Synthesis and Characterization of Nanosilica-zinc Coatings with Silane Coupling Agents on Glass Substrates

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By

Haile Asmelash

School of Mechanical, Chemical and Materials Engineering

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Abstract

Functional coatings were used as thin films on a lot of objects and substrates, such coatings were used as surface engineered materials to form advanced materials. Modified silica nanoparticles with amino group, zinc acetate dehydrate and γ-glycidoxypropyltrimethoxysilane (GPS) were used in this research to form functional coatings. The amino and epoxy groups from the modified silica nanoparticles and the GPS, respectively, forms a multifunctional smart coatings on microscope glass slides. We have used one step dip-coating and flow-coating process to fabricate superhydrophobic silica, nanosilica-zinc hybrids, and Nanocomposite films on glass substrates. It can be applied over different surfaces, such as glass, plastic substrates, semiconductor or electronic components and metal surfaces. Zinc acetate dehydrate [$Zn(CH_3OO)_2(H_2O)_2$] was used to interact with the modified silica sol, yielded films of a zinc acetate/silica composite network while the hydrophilic part associate with Zn helps in binding the hydroxyl groups (silanols) present on the glass surface. Nanocomposited coating using nanosilica, nanosilica-zinc and nanosilica-zinc-γ-glycidoxypropyltrimethoxysilane (GPS) coatings on glass substrate can improve the interfacial network or bridge region of organosilanes compounds. Optical microscope was used to see surface and morphology of films coated on glass substrates. X-Ray Diffraction (XRD), optical transmission by UV VIS-Spectroscopy and Fourier Transform Infrared (FTIR) Spectroscopy and peel test characterization were used to characterize samples.

Keywords: Functional, SH-silica, Nanosilica-Zn, GPS, Nanocomposite, Coatings, Surface, Modification, Transparent, Hybrid.

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Abbreviations and Symbols

SCA	Silane coupling agent
GPS	γ-glycidoxypropylmethoxytriethoxysilane
APS	γ-aminopropyltrimethoxysilane
APTES	3-aminopropyltriethoxysilane
APTMS	3-aminopropyltrimethoxysilane
HMDS	Hexamethyldisilane
TMCS	Trimethylchlorosilane
OR	Alkoxy group
OR'	Hydrolyzable group
X	Non-hydrolyzable organic moiety
R	Spacer
TEOS	Tetraethylorthosilicate
Nanosilica	Silicon dioxide nanoparticles
ZnO	Zinc oxide
SH	Superhydrophobic
WCA	Water contact angle
WSA	Water sliding angle
ITO	Indium thin oxide
TTFT	Transparent thin films transistor
EEC	Electro-elastocapillarity
AR	Anti-reflectivity
OINC	Organic inorganic nanocomposite
I/O	Organic inorganic
UV	Ultraviolet
NIR	Near-infrared
PC	Polycarbonate

PU	Polyureathane
PET	Polyethyleneterephthalate
PEG	Polyethylene glycol
PMMA	Polymethylmethacrylate
DLVO	Derjaguin, Landau, Verwey and Overbeek
ζ	Zeta potential
σ_o	Surface charge
F	Faraday constant
V_T	Total potential energy
V_A	Attractive potential
V_R	Repulsive potential
V_S	Potential energy due to the solvent
π	Solvent permeability
A	Hamaker constant
κ	Ionic composition
a	Particle radius
D	Particle separation
DL	Double layer
EDL	Electrochemical double layer
IHP	Inner Helmholtz plane
OHP	Outer Helmholtz plane
SEM	Scanning electron microscope
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
TG-DTA	Thermo gravimetric differential thermal analysis.

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CHAPTER ONE INTRODUCTION TO MULTIFUNCTIONAL SMART COATINGS

1.1 Introduction

Coating is a covering that is applied to the surface of an object, usually referred to as the substrate, and coatings are applied to improve surface properties of the substrate, such as appearance, adhesion, wettability, corrosion resistance, wear resistance, and scratch resistance [1]. Coating science and technology is an old field; however, it has not reached a perfect maturity. In particular, with increasingly strict environmental protection laws and rules enforced in various countries and the demands of continuously developing hi-tech industries, coatings with better or novel performances are highly expected. Coatings will be evolved to provide environmentally friendly coatings, which require synthesis of novel nanoparticles or nanopowders for superhydrophobic surfaces, thermal-insulating, air-purifying coatings, and so on; to enhance the performances of current coatings, including better scratch and mar resistance, enhanced corrosion-resistance, aging and heat resistance, anti-fingerprint performances, and so on; and to develop multifunctional even smart coatings, including self-cleaning coatings, temperature controllable coatings, bionic anti-fouling coatings, self-healing coatings, light or heat electricity switching coatings, sensory coatings, and so on [2]. These functions of coatings are not easily achievable by conventional synthesis methods and formulation techniques, but they can be possibly realized by application of modern science and technology, that is, organic–inorganic hybrid, self-assembly and nanotechnology for special coating functions. In addition, the use of new pigments and modification methods and construction of nano and micro surfaces can potentially afford coatings with enhanced and multifunctional properties [2]. Modern coating technology is gaining an increasing relevance in material and product development and occupies more and more key positions in the fields of materials and surface engineering. In particular, oxide layers play a dominant role in the improvement of the chemical and physical properties of glass surfaces, because they have the important characteristics of glass, such as transparency in the visible spectrum, and there are various deposition techniques can be applied to the production of oxide layers on glass [3]. Multifunctional hybrid materials have been synthesized successfully using various types of functional groups [4,5]. It forms functional coatings on glass surfaces, and it had wide applications over different materials and products which are presented in figure 1.1.

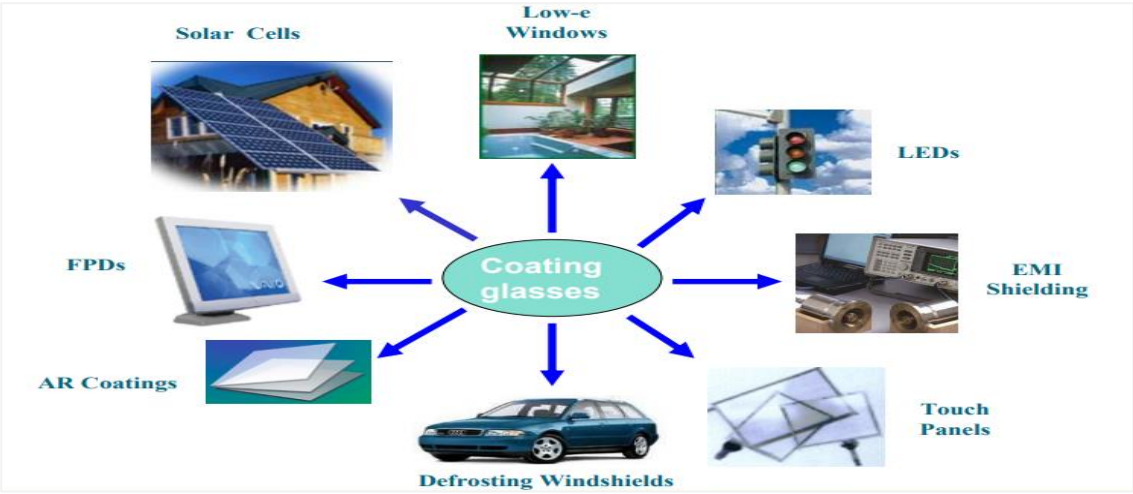


Figure 1.1 Application of functional coatings on glass surfaces of different materials and fields [1].

