quality [120]. The thermal treatment stage brings the coating process to a close. Typically, coatings made from

sol-gel are amorphous. Controlled heat treatment is used, if required, to introduce crystallization. Thin films are dried and calcined to remove solvent and organic residue [118,119].

The dip-coating method can work in one of two ways: either by raising the substrate out of the coating solution and drawing it away, or by keeping the sample in place and slowly drawing the liquid away. The method used in this paper is the pullout procedure, which is more economically practical. The five steps of the dip coating process (immersion, start-up, deposition, generating the drainage, evaporation, and the humid layer where the boundary layer forms) [120,121,122] can be separated into discrete stages. The various phases of the dip coating process are depicted in Figure (2.10). Evaporation is a natural part of start-up, deposition, and drainage processes and is dependent on solvents being employed. This causes the moist layer to aggregate and gel. A dense film is left on the substrate once it collapses.

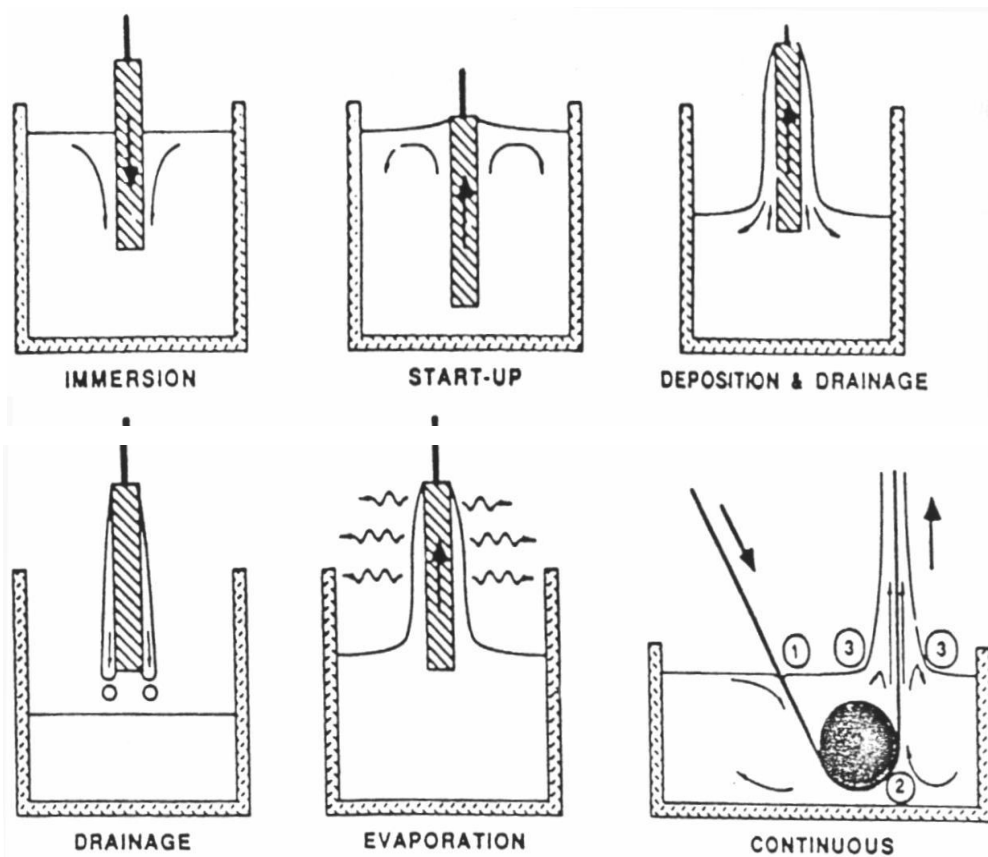


Figure 2.10. Different stages of the dip coating process[121].

Five competing elements in dip coating affect film thickness. The net impact influences streamline position and film thickness. These forces are gravity, surface tension, gravity, boundary layer liquid inertia, and disjoining or conjoining pressure [121]. The first force is the viscous drag that the moving substrate and liquid container exert upward on the liquid. The effectiveness of the resulting thin coatings depends on how well the liquid container is removed. As a consequence of this, the equipment used for dip coating is typically located in a chamber that is free from vibrations in order to reduce the amount of vibrations and prevent any interaction with the apparatus.

2.16.2. Advantages of Dip Coating

Tubes, pipelines, rods, fibers, and other planar and axially symmetric substrates that are difficult to handle by a more conventional coating process can be coated on both sides of large substrates in one step at room temperature using the dipping process, which is straightforward, inexpensive, and effective [123]. Due to the fact that the price of the procedure often increases with the substrate size, this is crucial for commercial applications. It is possible to achieve a high level of film homogeneity and to easily adjust the thickness of the films. The use of a dip coating enables the formation of many layers. with a wide range of optical properties, unlike spin and spray coating [88].

2.17. THE THICKNESS OF THE FILM

The separation of the layers that are travelling upward and the layers that are traveling downward leads to an increase in the thickness of the film. The deposited liquid's outermost layer is the one that is returned to the container, while the deposited liquid's innermost layer rises upward with the substrate. The position of the dividing line between layers that are flowing upward and layers that are moving downward has a direct correlation to the film's thickness [126].

The viscosity of the solution, the rate at which the solvent is evaporated, and the speed at which the substrate is moving all have an effect on the thickness of the

coating. The thickness of the deposited film is primarily determined by the liquid viscosity and the speed of the substrate, which are the two most critical parameters. The Landau-Levich equation, which depicts the link between film thickness and dip speed for Newtonian fluids, can be used to determine it. This equation can be found [here](#)[127].

PART 3

EXPERIMENTAL WORK

3.1. EXPERIMENTAL PROCEDURES

This chapter deals with the details of the experimental procedure used to synthesize an anti-corrosive hybrid coating using the sol-gel process. In addition to describing the main materials used in this study, the characterization techniques that were employed to analyze the protection coating performance, including their principles, are described.

3.2. SUBSTRATE MATERIAL

In this study, low-carbon steel reinforcement of Ukrainian origin was used as substrate material for coating with a 2-inch diameter as shown in Fig.3-1



Figure 3.1. Low Carbon Steel (Mild steel).

Mild steel samples with a circular cross section shape were mechanically cut with dimensions of 2 cm in diameter and 1 cm in thickness fig (3.2). with a hole drilled at one end to enable suspension of the specimens in the sol. The chemical composition (wt.%) of the mild steel used (low carbon steel) (C) 0.043, (Si) 0.022, (Cr) 0.035, Sulphur (S) 0.007, phosphorous (P) 0.007, (Mo) 0.002, (Ni) 0.008, (Al) 0.016, (Cu) 0.011, Manganese (Mn) 0.0238, and balance (Fe).

We polish the mild steel samples using different grades of silicon carbide starting from 320,600,1200 followed by polishing diamond paste to obtain a surface free of impurities. The abraded mild steel substrates were wiped with acetone several times and finally cleaned with ethanol for 5 min and deionized water for degreasing and to make the surface diffuse free, then dried in air.

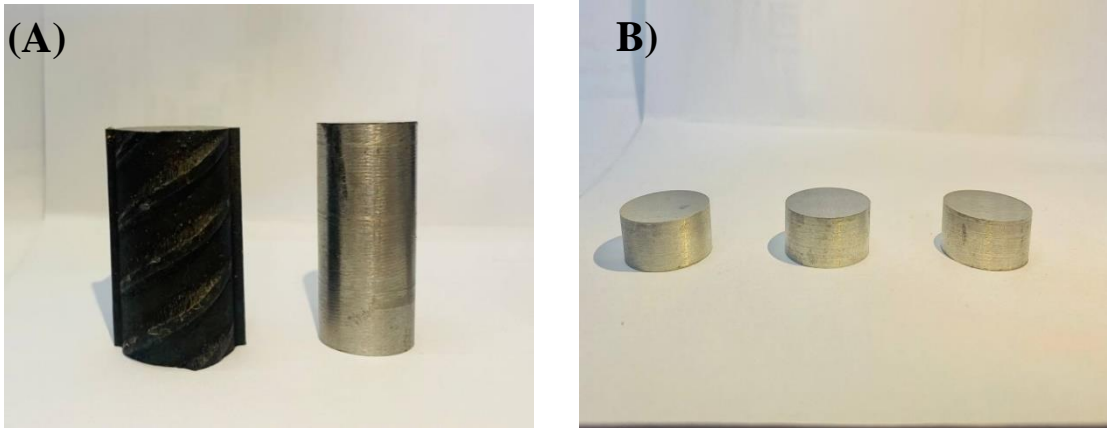


Figure 3.2. (A) Sample before cutting and polishing, (B) Sample before cutting and polishing

3.3. CHEMICAL MATERIALS

the laboratory-grade chemicals used came from China which is the main source of all chemicals used in synthesizing hybrid coatings. Shown (table 3.1) All chemicals used were commercially available."3-Methacryloxy-propyltrimethoxysilane ($\text{CH}_2\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ (MPTS), tetraethyl orthosilicate ($\text{Si}(\text{OCH}_2\text{CH}_3)_4$ (TEOS)" and Phenyltrimethoxysilane $\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$ (PhTMS), Ethanol $\text{CH}_3\text{CH}_2\text{OH}$ (EtOH) (Honeywell Co.) 98.8%, Hydrochloric acid (HCl) (Honeywell Co.) 98.8% were used as received without further purification.

Table 3.1. Chemical materials.

<i>Raw Material</i>	<i>Molecular Formula</i>	<i>Supplier</i>	<i>Purity</i>
TEOS	(Si(OCH ₂ CH ₃) ₄)	China	98.8%
MPTS	(CH ₂ C(CH ₃)COO(CH ₂) ₃ Si(OCH ₃) ₃)	China	98.8%
PhTMS	C ₆ H ₅ Si(OCH ₃) ₃	China	98.8%
Sodium Chloride	NaCl	Honeywell Co.	99.5%
Hydrochloric acid	HCl	Honeywell Co.	99.5%
Ethanol(EtOH)	CH ₃ CH ₂ OH	Honeywell Co.	99%