1.2 Background of study

The evolution of engineered surfaces through coating design is what makes the difference for mainstream and custom added value solutions in modern glass constructions. The rising environmental and convenience standards are driving the glass industry in an emerging field of functional design on the scientific discoveries of new materials at a nanoscale, and the right coating solution also has to take into account secondary processing operations.

In recent research, nanoparticle is a promising material to prepare superhydrophobic coatings, because the nanoparticle aggregates usually have multi-scale roughness including the nanoscale of primary nanoparticles and the micro-scale roughness of nanoparticle aggregates. The general process of fabricating superhydrophobic surface using nanoparticles involves two steps which are the hierarchical rough surface is created with nanoparticles and then modified with low surface energy materials. In order to simplify the general two-step process, hydrophobic nanoparticles were used directly to produce the superhydrophobic surface in one step without post-treatment, because of the assembly of hydrophobic nanoparticles could provide both surface hydrophobicity and surface roughness [6].

In natural environment, lotus leaf has been set as a benchmark for the scientists to fabricate the hydrophobic surface property. It can maintain its cleanliness even though it grows in muddy and dirty ponds because the contact angle is higher than 160°. Lotus leaf acts as self-cleaning by

beads up the water droplets into spherical form and rolls off to collect the dirt and debris along the surface. The combination of extreme water repellency and self-cleaning properties is known as "Lotus Effect" [7]. The butterfly wings are covered with grooved multilayered cuticles that help keeping the wing surface water free and preventing them from sticking together [8]. Water striders also developed a peculiar hierarchical structure on their legs, allowing them to walk on water. Lotus leaf, wings of butterfly and water striders leg are represented in Figure 1.2.

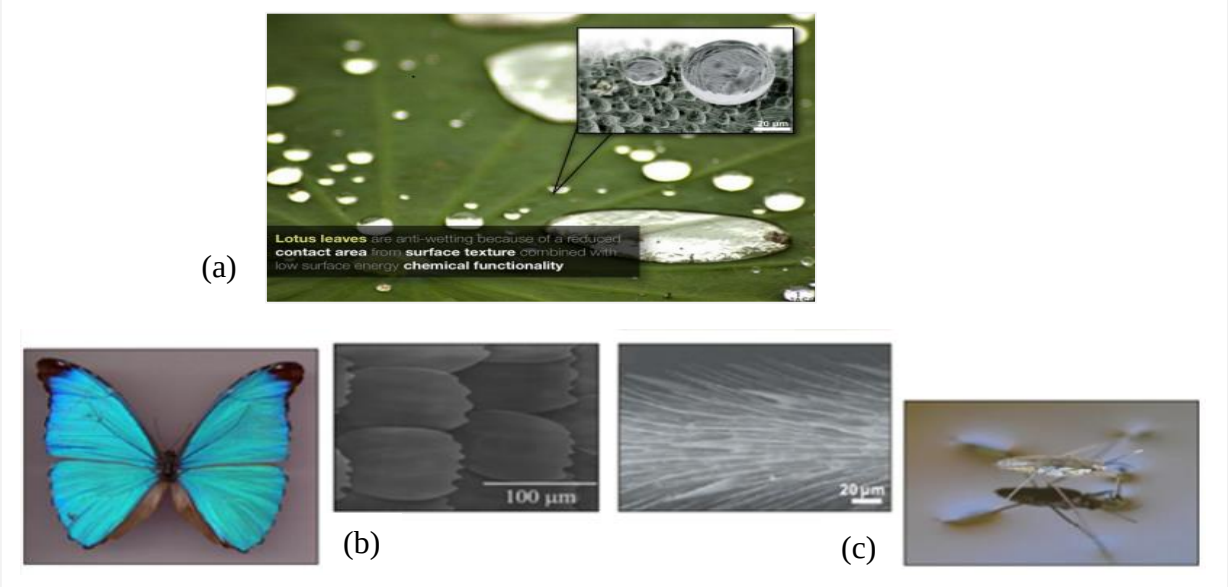


Figure 1.2 Photographic images and Scanning Electron Microscopy (SEM) images of (a) Lotus leaf, (b) butterfly wings and (c) water strider's leg.

Silica nanoparticles provide the topography required for superhydrophobic surfaces and the amino group attached to the surface renders the particles hydrophobicity. In addition, Silica nanoparticles do not scatter light and the linker can be constructed by a coupling agent that has a group for bonding to the substrate. Transparent superhydrophobic surfaces have a coating of ceramic nanoparticles attached to a transparent substrate that are bound to the substrate through a flexible linker and an amino group and epoxy is bound to the surface of ceramic nanoparticles.

1.2.1 Silane Coupling Agent

Organosilane coupling agents are finding increased use in ceramic particle-based coatings. These molecules were originally designed to improve interfacial strength between inorganic and organic phases in composite coatings, but now they are gaining popularity in coating applications.

Coatings can be prepared by depositing a suspension containing nanosilica colloids and an organosilane coupling agent onto a substrate, and then drying and curing. The addition of coupling agents to nanosilica particle-based coatings leads to the potential benefit of retaining the desired properties of the ceramic (e.g., hardness, index of refraction) and avoiding the problems usually associated with ceramic processing (e.g., high temperatures, cracking). Organosilanes react at temperatures low enough for the preparation of coatings on glass substrates [9-11]. Since silanes provide the benefits and adhere well to inorganic surfaces as well as react with polymeric molecules, their use in coatings should continue to grow. Scientific studies aimed at understanding the particle silane interactions in suspension and in the coatings are necessary to improve processing and coating properties.