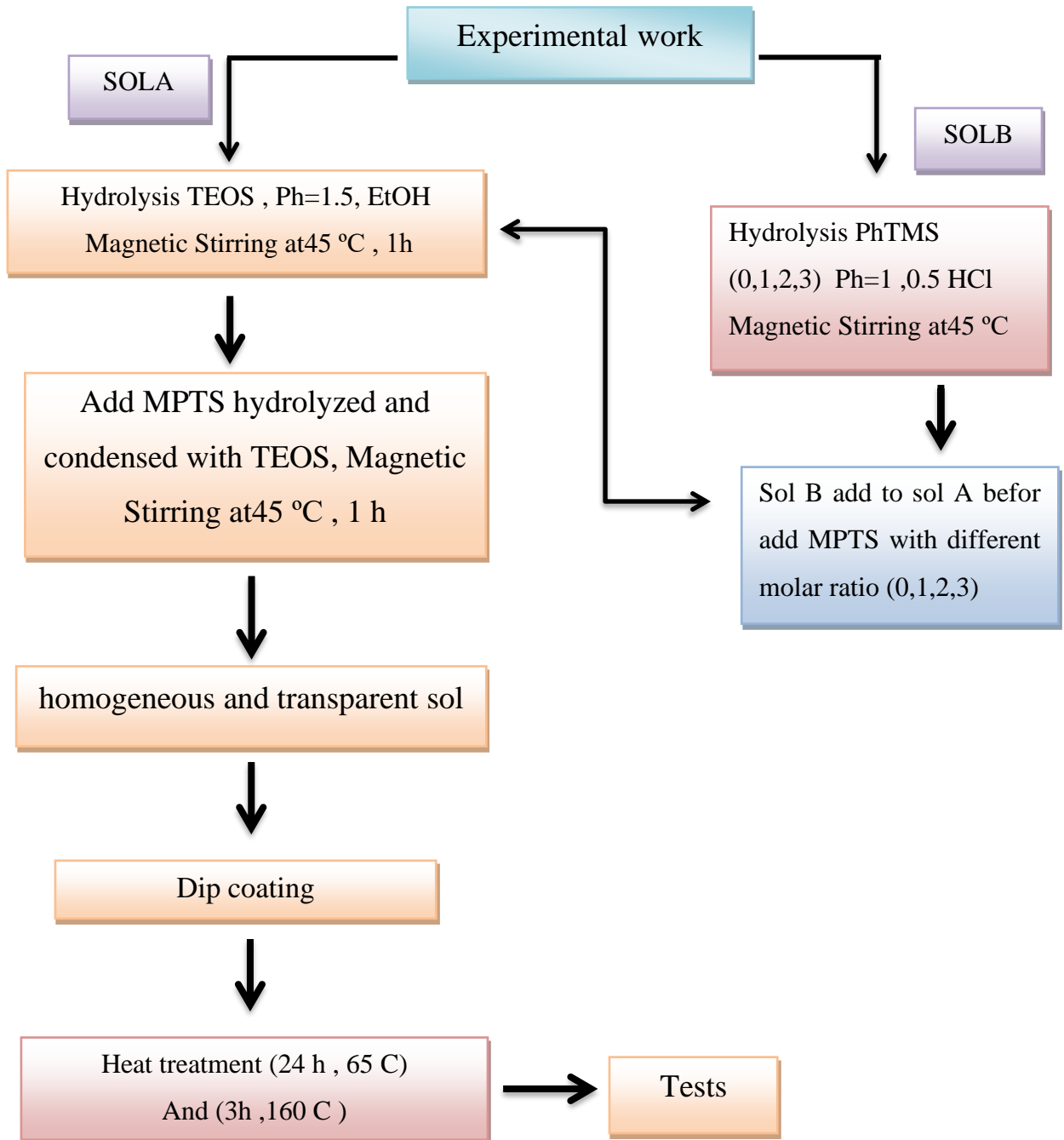
3.4. SOL-GEL ROUTE

The sol-gel route for coating preparation was performed by the mixing of two or three different solutions. For the first solution, **sol (A)**, By adding acidified water (pH = 1) to an ethanol solution, the hydrolysis of TEOS was carried out. Using 0.1 M hydrochloric acid (HCl) to assist the hydrolysis stage as a catalyst. Following a one-hour reaction at 45 degrees Celsius with continual shaking inside a flask, the MPTS was added into the reflux flask as a final step. At this point, the modified MPTS undergoes a partial hydrolysis reaction at 45 °C for 1 hour before condensing with the TEOS to create a homogeneous, transparent sol for dip-coating the films onto the substrate. Thermal curing is then applied to ensure that the hybrid structure has been polymerized.

The second solution sol (B), the sol was prepared by the acid-catalyzed hydrolysis of trimethoxyphenylsilane (PhTMS) (with deionized water in the presence of HCl, PH=1. This mixture was kept under stirring for 1 hour at 45 °C. To identify how the organic phase affects the structural characteristics and corrosion prevention behavior, Sol B will be mixed with Sol A before adding MPTS to it. This sol was prepared using three different molar ratios of PhTMS/TEOS [0, 1, 2, 3] to monitor the changes in the results and the surface of the metal and carry out the necessary tests. After mixing sol A with sol B until homogenization occurred, MPTS was added to the mixture and then thoroughly stirred with a magnetic stirrer for another hour at 45 °C. The hybrids were created using the following molar ratio of all the chemicals employed in order to explore the impact of the organic component on the film structure and electrochemical characteristics. [TEOS: MPTS: PhTMS: EtOH: H₂O]

was [1:1:(0,1,2,3):4:4]. The flow chart below Fig (3-2) summarizes the sol-gel route for preparing the hybrid coating.

3.5. FLOW CHART OF THE PRESENT STUDY



3.6. COATING DEPOSITION AND CURING PROCESS

The dip coating method was used to coat the mild steel substrates with silane solution. Following sol preparation, the mild steel was coated immediately as well as direct and after 12 hours. A constant velocity of 15 cm/min was used to dip and remove the substrate from the hybrid sol three or five times in a row, with an approximately 10-minute air drying period in between fig (3.3 b). The excess solvent was then removed from the coated substrates for 24 hours by heating them to 60 °C, and the condensation process was aided for 3 hours by curing the substrates at 160 °C (Fig 3.3 a). These processes encourage free radical generation, condensation, and solvent evaporation, which results in the polymerization of monomers and densification of the hybrid network.

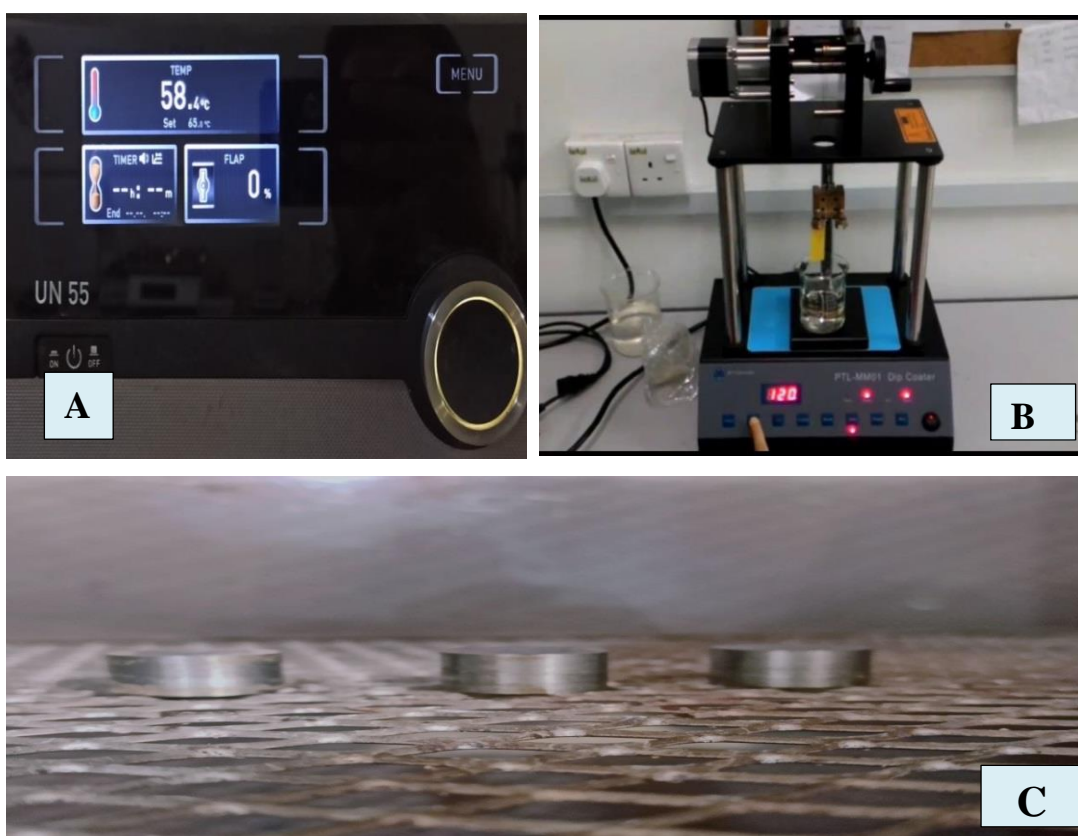


Figure 3.3. (A) drying oven (b) Dip coating device (C) Samples after drying in oven.

3.7. CHARACTERIZATION STUDIES

3.7.1. Polarization Test

Testing for electrochemical corrosion determines and regulates the rate of oxidation/reduction reactions. Most research apply a voltage to the working electrode before measuring the current. An electrochemical process that involves the creation of an electrical connection between areas of active corrosion (anodes) and passive areas is called embedded steel corrosion (cathodes.)

Corrosion processes' effects can be amplified directly by electrochemical tests. This is due to the fact that all electrochemical experiments employ a basic model of the electrode kinetics connected to corrosion processes in order to calculate corrosion rate. Tafel extrapolation method finds corrosion rate using mixed potential theory. This approach employed cathode/anode polarization values. The corrosion current and potential are calculated using this technique. The electrochemical cell and electrodes are what make up the testing device. (Mlab 200 Potentiostat Banch Elektronik GMP, Germany), as shown in Fig (3.4).

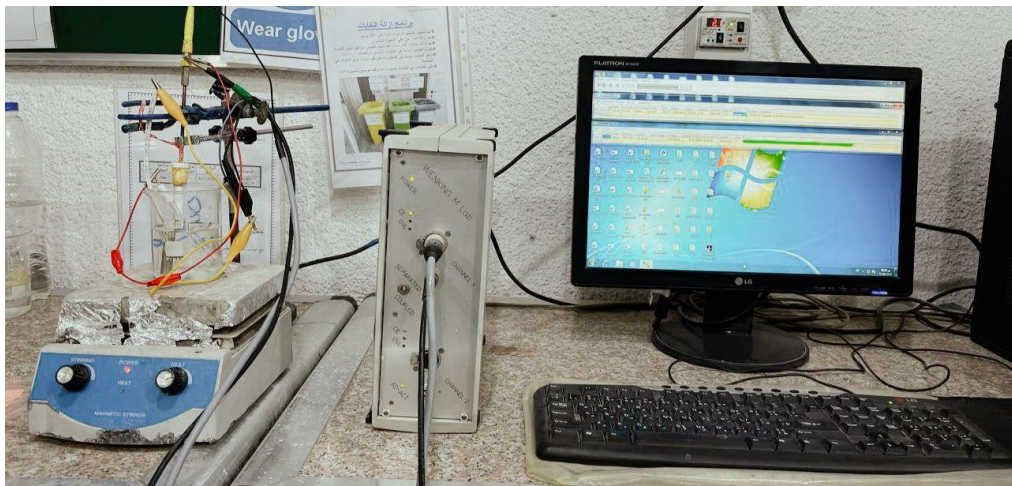


Figure 3.4. Polarization Test device (tafel).

3.7.2. Scanning Electron Microscopy (SEM)

The surface of a specimen was examined in detail using scanning electron microscopy (SEM). Signals are produced across a specimen's surface using a concentrated beam of high-energy electrons. Three-dimensional images were created from the electrical signals that were released as a result of the specimen's interaction with the electron beam. Images show topographical, morphological, chemical, and grain or crystallographic orientation. [128] Electron beam interaction with specimen surface produces secondary electrons, backscattered electrons, and X-rays.

The components of a typical SEM setup are represented in Figure 3.5.

This study we used, VEGA3 SBU/NO.118-0014/, electron microscopy was performed on the samples before and after the corrosion process. for both direct coating and after 12 hours with solution A as well as with solution B. We compared the results obtained from this test with those from the hybrid coatings' cross-sectional study. A very thin layer of gold was spread across the surface of the substrate. according to Figure (3.6).



Figure 3.5. Scanning electron microscopy (SEM).



Figure 3.6. Gold coated substrate surface device.

3.7.3. Contact Angel Test

A liquid drop applied to a surface of a material produces a contact angle, sometimes referred to as a wetting angle. Due to the liquid's surface tension and attraction to the surface, the drop condenses into a dome shape. If the drop is modest and the liquid's surface tension is high, a perfect hemisphere will develop. The intersection of a liquid drop's perimeter, liquid-solid interface, and solid is known as the three-phase contact point. The contact angle at this point is the angle formed by a tangent to the liquid surface and the solid surface [129]. In this test, the most widely used method for measuring contact angles—the lattice drop method—was used. This approach calculates the contact angle by averaging the angles of two fixed locations on a drop that are 180 degrees apart. Using a T-200 basic Theta Optical Tensiometer (Biolin Scientific, Stockholm, Sweden) outfitted with an LED blue light source and a regular 60 fps camera with a customized zoom lens, the contact angle was measured as shown in fig (3.7). For each composition sample, three measurements were made, and the values were then averaged.



Figure 3.7. Contact angel test device.

3.7.4. X-ray Diffraction Analysis

By subjecting a sample surface to x-rays and then detecting the photoelectron's kinetic energy as it left the sample surface, a technique known as photoelectron spectroscopy (XPS) can be used to determine the elements that make up the surface of the sample, its structure, and its chemical bonding condition. In general, an XPS device may learn about components within a few nm of the sample surface. The powder formed after the process of heating and sintering the coating solution and grinding it sieve 200, Bragg angle (2θ) range (10.0- 50.0) degree. Operating at scanning speed of 5.00 deg/min, That done by uses D PHASER as shown in Figure(3.8), This test was done at the University of Babylon –material engineering.



Figure 3.8. X-ray Diffraction Analysis device.

3.7.5. Fourier Transformed Infrared (FTIR) Spectroscopy

A method for obtaining a compound's absorption spectra is Fourier transformed infrared (FTIR) spectroscopy. Electromagnetic radiation in the infrared portion of the spectrum is applied to a sample. Some radiation travels through the sample while some is absorbed by it (is transmitted). The wavelengths that the sample absorbed, which serve as a chemical "fingerprint" of the material. The device shown in the figure (3.9) spectroscopy (FT-IR) spectra were recorded between 400 and 4000 cm^{-1} . The development of hybrid coatings and the bonding characteristics of the sol solutions were examined in this work using FTIR. The spectrum acquired was used to study the precise chemical changes that occurred during the sol synthesis and creation of hybrid coatings. Figure (3.10) illustrates the process of sintering and heating the gel to transform it into a powder.



Figure 3.9. Fourier transformed infrared (FTIR) spectroscopy.

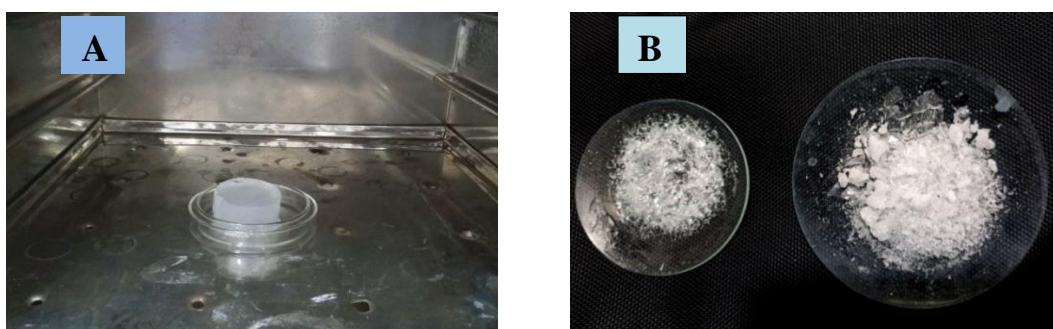


Figure 3.10. A. Gel before heating and sintering process, B. Powder formation after heating and sintering process.

PART 4

RESULTS AND DISCUSSION

4.1. INTRODUCTION

This chapter describes the results obtained in the experimental part of all tests performed and discusses these results Such as :

- SEM test.
- X-ray diffraction test results.
- FTIR
- Contact angel
- Tafel induction test

4.2. CHEMICAL COMPOSITION OF STEEL

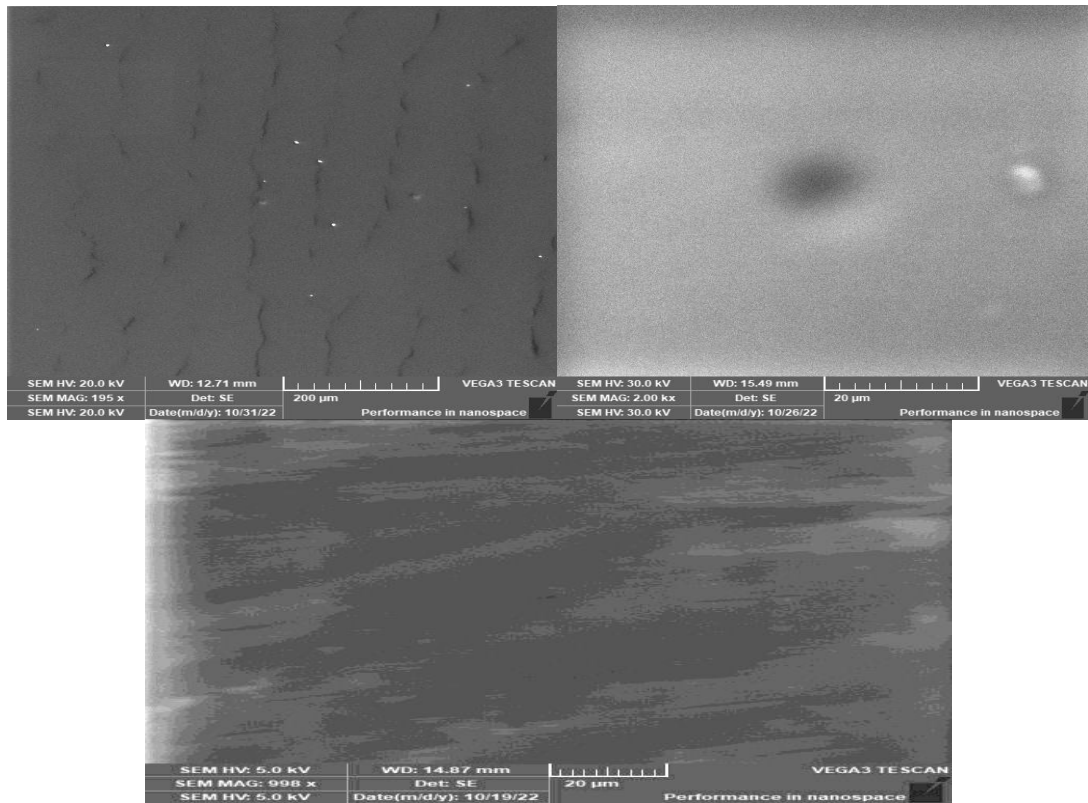
The chemical Composition of mild steel used in the experiment, which comes from samples from the original rod, showed that the percentage of carbon is The amount of each chemical present in the used mild steel (low carbon steel) : (C) 0.043, (Si) 0.022, (Cr) 0.035, Sulphur (S) 0.007, phosphorous (P) 0.007, (Mo) 0.002, (Ni) 0.008, (Al) 0.016, (Cu) 0.011, Manganese (Mn) 0.0238, and balance (Fe).As shown in Table (4-1):

Table 4.1. The Chemical composition of the mild steel rod.

Sam.%	C	Si	Cr	S	P	Mo	Ni	Al	Cu	Mn	Fe
Pers.	0.043	0.022	0.035	0.007	0.007	0.002	0.008	0.016	0.011	0.023	Bal

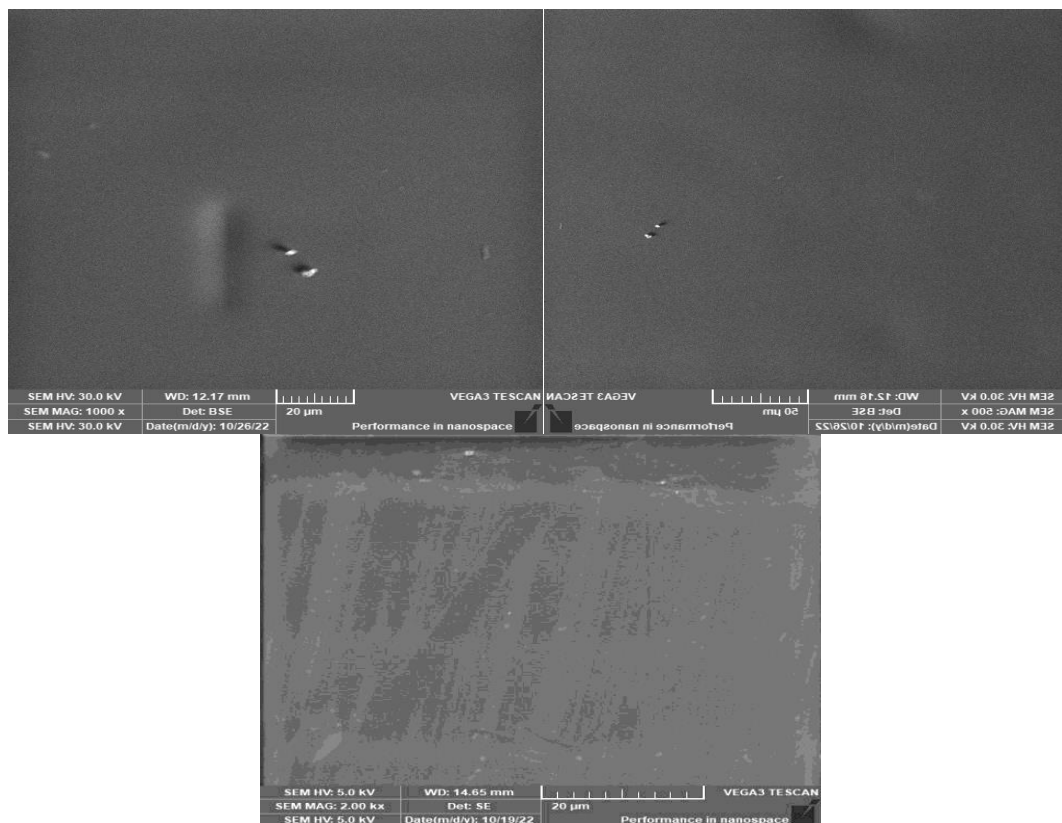
4.3. SEM ANALYSIS

The System (A) [TEOS/ MPTS/(EtOH)/H₂O] for direct coating and after 12 h, were comparative. In one of them, TEOS is the inorganic component that has been diluted. In both situations, coatings were uniform and clear in appearance. Provides scanning electron micrographs of the surface of the system (A). To facilitate direct comparison, we ensured that all photos were captured at the same magnification. However, the direct coating produced a surface that had wavy lines system A and was smooth and crack-free. Shown in (fig 4.2). As well as pores and roughness on the surface in were observed for [PhTMS+TEOS+MPTS] direct coating system B finger (4.1).



(A)

Figure 4.1. Surface SEM images of the system [TEOS+MPTS+H₂O+EtOH], 0h



(A)

Figure 4.2. Surface SEM images of system TEOS+MPTS , 12 h.

The system (B) with [PhTMS /TEOS/ MPTS/(EtOH)/H₂O] for 12 h coating, shows surfaces better than direct coating that contains fine cracks and increasing bubbles. Both the rate of gelation and the structure of the result can be greatly influenced by the use of solvents. They work in the same manner as genuine chemical additives and have the ability to react with alkoxide precursors, hence altering the molecular structure of the latter. Distinct morphologies can be produced as a result of different reactions being favored by the solvent and the metal. These reactions include alkoxy bridging, solvation, and alcohol interchange. The nature of the solvent has a role in the creation of solvates. As a result, variable hydrolysis rates are to be anticipated, which will ultimately result in distinct oxide materials. Because of this, the atomic makeup of alkoxide precursors is determined by the composition of the solvent in which they are dissolved [130, 131].