γ-aminopropyltrimethoxysilane (APS) and γ-glycidoxypropylmethoxytriethoxysilane (GPS) are silane coupling agents used for functionalization of nanoparticles. They endow nanoparticles with amino and epoxy groups, respectively, and hence chemical reactivity with the organic binder [12]. The GPS-modified nanoparticles can be readily embedded into epoxy coatings, and GPS-based polysiloxane coatings are part of the cross-linking network [13]. More interestingly, the prehydrolyzed GPS is amphiphilic can modify the aqueous nanoparticle sol [14]. The silylated colloidal particles thus have improved cross-linking ability with themselves or with other polymer binders via the grafted epoxy and/or silanol groups. The APS-modified nanoparticles can be applied to epoxy coatings [15].

1.3. Statement of the Problem and Approaches to Solve

When coatings were used as a barrier layers or sacrificial materials, it may affect the structure, properties, and application of the coated materials or the substrate, and it declines performance of materials. Conventionally, we apply thin films on glass substrates and other substrates during engineering of materials or manufacturing of products for protection of the substrate or to decorate the substrate, but coating materials developed on substrates instead of playing specific functional performance and widening its application fighting with its surrounding environment like humidity and water condensation, it gets contaminated with solid particles and it is prone to damage, resulting in loss of its coating life durability or a decline in its application as a barrier on the substrate, and causes deterioration of its surface or coated material surface.

Applying functional coating on glass surface and other substrates could solve some of problems mentioned in the above statement. Coatings developed with layers of inorganic-organic compounds (functional groups) which is comfortable to the substrate and uncomfortable for surrounding environment to form a reaction, so functional coatings give a life for coating instead of using as barrier or sacrificial material. Modified silica particles are used to form functional coatings on glass surfaces, zinc acetate dehydrate is used for glass coating applications. Modified silica particles, zinc acetate and γ-glycidoxypropylmethoxytriethoxysilane (GPS) form interfacial network (region) on glass surface. The functional groups on modified particles and surfaces with coating materials of silica and zinc could able to form a multifunctional coatings or smart coatings on glass substrates.

1.4. Objective of the Study

1.4.1 General Objective

The main goal of this study was formulating functional coatings on glass substrates. Modified silica nanoparticles, zinc acetate dehydrate and GPS were used to construct functional and multifunctional coatings on glass substrates. Inorganic substrate or components and organic compounds combine together by organosilanes compounds and it form interfacial region and bonding.

1.4.2 Specific Objective

Synthesizing the right coating solutions for functional coating, and apply coating solutions on glass substrates by dip-coating and flow coating techniques. Amino and epoxy groups in coating materials and on glass surface provide structure-property relationships for desired applications. Constructing interfacial network on glass surface by using only modified silica nanoparticles, or its hybrid form with zinc acetate dehydrate, and the other interfacial region was constructed by depositing coating solution of nanocomposited on GPS coated glass substrate. The interfacial region enhances to form a bond between glass surface and coating materials.

1.5 Application of Nano Coatings for Finding Advanced Materials

Advanced processing technologies were used for producing advanced materials in high-tech industries. Nanotechnologies are used to produce new nanomaterial and these technologies are

also used to improve properties of manufactured materials and upgrade performance of materials. Nanocoating is one of technologies developed for producing advanced materials, these coatings are used to form interior and exterior coatings on parts of engineered materials, and it makes a difference because of its high surface volume ratio. In this 21st century, the interactions between the surface of engineered materials and their surrounding environment, and interactions across engineered materials and human beings are rising, such active interactions cause problems, such as contamination, staining, condensation reactions, radiation, corrosion, failure of coating, degradation of materials, and it causes series problems in human life also. In addition, the outcome of climate change, global warming, and weathering cause vast impacts on materials and human's life. Materials surface have to be modified with a superhydrohydrophobic particles, and films, and such surfaces provide self-cleaning, antibacterial properties, corrosion resistance, scratch resistance. The functionalization of particle surfaces is one method for tuning the overall properties of particles to fit targeted applications, and used as advanced materials which can compensate their structure-property relationships, even in severe environments. Silica and zinc are an abundant material and we found it in different forms. Silica and zinc are known as coating material. Coatings are mostly applied on objects for decoration or protection purpose, but these coatings sometimes suffer because of changes in environmental conditions, and coated surface losses their protections as well as beauty, loss of capacity/tendency to resist the coming interactions/affections with the surrounding environment, and we need to develop materials which can able to respond. So, a well-developed thin films on objects which sustain performance of material during service life time. A multifunctional smart coating with organosilanes can able to form an outstanding coating with functional groups, and increase more functionality. In recent years, there has been an increased interest in the surface modification of inorganic nanoparticles with organic materials in numerous areas including photocatalysts, sensors, pharmaceuticals, and electronic devices.

1.6 Outline of the Thesis

We were working on Synthesis and characterization of Nanosilica-zinc coatings with silane coupling agents on glass substrates, and further development of this science for smart coatings with additional features and functionalities. Chapter two of this thesis is literature review about science of nanosilica and surface modified silica nanoparticles, organosilanes chemistry and glass surfaces, and colloidal science. Chapter three and four of this thesis describes experimental work,

result and discussion. Chapter five of this thesis states conclusion. We categorized the films developed in this research into three types, which are Nanosilicasilica, Nanosilica-zinc hybrid coating, and Nanosilica-zinc hybrid solution with $GPSiO_2$ colloidal solution (Nanocomposite).

CHAPTER TWO LITERATURE REVIEW

2.1 Science of Nanosilica

Silica is one of the main components of the crust of the earth. Our civilization has been using silica in different forms for a long period of time e.g. as flint for tools and weapons. In present technology the great variety of application includes catalyst in oil refinery, microcircuits and fiber optics [16]. The stober process is used to synthesize silica nanoparticles, even with particular size range. Once the xiloxane groups form, the entire structure of silica nanoparticles were formed.

$$Si(OC_2H_5)_4 + H_2O \xrightarrow{\text{hydrolysis}} Si(OC_2H_5)_3OH + C_2H_5OH$$

$$\equiv Si\text{-}O\text{-}H + H\text{-}O\text{-}Si \equiv \xrightarrow{\text{water condensation}} \equiv Si\text{-}O\text{-}Si \equiv + H_2O$$

$$\equiv Si\text{-}OC_2H_5 + H\text{-}O\text{-}Si \equiv \xrightarrow{\text{alcohol condensation}} \equiv Si\text{-}O\text{-}Si \equiv + C_2H_5OH.$$

Hydroxyl groups in the synthesized silica nanoparticles form hydrophilic and moisture instable properties because the hydroxyl groups which exists in isolated silanols, vicinal silanols, geminal silanols adsorb water as shown in figure 2.1.

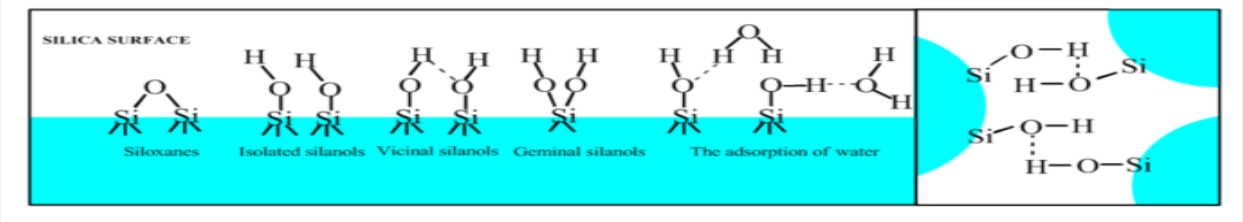
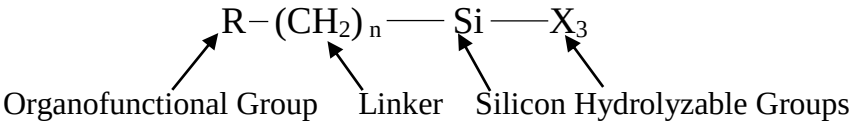


Figure 2.1 Surface structure of silica particles.



Organophiliation of nanoparticles with small molecules can be adopted for functionalization of nanoparticles. The small molecular modifiers in silane coupling agents (SCAs) are the most frequently used for surface modification of silica nanoparticles. These short organic segments can attach to the surface of nanoparticles through versatile means. Functionalization of some organic groups, like amino group, can be done during the nanoparticle synthesis. The alkoxyl groups of

SCA molecule can react with the hydroxyl groups of nanoparticles while their organic chains have epoxide and/or amine end groups that can provide chemical interaction and/or compatibility.

Organotrialkoxysilane ($RSi(OR)_3$) compounds can treat the surface of silica, and the silanol groups can be modified to various functional groups. 3-aminopropyltrimethoxy silane (APTMS) and 3-aminopropyltriethoxysilane (APTES) were widely explored by many researchers to modify the surface of silica nanoparticles. The amino functional groups are known to enhance dispersibility and miscibility of silica fibers [17], and to be used as a linkage unit to attach other functional molecules [18].

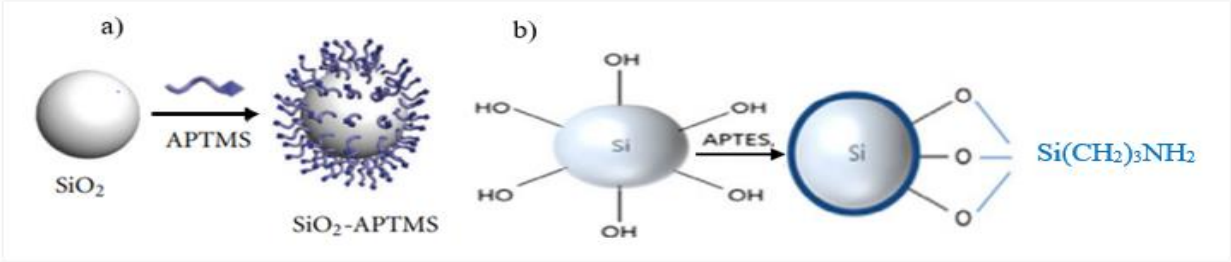


Figure 2.2. Surface modification of silica nanoparticle by APTMS (a), and APTES (b)

Modified silica nanoparticles can be serve as superhydrophobic surface as thin film on the glass surface and to form self-cleaning surfaces. Scratch resistant coatings were formed by using small amount of surface modified silica nanoparticles, Zinc acetate could able to form the crosslink network within the coating materials of silica and enhances the scratch resistance of coating material. The adsorption of silanes on inorganic surfaces is important to the mechanical properties of composites. The coating production occurs during silane adsorption, and relating coating processing and microstructure to coating properties, specifically scratch resistance. The adsorption behavior of an organosilane onto colloidal silica is related to the coating microstructure [11].

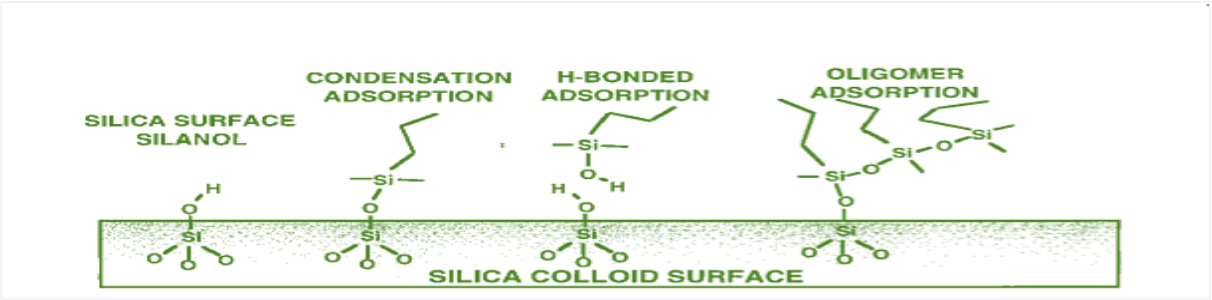


Figure 2.3 Possible adsorption configurations for a silane coupling agent on a silica surface.

Transparent barrier nanocomposite coatings are also formed by silica nanoparticles. A coating layer is usually cast on a package to enhance the barrier properties. Consumers demand high product visibility, as in food packaging. This requires a coating layer with good and sometimes selective barrier properties in combination with high transparency, good print quality, etc. Currently, there is a trend toward chilled and possibly modified atmosphere packaging.

2.2 Organosilanes Chemistry and Glass Surfaces

Glass is a durable long life material that can save energy in an installation. Certain properties of glass like strength, chemical stability and surface chemistry dictate its use based on the intended implementation in a wide variety of applications [19]. It is a critical component in fields such as building materials, energy conservation, medical products and consumer goods. Glasses have wide applications as represented in figure 2.4.