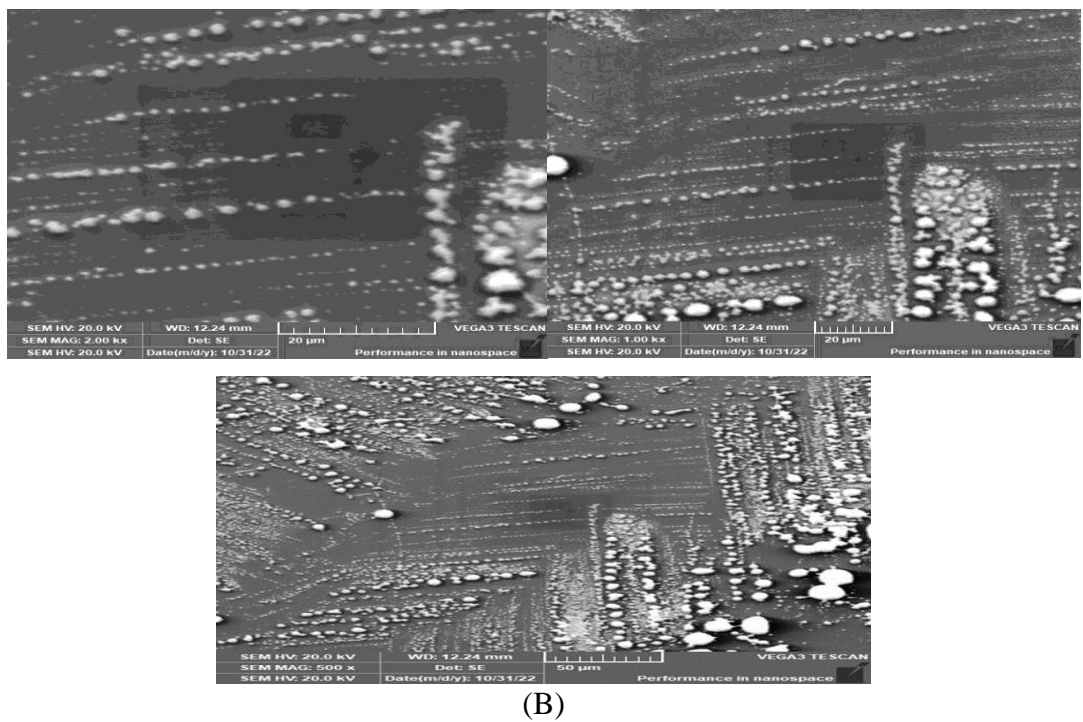


Figure 4.3. Surface SEM images of system TEOS+MPTS +PhTMS , 0 h

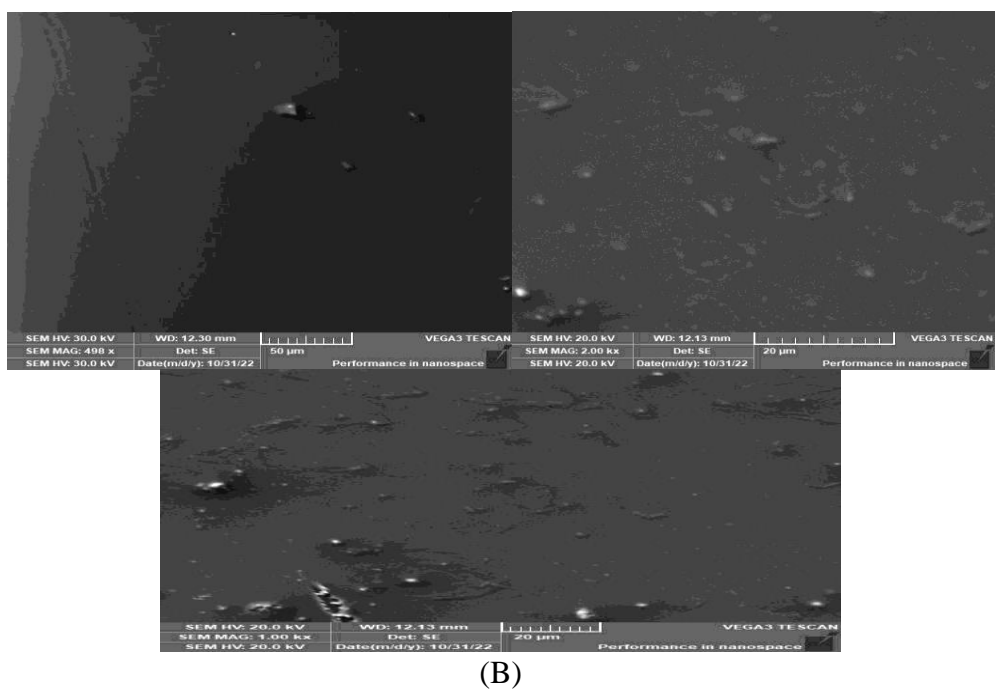


Figure 4.4. Surface SEM images of system TEOS+MPTS +PhTMS , 12 hÇ

4.4. X-RAY DIFFRACTION

The X-ray diffraction analysis was obtained on the TEOS/MPTS (fig 4.5 b) and TEOS/MPTS/ PhTMS fig (4.5 a) powder samples . It appears that powder is x-ray amorphous. This indicates that no crystalline phase was formed during the initial drying of thin films prepared with TEOS . As can be seen, the samples' amorphous nature prevents the observation of any distinctive crystalline peaks. All samples presented in figure 1 have an amorphous or semi-amorphous structure, as evidenced by the large peak in the XRD pattern that is centered about 20 degrees (4.5).This indicates a high consistency between the sample and the coating.

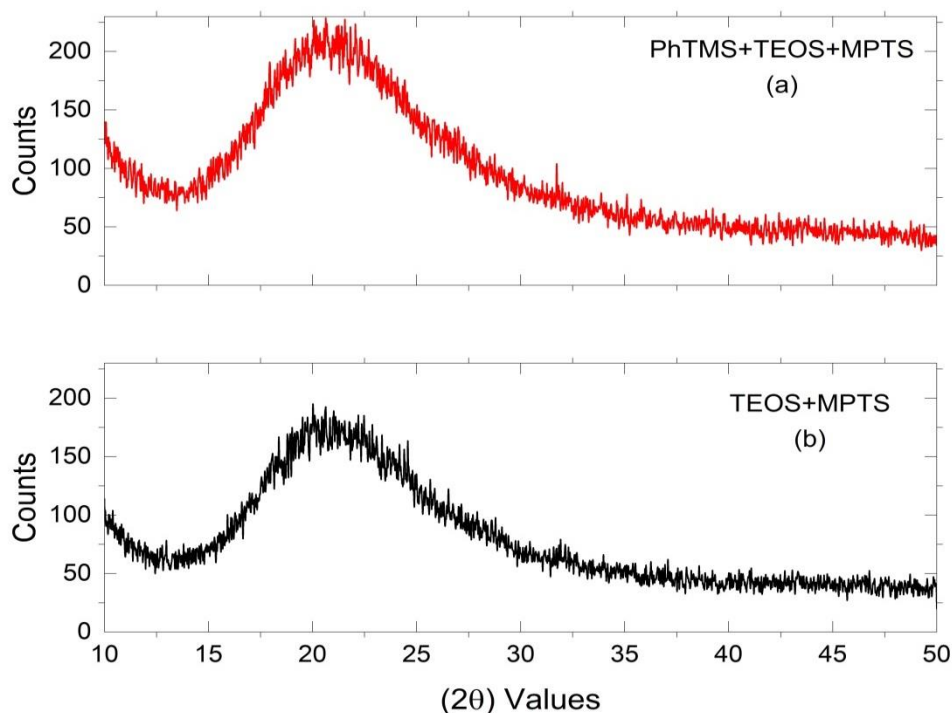


Figure 4.5. The diffraction X-ray pattern of the hybrid composite (system B&A).

4.5. FOURIER TRANSFORM INFRARED SPECTROSCOPY FTIR

Melting gels were analyzed with FTIR spectroscopy. This showed that phenyl-substituted siloxanes, tetra-functional siloxanes, co-solvents, and groups formed during water reactions (hydrolysis) corresponded to various chemical groups (poly condensation). Similar systems were found to have vibration bands with about the

same frequencies, but with different strengths. These shifts in intensity and position are the key to knowing the chemical processes that occur in the solid network and, by extension, the chemical groups that make up the network. Different types of precursors and different rates of hydrolysis lead to different network structures.

Organic-inorganic coatings' FTIR spectra are displayed in Figure 4.6. Looking at Fig. 4.6, The frequency of the Si-O bending mode vibration was noticed between 650 and 850 cm^{-1} for system A [132]. Due to the fact that very few organic molecules exhibit absorption in this region, this has the potential to be a significant diagnostic tool. The C-H bands are responsible for the absorption peak that may be seen between 2900 cm^{-1} to 3000 cm^{-1} (CH_2 and CH_3) [132,135].

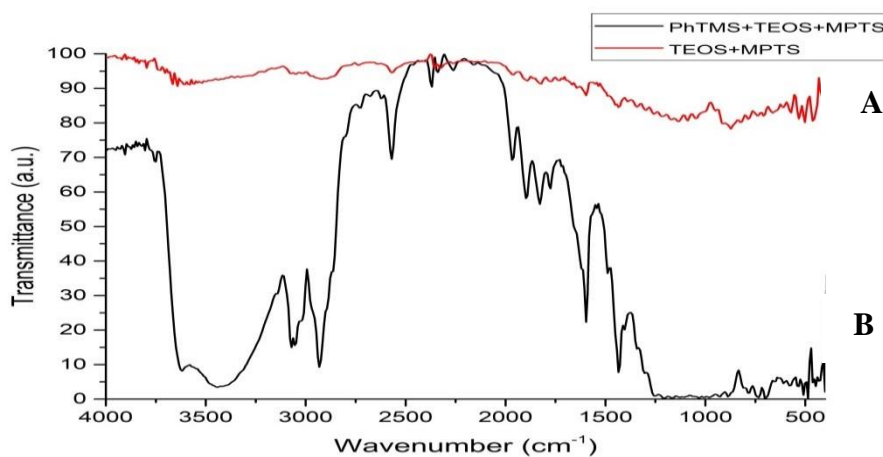


Figure 4.6. FTIR spectra of Sol A and B.

It is believed that the formation of a conspicuous peak at approximate 1049 cm^{-1} is a result of (Si-O-Si) stretching, which can be linked to the cross-linking density of silane coatings. This peak can be found at approximately 1049 cm^{-1} [132]. This signal is consistent from two hydrolysis times, showing the same Si-O-Si chains produced. C=O anhydride absorbs weakly between 1720 cm^{-1} and 1850 cm^{-1} . A large absorption peak at absorbed O-H stretching at 3300-3500 cm^{-1} moisture and unreacted silanol groups, indicates the films are not entirely cured [134].

The presence of phenyl groups that were connected to silica matrix was indicated by the vibration, and this presence was denoted by the presence of the phenyl groups.

The strength of the peak, which can be observed at a wavelength of 1435 cm⁻¹, can be attributed to the phenyl bond in silicon. Peaks in the frequency spectrum of silicon dioxide are observed at around 1000, 800, 500 cm⁻¹, respectively. These peaks are the result of asymmetric and symmetric, and bending modes of the material [133].

In conclusion, the sol-to-gel transformation is driven by the consumption of ethanol and TEOS and the creation of Si-O-Si bonds. This can be deduced from the disappearance of the bands related to ethanol and TEOS and the concurrent formation and intensity of the bands related to siloxane (Si-O-Si).[137,138]

Table 4.2. FTIR bands that match the hybrid silanol coating and the bond between the silanol coating..

Peak position (cm ⁻¹)	Peak assignment	Ref
[620-700]	C-H (Si-CH ₂ - CH ₂ -Si) expansion	[132]
[1000-1200]	Si-O-Si crosslinked Si-O expansion	[135]
[1300-1400]	CH ₂ and CH ₃ scissoring	[132]
[1600-1670]	C=C-H bond	[134]
[1700-1750]	C=O bond	[135]
[2900-3000]	C-H (CH ₂ , CH ₃) symmetric and asymmetric stretching	[134][135]
[3200-3700]	Si-OH axial deformation	[133]

4.6. CONTACT ANGLE

A good cross-linked film has a contact angle of about 90 degrees of order. The bare steel surface demonstrated a water contact angle of 73.7 degree, The TEOS/MPTS hybrid coating for TE3 sample (direct ,5 dip) shows a water contact angle of 89.8° Fig (4.7 a-c). The hybrid film had the largest contact angle value and, as a result, exhibited decreased wettability. This indicates that a rise in the total number of dipping causes a corresponding rise in the contact angle of system A. This effect can be explained by the creation of more siloxane groups in the system when TEOS is present. This results in the formation of a more compact network, which prevents the film from absorbing water and makes it more hydrophobic. When silane films are cross-linked enough, they don't let water through. Therefore, a film that has good cross-linking has a contact angle of approximately 90 degrees. But when this value is put into an aqueous solution, it goes down, showing (Si-O-Si) bond is not

stable[139]. Since the instability of these bonds, hydrolysis can damage the Si-O-Si interactions by generating Si-OH hydrophilic groups that permit water and ions to infiltrate and react with the interface [136].