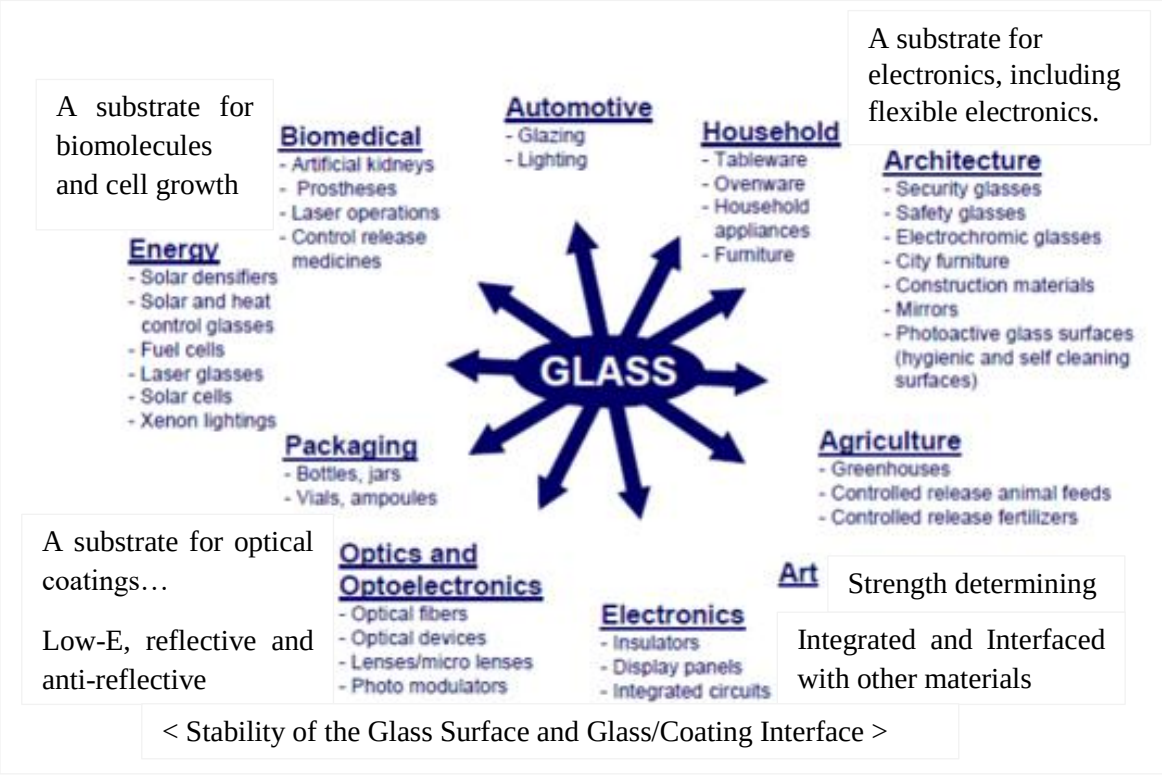


Figure 2.4 Glass surfaces, coatings and interfaces.

Glass surfaces are often chemically functionalized to improve product performance and style. Along with the continuous demand for improved performance, coating formulations constricted

with ever-tightening environmental protection regulations. One such functionalization is conducted by application of organosilanes in a process known as silanization. Monomeric silicon chemicals are known as silanes. A silane that contains at least one carbon-silicon bond (Si-C) structure is known as an organosilane. The organosilane molecule has three key elements: X-R-Si(OR')3, where "X" is a non-hydrolyzable organic moiety, this moiety can be reactive toward another chemical (e.g., amino, epoxy, vinyl, methacrylate, sulfur) or nonreactive (e.g., alkyl), "R" is a spacer, which can be either an aryl or alkyl chain, typically propyl, and "OR'" is a hydrolyzable group like an alkoxy group (e.g., methoxy, ethoxy, isopropoxy) or an acetoxy group that can react with various forms of hydroxyl groups present in mineral fillers or polymers and liberates alcohols (methanol, ethanol, propanol) or acid. These groups can provide the linkage with inorganic or organic substrates [20,21]. Organosilanes serve as bridges between inorganic or organic substrates (such as minerals, fillers, metals and cellulose) and organic matrices can dramatically improve adhesion between them [22,23], which is shown in figure 2.5. Silanes can tailor glasses to have a hydrophobic or hydrophilic surface. It has been used as water barrier to reduce corrosion of materials such as glasses and metals. The silanol group in silane molecule bonds to the glass, and then the polymer can bond to the organic end-group on the silane [24].

Figure 2.5 The bridge formation of an organosilane molecules.

Functionalization with another substance presents a modified surface for interactions with a target substance, which would otherwise not interact desirably with the original surface. The use of organosilanes in primers and their proven benefits for offering a healthier and more environmentally friendly alternative to chrome-based compounds in corrosion protection of metals [25]. They also improve cure (by reducing catalyst inhibition) and electrical properties. The organic group on the silane which is nonreactive are often used as dispersing or hydrophobing agents. They feature a nonreactive organic group, which is compatible with the matrix, and an alkoxy group, which reacts with the substrate [22]. Amino functional silanes are reactive at both ends and are useful in improving the adhesion of all kinds of coatings [26].

Surface composition of the glass is expected to have a major impact on adsorption. The silicate surfaces are known to be chemically heterogeneous, and adsorption on a glass is directly related to its surface reactivity, specifically to the accessibility of the surface reactive sites to adsorbates such as organic molecules and organosilanes [27].

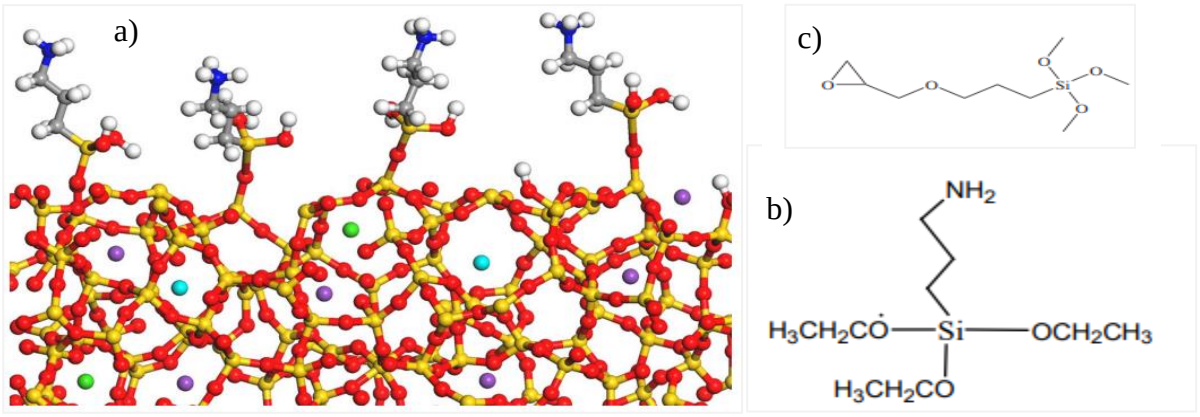


Figure 2.6. (a) Organofunctionalization of a glass surface, (b) structure of APS and GPS (c).

In applications where the glasses come into intimate contact with another material, for example, organic-inorganic hybrids such as siloxanes, the coatings are usually intended to be strongly adhered. Therefore the interaction between the glass surface and the functional reactive groups in the coating needs to be understood, specifically those that determine the hydrolytic stability of the interface between the glass and coating [21].

2.3 Colloidal Science

Colloidal particles are considered to range from 1 to 1000 nm in size and consist of 10^3 to 10^9 atoms. These particles are small enough that they remain suspended indefinitely due to Brownian motion. Several interaction forces operate in suspensions, such as the gravity, the Brownian motion, the attractive interaction by van der Waals forces, and the repulsive interactions necessary to overcome attraction and to avoid agglomeration [28]. Brownian motion caused kinetic energy, it drives the particles to move randomly in the solution (figure 2.7). This lead to collisions and depending on the forces between the particles they either attract or repel each other. The repulsive forces between two particles in a colloidal suspension need to be larger than the attractive forces to keep the particles from aggregating. The Repulsive Electrostatic Potential Hydrous oxide surfaces are amphoteric and can be modeled by the following acid base reactions:

$MOH + H^+ \rightleftharpoons MOH_2^+$

$MOH + OH^- \rightleftharpoons MO^- + H_2O$

Where protons and hydroxyl ions can specifically adsorb. For this reason, H^+ and OH^- are referred to as potential determining ions. The surface charge (σ_o) can be expressed by the difference in adsorption density between H^+ and OH^- adsorbed on the surface (Γ_H^+ andΓ_{OH}^-, respectively), which is proportional to the adsorption density of cationic and anionic species.

$$\sigma_o = F(\Gamma_{H^+} - \Gamma_{OH^-}) = f(\Gamma_{MOH_2^+} - \Gamma_{MO^-})$$

F being the faraday constant (96,485 C).

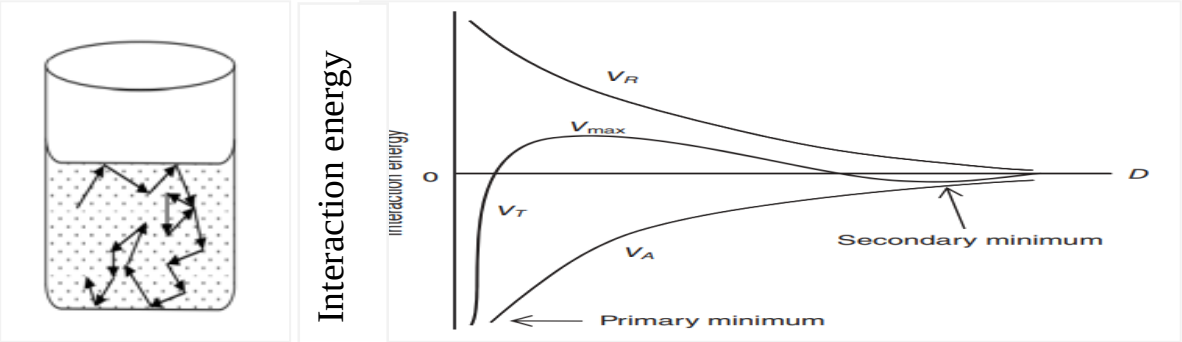


Figure 2.7 Brownian motion of colloidal particles.

Figure 2.8 Potential energy of interaction as a function of distance according to the DLVO theory.

The zeta potential determines the surface charge properties of silica particles in suspension. When the solution pH is lower than the isoelectric point of silica, hydroxyl groups on the silica particles are deprotonated, producing negative charges on the surface. Since the silanol groups on the silica particles are used as reactive sites in surface modification, there should be fewer silanol groups left on the modified particles than on the pure silica particles. Thus, it is expected that there would be fewer negative charges on the modified particle surface. The surface charge is negative at high pH values and the protons are attracted. When the concentration of the potential determining ion is altered, the relative adsorption of ions on the surface varies. There is a definite concentration for which the activities of positive and negative species are equal and the surface potential will be zero [29]. Zero point of charge (ZPC) defines the maximum destabilization, as there is no net surface charge. Hence, suspensions are stable only if the pH is kept far enough from

the ZPC, as illustrated in Figure 2.9. In general, the ZPC decreases as the charge of the cation increases, 2-3 for SiO_2.

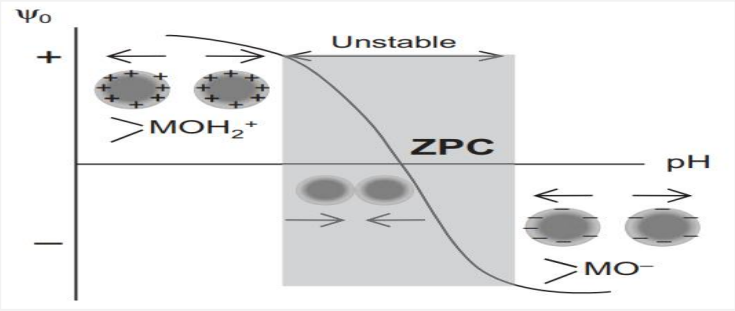


Figure 2.9 Variation of surface potential with pH.

When there is no specific adsorption, the isoelectric point and the ZPC are the same. When specific adsorption occurs, the measurements of the zeta potential show that the isoelectric point shifts toward acidic pH values if the adsorbed species are anionic and toward basic pH values when the adsorbed species are cationic. [30,31].

Functional groups form charges during reaction, which is acidic or basic surface groups. Acidic groups such as carboxylic dissociate when in contact with water, i.e. the H^+ ion is released into the surrounding water and the surface assumes a negative charge. Basic groups such as amine groups get protonated when in contact with water, i.e. the surface assumes a positive charge. (Figure 2.10). The surface charge and its changes due to liquid-on-solid surface adsorption is important for tuning material properties and optimizing processes.

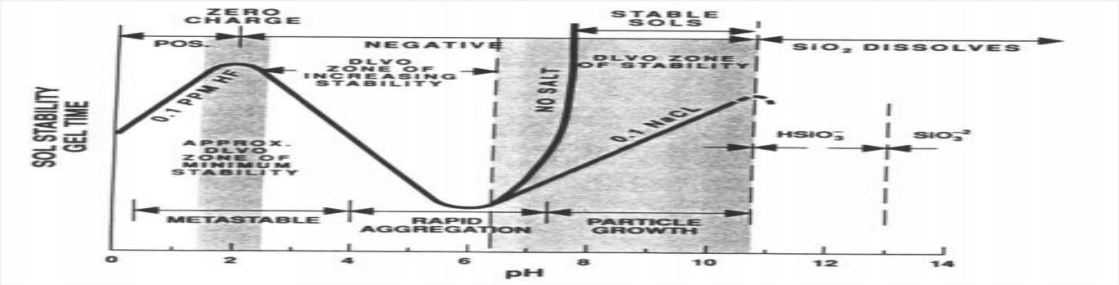


Figure 2.10 Effect of pH on the stability of the colloidal silica-water system. Shaded and white areas are approximate zones corresponding to behavior predicted by the DLVO theory, minimum stability predicted at pH around 2 and 3, increased stability at pH between 3 and 6-8, and maximum stability at pH higher than 8.