Because Si-O-Si bonds are vulnerable to hydrolysis reactions, hydrophobic silane films protect metals better. This is Due to the fact that the barrier and adhesion qualities change with time, when exposed to air or water.

For system B, the angle of contact is higher than it was for the uncoated sample, but it doesn't reach the hydrophobic limit (see Fig (4.7 b). The diagrams (4.8 and 4.9) show what happens to the mild steel when the number of coatings and time spent in the water are increased.

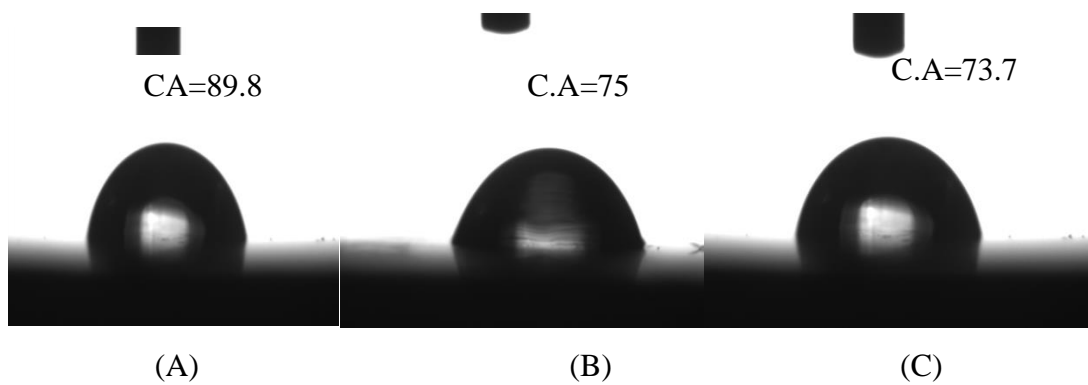


Figure 4.7. (a) TE3 (b) ph5 (c) pure.

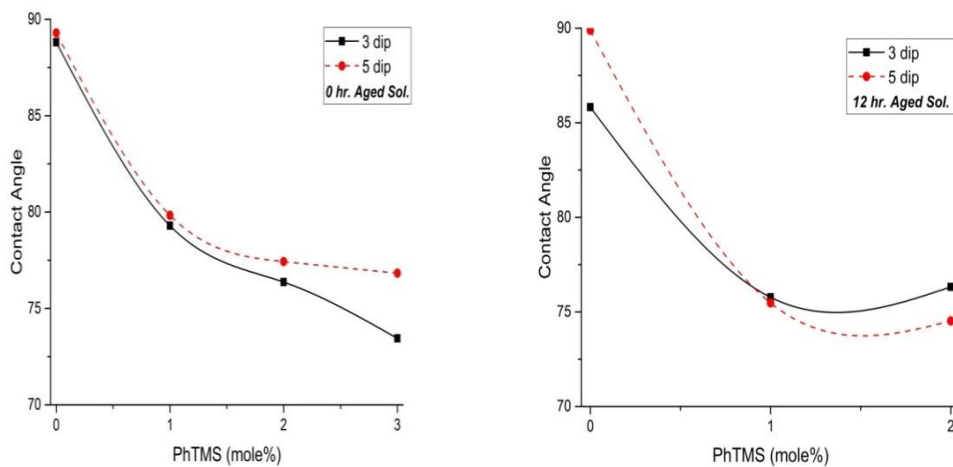


Figure 4.8. A: contact angel for system A, B:contact angel for system B.

Table 4.3. A table showing the contact angle values for both systems

PURE															
73.7															
TEOS+ MPTS				TEOS+ MPTS+PHTMS											
				1M				2M				3M			
Direct		12hr		Direct		12hr		Direct		12hr		Direct		12hr	
3dip	5dip	3dip	5dip	3dip	5dip	3dip	5dip	3dip	5dip	3dip	5dip	3dip	5dip	3dip	5dip
TE1	TE4	TE2	TE3	PH4	PH7	PH5	PH8	PH3	PH9	PH1	PH10	PH2	PH6	No Coting	
88.8	89.2	85.8	89.8	79.2	79.8	75.7	75.4	76.3	77.4	76.3	74.5	76.4	76.8		

4.7. TAFEL EXTRAPOLATION

Theory of mixed potential is considered as the base of the Tafel extrapolation to determine the corrosion rate. In this method, adding the corrosive solution (3.5% NaCl) in corrosion cell ,The corrosion curves in the figures (4.9-4.12) below were recorded for both systems a and b and compared with the uncoated sample. shows that the current density is very high in the absence of coating, implying the rapid corrosion of the metal. This has been attributed to the weak ability of the alloy by default to resist corrosion. The Cl⁻ has great penetrative action in the metal, causing corrosion as well as increasing the conductivity of the solution.

We notice that the current density decreases when coated samples are due to the growth of a protective oxidized layer during the anodic scanning, and this means greater corrosion resistance. Table (4.2) also includes data on the polarization parameters of corrosion current rate density (I_{corr}.) obtained by Tafel lines extrapolation, corrosion potential (E_{corr}.), We note that the best current reading is in the sample TE3, where the current is 8.13 mA/cm² and the voltage is -725.7 in A system. As for the uncoated sample, the current was 92.3 and the voltage is -718.

The usual polarization curves of bare and coated surfaces (0h -3 dip) sol-gel coated mild steel substrates are shown in (Fig4-9), respectively. The polarization curve of the coating made of sol-gel was noticeably distinct from the polarization curve of the mild steel substrate in its natural state. To begin, the open circuit potential, denoted

by E, of sol-gel coatings was found to be a sizeable amount lower than that of the mild steel substrate in its uncoated state. There is a possibility that the successful suppression of the cathodic process is the cause of the reduced open circuit voltage. Second, there was a passivation zone that had a relatively low passivation current density, which suggested that the sol-gel coatings did in fact provide a physical barrier that blocked the electrochemical process. The potentiostat polarization curve of the bare mild steel substrate was notably different from any other curve, and there was no clear passivation zone detected. The early sign of an active electrochemical process was a rapid increase in the current density, which occurred when an electric field was allowed to develop beyond its E value.

On the other hand, being older would cause an additional condensation reaction. It was found that the passing of time has a major impact on the corrosion protection offered by sol gel coatings. For instance, the corrosion resistance of the coatings produced by fresh sols was significantly higher than that of the coatings produced by aged sols. Fig. (4-10) 12hr -3dip depicts the polarization curves of two different coatings, one of which had just been freshly made, and the other of which had been aged for 12 hours at room temperature. The differences in the breakdown potential, passivation region and passivation according to current density, a coating made from old sols is less effective in preventing corrosion than a coating made from fresh sols. The coatings produced from a fresh sol may have had lower porosity and/or a bigger thickness than the coatings produced from an aged sol, which may be one explanation for the observed difference. Because the viscosity of a sol grows with age due to the ongoing condensation reaction, it is highly unlikely that new sol could be used to create thicker coatings. The passage of time brought about an extension of the condensation reaction, which led to the development of silica polymers that were larger and the production of a gel network that was more robust. When the solvent is removed during the drying process, older sols that have the capillary-driven collapse of the gel network will be less likely to occur in the presence of bigger polymers and a stronger gel network. This will result in production of a structure that is more porous. This demonstrates that a coating system consisting of many layers does, in fact, increase the difficulty that active chloride ions have in migrating from the

solution to the metal surface in order to further increase the corrosion resistance of mild steel substrates.

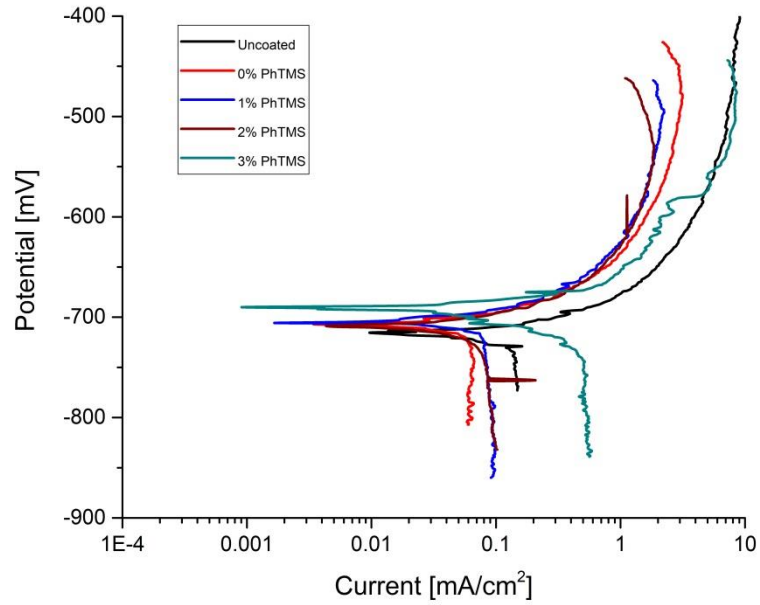


Figure 4.9. Potentiodynamic polarization curves of bare mild steel, coated with polysiloxane hybrids prepared with TEOS/MPTS . 0hr-3dip

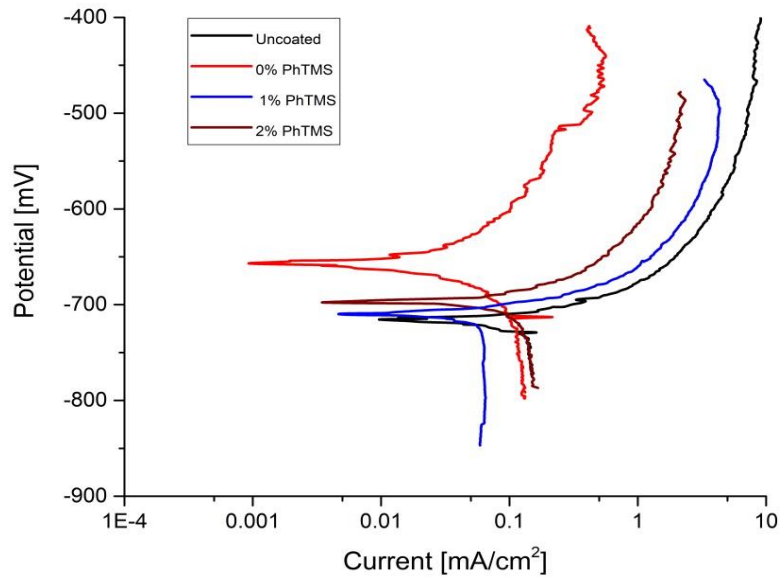


Figure 4.10. 12hr -3dip.

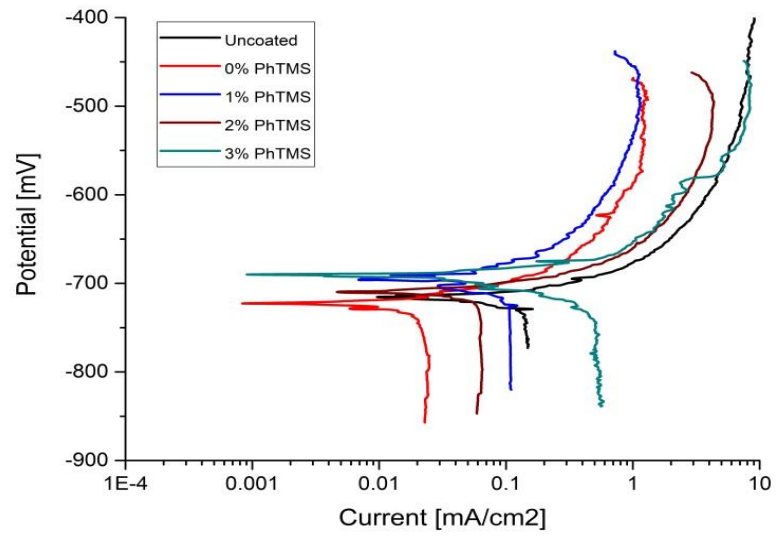


Figure 4.11. 0hr -5 dip.