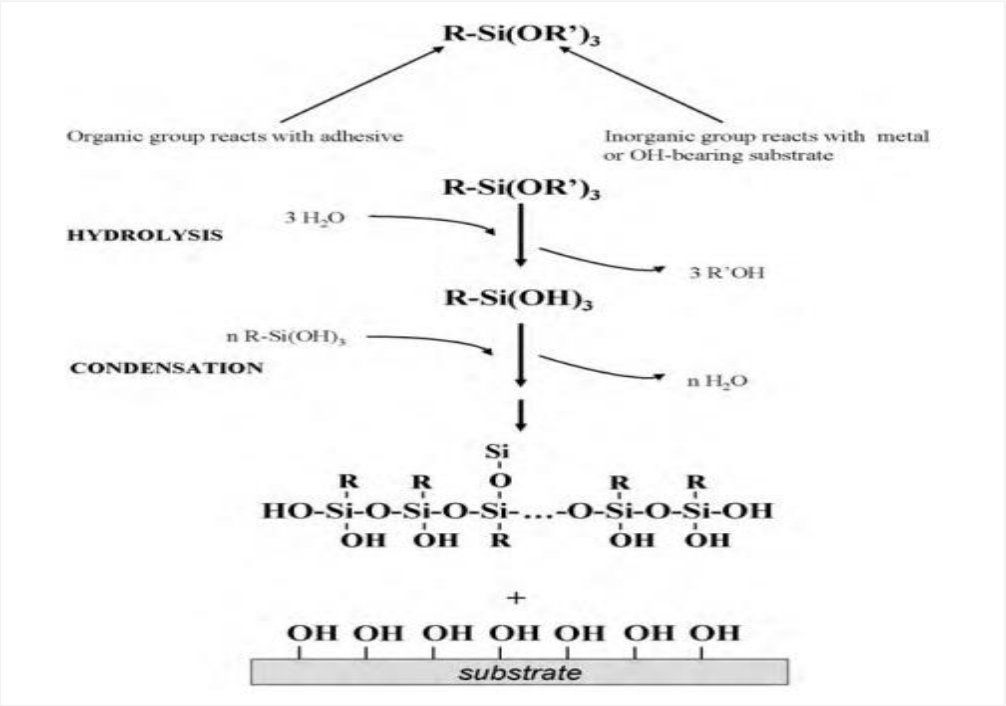
The main concern in chemical synthesis/solution preparation is the mixing process and to obtain homogeneous silica dispersion in the solution or solvent. The simplest method is direct mixing of silica into solution blending. Besides blending, sol-gel process is also widely used.

Solution blending is a liquid-state powder-processing method that allows a good molecular level of mixing. The blending approach is the faster and simpler method to prepare hybrid materials, but it is sometimes difficult to obtain hybrid films with good mechanical properties and high optical transparency, due to the formation of nanoparticles aggregation. Magalhaes et al. prepared self-cleaning hybrid coatings using functionalized fumed silica. The use of fumed silica with an acrylate functionalization at the surface facilitated the compatibility and promoted interaction with the polymer matrix during the blending process. Melt blending is also the most commonly used method in composite preparation due to its efficiency and operability [32].

Sol gel process is widely known as practical and useful way for fabricating thin film on various substrates [34]. Sol-gel methods are composed of three reactions such as hydrolysis, adsorption, and condensation. Alkoxy groups of the organic binder (trialkoxysilanes) are hydrolyzed in water to build the silanol groups. Acid and base catalyze the hydrolysis reaction. The hydrolysis is fast at acids of low pH, but is slow at pH 7 [11]. The hydrolysis reaction is controlled irreversibly by a large excess of water and followed by condensation and adsorption. Since silanols have three functional groups, large crosslinked network polymers are possible. At the strong acidic conditions, the organic binders are adsorbed on the surface of silica particles through the silanol reactions, while another alkoxy group remains available for the reaction with the matrix resin. The condensation process transforms the silanol groups to form polysiloxanes [35]. These reactions can be shown schematically in 2.1, which shows different reaction pathways. Acidic media enhances the hydrolysis of the alkoxysilane and stabilize the resulting formed silanols, thus limiting self-condensation reactions. The interfacial bonding formed between a silane film (organic group) and glass substrate.

$$R'Si(OR)_3 + \text{excess } H_2O \Leftrightarrow R'Si(OH)_3 + 3ROH$$

$$RSi(OH)_3 + RSi(OH)_3 \Leftrightarrow RSi(OH)_2OSi(OH)_2R + H_2O.$$



Scheme 2.1. Hydrolysis and condensation reactions of trialkoxysilanes, as a function of the amount of water and the nature of the organic group [31].

2.4 Coating Formulations on Glass Surface

2.4.1 Superhydrophobic Surface

Superhydrophobic layer or film spread over a surface to combine physical and chemical properties of a coating, such coatings typically improve the surface properties of the substrate where it is applied, from its global appearance to its resistance to corrosion, scratch or wear [36]. The wettability of the substrate, i.e. its ability to maintain contact with a liquid, can also be influenced by such layer. A surface is classified as either hydrophilic or hydrophobic by how it sticks to water drops. If a water drop has a tendency to stick to itself more than it sticks to a given surface that surface is called hydrophobic and the water drop will bead up with a CA greater than 90°. Conversely, if a water drop tends to stick more to a given surface than it sticks to itself, that surface is called hydrophilic and the drop will have a contact angle of less than 90°. A water drop that completely wets a surface will have a contact angle of ~0°, while a drop that has no interaction with a surface will bead up into a prefect sphere and will have a contact angle of ~180°. The images in figure 2.11 show these conditions [37].

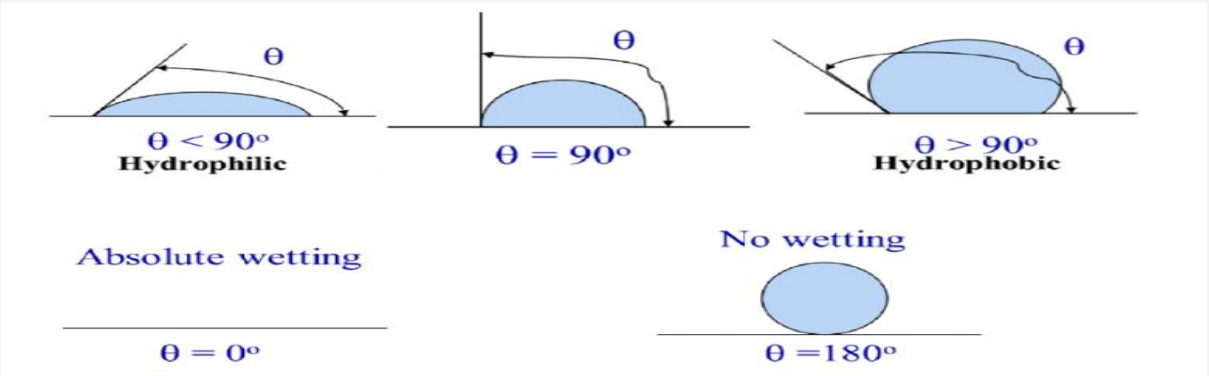


Figure 2.11. Hydrophilic and hydrophobic wetting conditions.