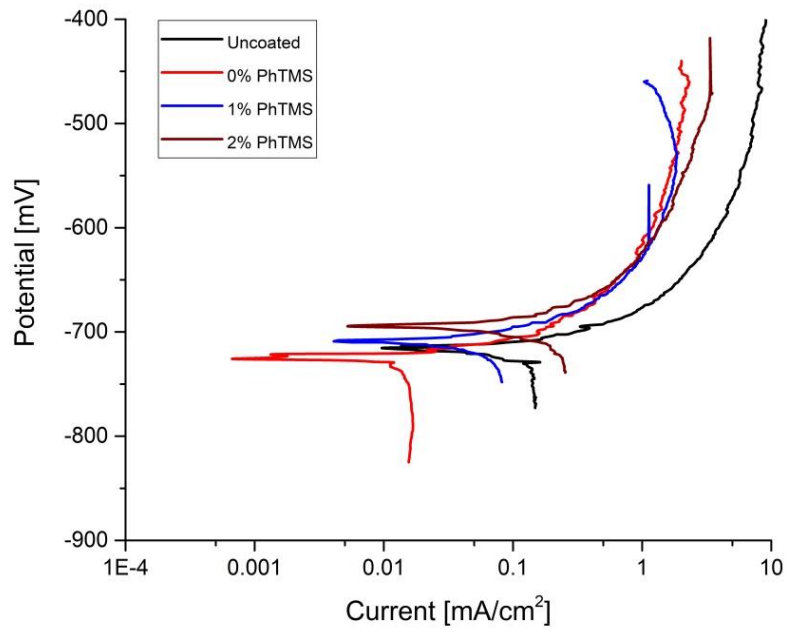


Figure 4.12. 12hr -5 dip.

Table 4.4. Result of Potentiodynamic polarization tafel test.

sample	E_{corr.} (mv)	I_{corr.} (mA/cm²)
PURE	-718.7	92.33
Ph1	-696.9	59.21
ph2	-694.2	39.4
ph3	-709.2	37.8
ph4	-702.6	35.39
Ph5	-709.1	37
Ph6	-710.1	38.4
Ph7	-694.2	32.81
Ph8	-719.7	36.7
Ph9	-709.1	37.2
Ph10	-695.3	87.2
TE1	-707.2	20.19
TE2	-657.4	11.96
TE3	-725.6	8.13
TE4	-723.1	8.32

PART 5

CONCLUSIONS & RECOMMENDATIONS

5.1. CONCLUSIONS

Based on the results of this work, the following points can be concluded:

- For all types of pre-treatments, SEM pictures revealed coatings free of cracks.
- According to the findings of the DC polarization tests, covering a metal substrate with a silane solution effectively inhibited corrosion on the substrate.
- Hybrid silane-based films demonstrated strong corrosion resistance and can be applied as a pre-treatment to protect coated mild steels against corrosion.
- According to the electrochemical tests, TEOS and MPTS by themselves increase the substrate corrosion resistance.
- It was also discovered that PHTMS plays a major part in the protective qualities of the coatings. This combination did, however, have a low thickness and long-lasting anticorrosion resistance.
- For this formulation, the numerous dipping operations did not result in an increase in coating thickness, most likely because the Van der Waals forces are weak and do not adequately fix the subsequent coating layers.

5.2. RECOMMENDATIONS

Sol-gel-produced organic-inorganic hybrid (OIH) coatings had good adhesion and corrosion protection with many metal substrates. Our melting gel materials successfully protected stainless steel from corrosion, but they need to be tested on other metals to prove their efficacy in preventing corrosive medium contact with the metallic substrate and ion migration through the coatings. Sol-gel OIHs are a new

generation of multifunctional materials with a wide range of useful properties and application potential that need to be studied.

- We recommend using different coating methods such as spin coating for better coating distribution.
- We recommend using other alkoxy silanes and studying their effects, such as VTMS or GPTMS, and others.
- We recommend painting after a period longer than 12 hours, as coating after 12 hours is better than direct coating according to the SEM images.
- We recommend using a substrate of different metals for the same coating solution being used.
- To investigate the possibility of making a melting gel using substituents other than phenyl, such as methyl or ethyl, or a mixture of those substituents with tetra-alkoxide, we will use these other substituents.

REFERENCES

- [1] Zandi Zand, R., Verbeken, K., & Adriaens, M. "Influence of the cerium concentration on the corrosion performance of Ce-doped silica hybrid coatings on hot dip galvanized steel substrates". *International Journal of Electrochemical Science*, 8(1), (2013). 548-563.
- [2] Ruhi, G., Modi, O. P., Sinha, A. S. K., & Singh, I. B. (2008). "Effect of sintering temperatures on corrosion and wear properties of sol-gel alumina coatings on surface pre-treated mild steel". *Corrosion science*, 50(3), 639-649.
- [3] Kirtay, S. (2014). "Preparation of hybrid silica sol-gel coatings on mild steel surfaces and evaluation of their corrosion resistance". *Progress in Organic Coatings*, 77(11), 1861-1866.
- [4] Jianguo, L., Gaoping, G., & Chuanwei, Y. (2006). "Enhancement of the erosion-corrosion resistance of Dacromet with hybrid SiO₂ sol-gel". *Surface and Coatings Technology*, 200(16-17), 4967-4975.
- [5] Suleiman, R., Khaled, M., Wang, H., Smith, T. J., Gittens, J., Akid, R., ... & Khalil, A. (2014). "Comparison of selected inhibitor doped sol-gel coating systems for protection of mild steel". *Corrosion Engineering, Science and Technology*, 49(3), 189-196.
- [6] Pagliaro, M., Ciriminna, R., Wong Chi Man, M., & Campestrini, S. (2006). "Better chemistry through ceramics: the physical bases of the outstanding chemistry of ORMOSIL". *The Journal of Physical Chemistry B*, 110(5), 1976-1988.
- [7] Pepe, A., Galliano, P., Ceré, S., Aparicio, M., & Durán, A. (2005). "Hybrid silica sol-gel coatings on Austempered Ductile Iron (ADI)". *Materials Letters*, 59(17), 2219-2222.
- [8] Fallet, M., Mahdjoub, H., Gautier, B., & Bauer, J. P. (2001). "Electrochemical behaviour of ceramic sol-gel coatings on mild steel". *Journal of non-crystalline solids*, 293, 527-533.
- [9] Izumi, K., Murakami, M., Deguchi, T., Morita, A., Tohge, N., & Minami, T. (1989). "Zirconia coating on stainless steel sheets from organozirconium compounds". *Journal of the American Ceramic Society*, 72(8), 1465-1468.
- [10] Kirtay, S. (2014). "Preparation of hybrid silica sol-gel coatings on mild steel surfaces and evaluation of their corrosion resistance". *Progress in Organic Coatings*, 77(11), 1861-1866.

- [11] Seok, S. I., Kim, J. H., Choi, K. H., & Hwang, Y. Y. (2006). "Preparation of corrosion protective coatings on galvanized iron from aqueous inorganic–organic hybrid sols by sol–gel method". *Surface and Coatings Technology*, 200(11), 3468-3472.
- [12] Garcia-Heras, M., Jimenez-Morales, A., Casal, B., Galvan, J. C., Radzki, S., & Villegas, M. A. (2004). "Preparation and electrochemical study of cerium–silica sol–gel thin films". *Journal of Alloys and Compounds*, 380(1-2), 219-224.
- [13] Kirtay, S. (2014). "Preparation of hybrid silica sol–gel coatings on mild steel surfaces and evaluation of their corrosion resistance". *Progress in Organic Coatings*, 77(11), 1861-1866.
- [14] Koh, Y. H., Kwon, O. S., Hong, S. H., Kim, H. E., & Lee, S. K. (2001). "Improvement in oxidation resistance of carbon by formation of a protective SiO₂ layer on the surface". *Journal of the European Ceramic Society*, 21(13), 2407-2412.
- [15] Qian, M., Soutar, A. M., Tan, X. H., Zeng, X. T., & Wijesinghe, S. L. (2009). "Two-part epoxy-siloxane hybrid corrosion protection coatings for carbon steel". *Thin Solid Films*, 517(17), 5237-5242.
- [16.] Brinker, C. J., & Scherer, G. W. (2013). "Sol-gel science: the physics and chemistry of sol-gel processing". *Academic press*.
- [17]. Pierre, A. C., & Pierre, A. C. (2020). "Hybrid Organic–Inorganic and Composite Materials". *Introduction to Sol-Gel Processing*, 421-455.
- [18]. Woodman, R. H. "Electrometric acidity determinations and acidity-property correlations in silica gels prepared from tetraethylorthosilicate-ethanol-water solutions". *Rutgers The State University of New Jersey-New Brunswick*. 653-662 (1996).
- [19]. Kane, R. D., Maldonado, J. G., & Ashbaugh, W. G. (2000). "Cracking down on corrosion". *Chemical Engineering*, 107(3), 74-77.
- [20]. Sørensen, P. A., Kiil, S., Dam-Johansen, K., & Weinell, C. E. (2009). Anticorrosive coatings: a review. *Journal of coatings technology and research*, 6, 135-176.
- [21]. Hafiz, M. H., Hamdan, W. K., & Kaskah, S. E. (2012). "Optimum Effect of Factors Influencing on Sacrificial Cathodic Protection for Steel Wall". *Engineering and Technology Journal*, 30(18).
- [22]. Craig, B. D., Lane, R. A., & Rose, D. H. "Corrosion prevention and control: A program management guide for selecting materials". *Advanced Materials, Manufacturing, and Testing Information Analysis Center (AMMTIAC)*. (2006).

- [23] Durán, A., Castro, Y., Conde, A., & de Damborenea, J. J. (2004). "Sol-gel protective coatings for metals". *Handbook of sol-gel science and technology. 3. Applications of sol-gel technology*, 1, 399.
- [24] Moosbrugger, C., Sanders, B. R., Anton, G. J., Hrivnak, N., Kinson, J., Polakowski, C., & Scott Jr, W. W. (2003). *ASM handbook* (Vol. 13). S. D. Cramer, & B. S. Covino Jr (Eds.). *Materials Park, Ohio: ASM international*.
- [25] Liu, Z. L., Wang, H. B., Lu, Q. H., Du, G. H., Peng, L., Du, Y. Q., ... & Yao, K. L. (2004). Synthesis and characterization of ultrafine well-dispersed magnetic nanoparticles. *Journal of Magnetism and Magnetic Materials*, 283(2-3), 258-262.
- [26] Craig, B. D., Lane, R. A., & Rose, D. H. (2006). "Corrosion prevention and control: A program management guide for selecting materials". *Advanced Materials, Manufacturing, and Testing Information Analysis Center (AMMTIAC)*.
- [27] Tang, F., Uchikoshi, T., Suzuki, T. S., & Sakka, Y. (2004). "Alignment of TiO₂ particles by electrophoretic deposition in a high magnetic field". *Materials research bulletin*, 39(14-15), 2155-2161.
- [28] Cao, G. (2004). "Nanostructures & nanomaterials: synthesis, properties & applications". *Imperial college press*.
- [29] Kaya, C., Kaya, F., Su, B., Thomas, B., & Boccaccini, A. R. (2005). "Structural and functional thick ceramic coatings by electrophoretic deposition". *Surface and Coatings Technology*, 191(2-3), 303-310.
- [30] Lind, C., Gates, S. D., Pedoussaut, N. M., & Baiz, T. I. (2010). "Novel materials through non-hydrolytic sol-gel processing": Negative thermal expansion oxides and beyond. *Materials*, 3(4), 2567-2587.
- [31] HEGAB, H.; PALMER, J.; NAPPER, S." Development of a nanosystems engineering degree". In: *ASME International Mechanical Engineering Congress and Exposition*. 2005. p. 11-16..
- [32] Chauhan, D. S., Quraishi, M. A., Ansari, K. R., & Saleh, T. A. (2020). "Graphene and graphene oxide as new class of materials for corrosion control and protection: Present status and future scenario". *Progress in Organic Coatings*, 147, 105741..
- [33] Lopez-Ortega, A., Bayón, R., Arana, J. L., Arredondo, A., & Igartua, A. (2018). "Influence of temperature on the corrosion and tribocorrosion behaviour of High-Strength Low-Alloy steels used in offshore applications". *Tribology International*, 121, 341-352..
- [34] Rana, M. Z., Mehmood, M., Ahmad, J., Aslam, M., Hasanain, S. K., & Hameed, S. (2011). "Synthesis of nickel nanoparticles in silica by alcogel electrolysis". *Journal of Nanoparticle Research*, 13(1), 375-384.

- [35] Rana, M. Z., Mehmood, M., Ahmad, J., Aslam, M., Hasanain, S. K., & Hameed, S. (2011). "Synthesis of nickel nanoparticles in silica by alcogel electrolysis". *Journal of Nanoparticle Research*, 13(1), 375-384.
- [36] Nakata, K., Liu, B., Ishikawa, Y., Sakai, M., Saito, H., Ochiai, T., & Fujishima, A. (2011). "Fabrication and photocatalytic properties of TiO₂ nanotube arrays modified with phosphate". *Chemistry Letters*, 40(10), 1107-1109.
- [37] Yao, L., Haas, T. W., Guiseppi-Elie, A., Bowlin, G. L., Simpson, D. G., & Wnek, G. E. (2003). "Electrospinning and stabilization of fully hydrolyzed poly (vinyl alcohol) fibers". *Chemistry of Materials*, 15(9), 1860-1864.
- [38] Burda, C., Lou, Y., Chen, X., Samia, A. C., Stout, J., & Gole, J. L. (2003). "Enhanced nitrogen doping in TiO₂ nanoparticles". *Nano letters*, 3(8), 1049-1051.
- [39] Brayner, R., Dahoumane, S. A., Yéprémian, C., Djediat, C., Meyer, M., Couté, A., & Fiévet, F. (2010). "ZnO nanoparticles: synthesis, characterization, and ecotoxicological studies". *Langmuir*, 26(9), 6522-6528.
- [40] Ciriminna, R., Fidalgo, A., Pandarus, V., Beland, F., Ilharco, L. M., & Pagliaro, M. (2013). "The sol-gel route to advanced silica-based materials and recent applications". *Chemical reviews*, 113(8), 6592-6620.
- [41] Mátková, V., Holubová, B., Krabicová, I., Kulhánková, J., & Řezanka, M. (2021). "Hybrid organosilane fibrous materials and their contribution to modern science". *Polymer*, 228, 123862.
- [42] Exarhos, G. J., & Zhou, X. D. (2007). "Discovery-based design of transparent conducting oxide films". *Thin solid films*, 515(18), 7025-7052.
- [43] Wang, D., & Bierwagen, G. P. (2009). "Sol-gel coatings on metals for corrosion protection". *Progress in organic coatings*, 64(4), 327-338.
- [44] Niznansky, D., & Rehspringer, J. L. (1995). "Infrared study of SiO₂ sol to gel evolution and gel aging". *Journal of non-crystalline solids*, 180(2-3), 191-196.
- [45] D. Niznansky and J. L. Rehspringer, J. "Sol-Gel Sci". *Technol.*, 180 (1995) 191.
- [46] Rampaul, A., Parkin, I. P., O'Neill, S. A., DeSouza, J., Mills, A., & Elliott, N. (2003). "Titania and tungsten doped titania thin films on glass; active photocatalysts". *Polyhedron*, 22(1), 35-44.
- [47] Brinker, C. J., & Scherer, G. W. (2013). "Sol-gel science: the physics and chemistry of sol-gel processing". **Academic press**.
- [48] Klein, L. C. (Ed.). (2013). "Sol-gel optics: processing and applications (Vol. 259)". **Springer Science & Business Media**.

- [49] Khobaib, M., Reynolds, L. B., & Donley, M. S. (2001). "A comparative evaluation of corrosion protection of sol-gel based coatings systems". *Surface and Coatings technology*, 140(1), 16-23.
- [50] Zheludkevich, M. L., Salvado, I. M., & Ferreira, M. G. S. (2005). "Sol-gel coatings for corrosion protection of metals". *Journal of Materials Chemistry*, 15(48), 5099-5111.
- [51] Galliano, P., De Damborenea, J. J., Pascual, M. J., & Durán, A. (1998). "Sol-gel coatings on 316L steel for clinical applications". *Journal of sol-gel science and technology*, 13(1), 723-727.
- [52] Vasconcelos, D. C. L., Carvalho, J. A. N., Mantel, M., & Vasconcelos, W. L. (2000). "Corrosion resistance of stainless steel coated with sol-gel silica". *Journal of non-crystalline solids*, 273(1-3), 135-139.
- [53] Mohammadloo, H. E., Sarabi, A. A., Alvani, A. S., Sameie, H., & Salimi, R. (2012). "Anti-corrosion and morphological analysis of a conversion coating based on nanoceramic hexafluorozirconic acid on a steel substrate". *J. Color Sci. Technol*, 6, 9-18.
- [54] Zheng, H., Du, Y., Damron, M., Wright, J., & Tang, M. (1998). "An alternative to anodization: Sol-gel solutions for metal finishing". *Metal finishing*, 96(12), 35-38.
- [55] Thim, G. P., Oliveira, M. A., Oliveira, E. D., & Melo, F. C. (2000). "Sol-gel silica film preparation from aqueous solutions for corrosion protection". *Journal of non-crystalline solids*, 273(1-3), 124-128.
- [56] Mayrand, M., Quinson, J. F., Roche, A., Roisne, V., & Guyon, H. (1998). "Heteropolysiloxane coatings on electrogalvanized steel: Elaboration and characterization". *Journal of sol-gel science and technology*, 12(1), 49-57..
- [57] Wang, D., & Bierwagen, G. P. (2009). "Sol-gel coatings on metals for corrosion protection". *Progress in organic coatings*, 64(4), 327-338.
- [58] Gallardo, J., Durán, A., García, I., Celis, J. P., Arenas, M. A., & Conde, A. (2003). "Effect of sintering temperature on the corrosion and wear behavior of protective SiO₂-based sol-gel coatings". *Journal of sol-gel science and technology*, 27(2), 175-183.
- [59] Niedziolka, J., Palys, B., Nowakowski, R., & Opallo, M. (2005). "Characterisation of gold electrodes modified with methyltrimethoxysilane and (3-mercaptopropyl) trimethoxysilane sol-gel processed films". *Journal of Electroanalytical Chemistry*, 578(2), 239-245.
- [60] Amato, L. E., López, D. A., Galliano, P. G., & Ceré, S. M. (2005). "Electrochemical characterization of sol-gel hybrid coatings in cobalt-based alloys for orthopaedic implants". *Materials Letters*, 59(16), 2026-2031.

- [61] Rubio, F., Rubio, J., & Oteo, J. L. (2000). "Effect of TiO₂ on the pore structure of SiO₂-PDMS ormosils". *Journal of sol-gel science and technology*, 18(2), 105-113.
- [62] Gallardo, J., Galliano, P., & Duran, A. (2001). "Bioactive and protective sol-gel coatings on metals for orthopaedic prostheses". *Journal of sol-gel science and technology*, 21(1), 65-74.
- [63] Voevodin, N., Jeffcoate, C., Simon, L., Khobaib, M., & Donley, M. (2001). "Characterization of pitting corrosion in bare and sol-gel coated aluminum 2024-T3 alloy". *Surface and Coatings Technology*, 140(1), 29-34.
- [64] Smarsly, B., Garnweitner, G., Assink, R., & Brinker, C. J. (2003). "Preparation and characterization of mesostructured polymer-functionalized sol-gel-derived thin films". *Progress in organic coatings*, 47(3-4), 393-400.
- [65] Liu, Y., Sun, D., You, H., & Chung, J. S. (2005). "Corrosion resistance properties of organic-inorganic hybrid coatings on 2024 aluminum alloy". *Applied Surface Science*, 246(1-3), 82-89.
- [66] Haas, K. H. (2000). "Hybrid inorganic-organic polymers based on organically modified Si-Alkoxides". *Advanced Engineering Materials*, 2(9), 571-582.
- [67] Martin, J. W. (2006). *Concise encyclopedia of the structure of materials*. Elsevier.
- [68] Wang, S., Wang, D. K., Smart, S., & Diniz da Costa, J. C. (2015). "Ternary phase-separation investigation of sol-gel derived silica from ethyl silicate 40". *Scientific reports*, 5(1), 1-11.
- [69] Nakanishi, K. (1997). "Pore structure control of silica gels based on phase separation". *Journal of Porous Materials*, 4(2), 67-112.
- [70] Kaji, H., Nakanishi, K., & Soga, N. (1995). "Formation of porous gel morphology by phase separation in gelling alkoxy-derived silica. Affinity between silica polymers and solvent". *Journal of non-crystalline solids*, 181(1-2), 16-26.
- [71] Mackenzie, J. D. (1988). "Applications of the sol-gel process". *Journal of Non-Crystalline Solids*, 100(1-3), 162-168.
- [72] Atanacio, A. J., Latella, B. A., Barbé, C. J., & Swain, M. V. (2005). "Mechanical properties and adhesion characteristics of hybrid sol-gel thin films". *Surface and Coatings Technology*, 192(2-3), 354-364.
- [73] Zheludkevich, M. L., Serra, R., Montemor, M. F., Salvado, I. M., & Ferreira, M. G. S. (2006). "Corrosion protective properties of nanostructured sol-gel hybrid coatings to AA2024-T3". *Surface and Coatings Technology*, 200(9), 3084-3094.

- [74] Malzbender, J., & de With, G. (2002). "Modification of the Mechanical Properties of a Sol-Gel Coating Using Silica Filler Nanoparticles". *Advanced Engineering Materials*, 4(5), 296-300.
- [75] Castro, Y., Ferrari, B., Moreno, R., & Duran, A. (2003). "Silica sol-gel coatings on metals produced by EPD". *Journal of sol-gel science and technology*, 26(1), 735-739.
- [76] Schmidt, H. K. (1997). "Organically modified silicates and ceramics as two-phasic systems: synthesis and processing". *Journal of Sol-Gel Science and Technology*, 8(1), 557-565.
- [77] Brooman, E. W. (2002). "Modifying organic coatings to provide corrosion resistance: Part II—Inorganic additives and inhibitors". *Metal Finishing*, 100(5), 42-53.
- [78] Brinker, C. J., & Scherer, G. W. (2013). *Sol-gel science: the physics and chemistry of sol-gel processing*. Academic press.
- [79] Yamazaki, S., Matsunaga, S., & Hori, K. (2001). "Photocatalytic degradation of trichloroethylene in water using TiO₂ pellets". *Water Research*, 35(4), 1022-1028.
- [80] Unger, K. K. (1979). Porous Silica (Journal of Chromatography Library, Vol. 16).
- [81] Pope, E. J. A., & Mackenzie, J. D. (1986). Sol-gel processing of silica: II. "The role of the catalyst". *Journal of non-crystalline solids*, 87(1-2), 185-198.
- [82] Brinker, C. J., Hurd, A. J., Frye, G. C., Ward, K. J., & Ashley, C. S. (1990). "Sol-gel thin film formation". *Journal of Non-Crystalline Solids*, 121(1-3), 294-302.
- [83] Brinker, C. J., Frye, G. C., Hurd, A. J., & Ashley, C. S. (1991). "Fundamentals of sol-gel dip coating". *Thin solid films*, 201(1), 97-108.
- [84] Ben-Nissan, B., & Choi, A. H. (2006). "Sol-gel production of bioactive nanocoatings for medical applications". Part 1: an introduction.
- [85] Lannutti, J. J., & Clark, D. E. (1984). "Sol-Gel Derived Ceramic-Ceramic Composites Using Short Fibers". *MRS Online Proceedings Library (OPL)*, 32.
- [86] Yoldas, B. E. (1980). "Formation of titania-silica glasses by low temperature chemical polymerization". *Journal of Non-Crystalline Solids*, 38, 81-86.
- [87] Dubois, M., & Cabane, B. (1989). "Light-scattering study of the sol-gel transition in silicon tetraethoxide". *Macromolecules*, 22(5), 2526-2533.
- [88] Brinker, C. J., & Scherer, G. W. (2013). *Sol-gel science: the physics and chemistry of sol-gel processing*. Academic press.44(6).

- [89] McDonald, P. D. (1980). A review of: "Porous Silica-Its Properties and Uses as Support in Column Liquid Chromatography, by KK Unger (Vol. 16, JOURNAL of Chromatography Library), *Elsevier Scientific Publishing Company, Amsterdam*, 1979, 336 pp."
- [90] Parkhill, R. L., Knobbe, E. T., & Donley, M. S. (2001). "Application and evaluation of environmentally compliant spray-coated ormosil films as corrosion resistant treatments for aluminum 2024-T3". *Progress in Organic Coatings*, 41(4), 261-265.
- [91] Castro, Y., Ferrari, B., Moreno, R., & Duran, A. (2003). "Silica sol-gel coatings on metals produced by EPD". *Journal of sol-gel science and technology*, 26(1), 735-739.
- [92] Roux, S., Audebert, P., Pagetti, J., & Roche, M. (2002). "Electropolymerization of carboxylic acid functionalized pyrrole into hybrid zirconium-silicon oxopolymer sol-gel coatings". *New Journal of Chemistry*, 26(3), 298-304.
- [93] Biswas, R. G., Woodhead, J. L., & Bhattacharaya, A. K. (1997). "Corrosion studies of inorganic sol-gel alumina coatings on 316 stainless steel". *Journal of materials science letters*, 16(20), 1628-1633.
- [94] Zheludkevich, M. L., Serra, R., Montemor, M. F., Salvado, I. M., & Ferreira, M. G. S. (2006). "Corrosion protective properties of nanostructured sol-gel hybrid coatings to AA2024-T3". *Surface and Coatings Technology*, 200(9), 3084-3094.
- [95] Wang, D., & Bierwagen, G. P. (2009). "Sol-gel coatings on metals for corrosion protection". *Progress in organic coatings*, 64(4), 327-338.
- [96] Menning, M., Schelle, C., Durán, A., Damborena, J. J., Guglielmi, M., & Brusatin, G. (1998). "Investigation of glass-like sol-gel coatings for corrosion protection of stainless steel against liquid and gaseous attack". *Journal of sol-gel science and technology*, 13(1), 717-722.
- [97] Fallet, M., Mahdjoub, H., Gautier, B., & Bauer, J. P. (2001). "Electrochemical behaviour of ceramic sol-gel coatings on mild steel". *Journal of non-crystalline solids*, 293, 527-533.
- [98] Amato, L. E., López, D. A., Galliano, P. G., & Ceré, S. M. (2005). "Electrochemical characterization of sol-gel hybrid coatings in cobalt-based alloys for orthopaedic implants". *Materials Letters*, 59(16), 2026-2031.
- [99] Gallardo, J., Durán, A., García, I., Celis, J. P., Arenas, M. A., & Conde, A. (2003). "Effect of sintering temperature on the corrosion and wear behavior of protective SiO₂-based sol-gel coatings". *Journal of sol-gel science and technology*, 27(2), 175-183.

- [100] Hawthorne, H. M., Neville, A., Troczynski, T., Hu, X., Thammachart, M., Xie, Y & Yang, Q. (2004). "Characterization of chemically bonded composite sol-gel based alumina coatings on steel substrates". *Surface and Coatings Technology*, 176(2), 243-252.
- [101] Ruhi, G., Modi, O. P., Sinha, A. S. K., & Singh, I. B. (2008). "Effect of sintering temperatures on corrosion and wear properties of sol-gel alumina coatings on surface pre-treated mild steel". *Corrosion science*, 50(3), 639-649.
- [102] Zheng, H., Du, Y., Damron, M., Wright, J., & Tang, M. (1998). An alternative to anodization: Sol-gel solutions for metal finishing. *Metal finishing*, 96(12), 35-38.
- [103] Khramov, A. N., Voevodin, N. N., Balbyshev, V. N., & Donley, M. S. (2004). "Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors". *Thin solid films*, 447, 549-557.
- [104] Zheludkevich, M. L., Salvado, I. M., & Ferreira, M. G. S. (2005). Sol-gel coatings for corrosion protection of metals. *Journal of Materials Chemistry*, 15(48), 5099-5111.
- [105] Brooman, E. W. (2002). Modifying organic coatings to provide corrosion resistance: Part II—Inorganic additives and inhibitors. *Metal Finishing*, 100(5), 42-53.
- [106] Zheludkevich, M. L., Shchukin, D. G., Yasakau, K. A., Möhwald, H., & Ferreira, M. G. (2007). Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor. *Chemistry of Materials*, 19(3), 402-411.
- [107] Hasegawa, I., & Sakka, S. (1988). "Influence of the type of alkyl group on hydrolysis and polycondensation of tetraalkoxysilane". *Journal of Non-Crystalline Solids*, 100(1-3), 201-205.
- [108] Frignani, A., Zucchi, F., Trabanelli, G., & Grassi, V. (2006). "Protective action towards aluminium corrosion by silanes with a long aliphatic chain". *Corrosion Science*, 48(8), 2258-2273.
- [109] Schmidt, H. K., Geiter, E., Mennig, M., Krug, H., Becker, C., & Winkler, R. P. (1998). "The sol-gel process for nano-technologies: new nanocomposites with interesting optical and mechanical properties". *Journal of sol-gel science and technology*, 13(1), 397-404.
- [110] Salve, A. A., Kozhukharov, S., Pernas, J. E., Matter, E., & Machkova, M. (2012). "A COMPARATIVE RESEARCH ON HYBRID AND HYBRID NANO-COMPOSITE PROTECTIVE PRIMARY COATINGS FOR AA2024 AIRCRAFT ALLOY". *Journal of the University of Chemical Technology & Metallurgy*, 47(3).

- [111] Kozhukharov, S. (2009). Relationship between the conditions of preparation by the sol-gel route and the properties of the obtained products. *Journal of the University of Chemical Technology and Metallurgy*, 44(2), 143-150.
- [112] Kozhukharov, S. (2009). Relationship between the conditions of preparation by the sol-gel route and the properties of the obtained products. *Journal of the University of Chemical Technology and Metallurgy*, 44(2), 160-170.
- [113] Kozhukharov, S. (2009). "Relationship between the conditions of preparation by the sol-gel route and the properties of the obtained products". *Journal of the University of Chemical Technology and Metallurgy*, 44(2), 143-150.
- [114] Kozhukharov, S. (2009). "Relationship between the conditions of preparation by the sol-gel route and the properties of the obtained products". *Journal of the University of Chemical Technology and Metallurgy*, 44(2), 143-150.
- [115] Bera, S., Udayabhanu, G., Narayan, R., & Rout, T. K. (2013). Sol-Gel Chemistry Materials for Anti-Corrosion Coatings. *Journal of Research Updates in Polymer Science*, 2(4), 209-231.
- [116] Izumi, K., Tanaka, H., Uchida, Y., Tohge, N., & Minami, T. (1993). "Hydrolysis of trifunctional alkoxy silanes and corrosion resistance of steel sheets coated with alkoxy silane-derived films". *Journal of materials science letters*, 12(10), 724-727.
- [117] Pope, E. J. A., & Mackenzie, J. D. (1986). Sol-gel processing of silica: II. The role of the catalyst. *Journal of non-crystalline solids*, 87(1-2), 185-198.
- [118] Brinker, C. J., Hurd, A. J., Frye, G. C., Ward, K. J., & Ashley, C. S. (1990). "Sol-gel thin film formation". *Journal of Non-Crystalline Solids*, 121(1-3), 294-302.
- [119] Brinker, C. J., Hurd, A. J., Schunk, P. R., Frye, G. C., & Ashley, C. S. (1992). "Review of sol-gel thin film formation". *Journal of Non-Crystalline Solids*, 147, 424-436.
- [120] L.C. Klein (ed.), "Sol-gel technology for thin films, fibers, preforms, electronics, and specialty shapes"; *William Andrew Publishing*, 1988.
- [121] J. Lannutti and D. Clark. "Sol-Gel Derived Ceramic-Ceramic Composites Using Short Fibers," *MRS Online Proceedings Library Archive* 32 (1984).
- [122] Pulker, H., & Pulker, H. K. (1999). "Coatings on glass (Vol. 20)". *Elsevier*.
- [123] Brinker, C. J., & Hurd, A. J. (1994). "Fundamentals of sol-gel dip-coating". *Journal de Physique III*, 4(7), 1231-1242.

- [124] Strawbridge, I., & James, P. F. (1986). "The factors affecting the thickness of sol-gel derived silica coatings prepared by dipping". *Journal of non-crystalline solids*, 86(3), 381-393.
- [125] Brinker, C. J., Hurd, A. J., Schunk, P. R., Frye, G. C., & Ashley, C. S. (1992). "Review of sol-gel thin film formation. *Journal of Non-Crystalline Solids*", 147, 424-436.
- [126] Wachtman, J. B., & Haber, R. A. (1993). "*ceramic films and coatings—an overview*". **Noyes Publications**: Park Ridge, NJ.29-36
- [127] Levich, B., & Landau, L. (1942). "Dragging of a liquid by a moving plate. *Acta Physicochim*". *URSS*, 17, 42.
- [128] SEQUEIRA, Ana Sofia da Silva. "*Desenvolvimento de uma membrana de fibras para conversão enzimática de CO2*". 2018. *PhD Thesis*.80-88
- [129]. Chau, T. T. (2009). A review of techniques for measurement of contact angles and their applicability on mineral surfaces. *Minerals engineering*, 22(3), 213-219.
- [130] Nabavi, M., Doeuff, S., Sanchez, C., & Livage, J. (1990). "Chemical modification of metal alkoxides by solvents: A way to control sol-gel chemistry". *Journal of non-crystalline solids*, 121(1-3), 31-34.
- [131] Livage, J., Henry, M., & Sanchez, C. (1988). Sol-gel chemistry of transition metal oxides. *Progress in solid state chemistry*, 18(4), 259-341.
- [132] Gasch, C., Salameh, B. A., Pradera, M. A., & Fuentes, J. (2001). "Isothiocyanatoulosonates, a new type of glycosyl isothiocyanate useful for the stereocontrolled synthesis of thiohydantoin spironucleosides". *Tetrahedron Letters*, 42(49), 8615-8617.
- [133] Silverstein, R. M., & Bassler, G. C. (1962). Spectrometric identification of organic compounds. *Journal of Chemical Education*, 39(11), 546.
- [134] Habsuda, J., Simon, G. P., Cheng, Y. B., Hewitt, D. G., Lewis, D. A., & Toh, H. (2002). "Organic–inorganic hybrids derived from 2-hydroxyethylmethacrylate and (3-methacryloyloxypropyl) trimethoxysilane". *Polymer*, 43(15), 4123-4136.
- [135] Martínez, J. R., & Ruiz, F. (2002). "Mapeo estructural de sílica xerogel utilizando espectroscopía infrarroja". *Revista mexicana de física*, 48(2), 142-149.
- [136] Lavorgna, M., Mascia, L., Mensitieri, G., Gilbert, M., Scherillo, G., & Palomba, B. (2007). "Hybridization of Nafion membranes by the infusion of functionalized siloxane precursors". *Journal of membrane science*, 294(1-2), 159-168.

- [137] Matos, M. C., Ilharco, L. M., & Almeida, R. M. (1992). The evolution of TEOS to silica gel and glass by vibrational spectroscopy. *Journal of Non-Crystalline Solids*, 147, 232-237.
- [138] Jitianu, A., Gonzalez, G., & Klein, L. C. (2015). "Hybrid Sol–Gel Glasses with Glass-Transition Temperatures Below Room Temperature". *Journal of the American Ceramic Society*, 98(12), 3673-3679.

RESUME

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