Transparency and surface roughness are contradictory properties. It is necessary to control the roughness below 100nm to effectively lower the intensity of Mie scattering while maintaining non-wettable characteristics [38]. It is difficult to achieve superhydrophobicity and high optical transmittance on the same surface. An increase in surface roughness leads to increased hydrophobicity and decreased optical transmittance due to Mie and Rayleigh scattering [39].

2.4.2 Nanosilica-Zinc Hybrid solutions and Coatings

Silica based materials have microeletronic, optical and optoelectronical applications. On the other hand zinc oxide is one of the most widely used inorganic semiconductors for many different applications such as solar cells, photodetectors, gas sensors, and photocatalytics. Silica and zinc oxide found usage in very different applications such as, photonic crystals, photocatalysts, gas sensors, vacuum fluorescent display and varistors [40]. Zinc oxide coated with silica is also serve as interconnector or nanoelectronic devices and biochemical capsules. The photocatalytic activity of ZnO and its poor compatibility to organic compounds that makes it to agglomerate in organic solution are just some problems that hinder some potential applications of ZnO [41]. Fortunately, these disadvantages of ZnO are avoidable through the process of surface modification and this can be achieved by coating ZnO particles by surface modifiers like silica or alumina, but silica is given much attention by most scientists due to its important properties such as high transparency for visible light, low chemical activity and compatibility to ZnO [41]. Recently, preliminary investigations are going on the synthesis of ZnO-SiO_2 both in powder form and deposited on glass substrates by using simple wet chemical deposition process [42,43]. The coating of SiO_2 on ZnO is also applied to protect organic material from the photocatalytic reaction of ZnO. Nanosilica-Zn

is seen to have significant potential application as an antibacterial coating, luminescent material, photocatalyst, and also as gas sensor because of the good sensing capability of ZnO which could be enhanced more with the presence of SiO_2 for size and shape control that could lead to better chemical activity at the surface. However, understanding the mechanism for the growth of ZnO-SiO_2 nanostructures is still a formidable task particularly on controlling its surface morphology [44,45]. In recent years, the silica-based nanocomposites are considered the most challenging systems for the quantum confinement of semiconductive nanocrystallites, for a better control of shape, size and properties [46]. Preparation of ZnO nanoparticles confined in silica matrix is investigated for high UV luminescence at room temperature.

2.4.3 Nanocomposite Coatings

Nanocomposites are mainly used in coatings whose characteristics cannot be produced by conventional means or can only be achieved by multiple coats. The possible routes to produce nanocomposite coatings are presented in figure 2.12. Silica-nanocomposites are preferred where high scratch and abrasion resistance is needed at the same time as transparency. Silicon dioxide nanoparticles are the most commonly used nanofillers in the fabrication of the nanocomposites due to their superior properties like very small dimensions and high surface free energy. Therefore, the final properties of the specimens will be declined.

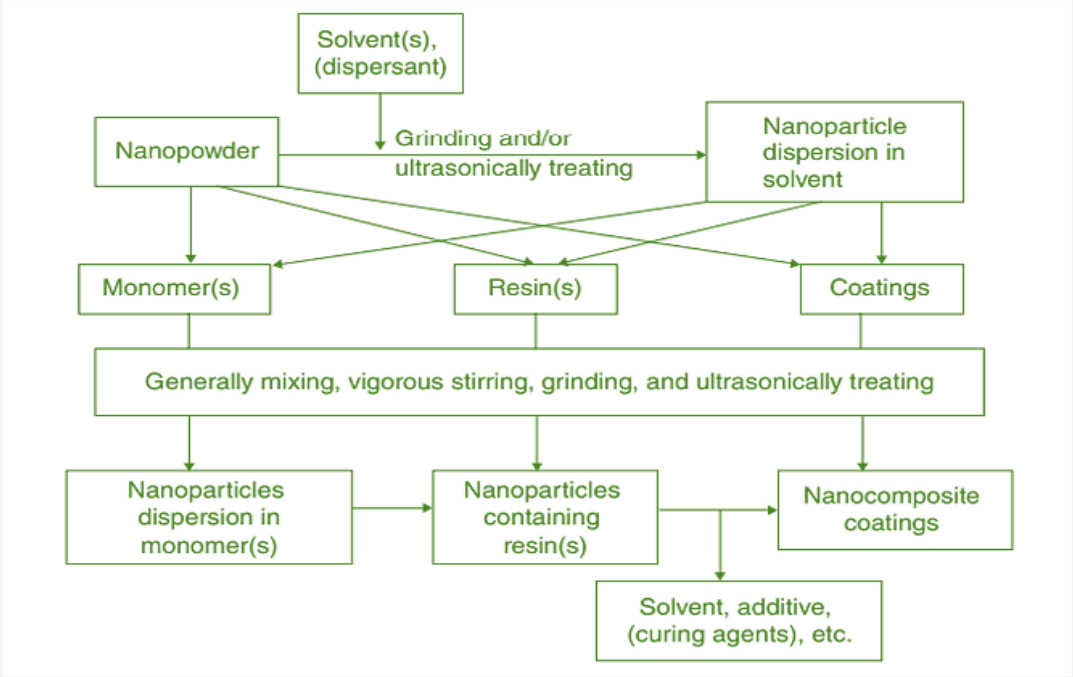


Figure 2.12 The possible routes for preparation of nanocomposite coatings from nanopowders.

Surface treatment of the nanosilica with coupling agents is one of the best methods to eliminate their negative effects on mechanical response [13,47]. They can be used in the form of liquid composites in many organic matrices in coating materials. They are favored in applications which require transparency and/or high abrasion resistance such as high-performance coatings or off-shore topcoats. 3-Glycidoxypropyltrimethoxysilane (GPS) is one of silane coupling agents used for surface treatment of silica nanoparticles. It was used as an organic binder, where GPS monomer has three methoxy groups for hydrolysis and one epoxy group for curing. The methoxy groups are hydrolyzed with silanol group and combine with the hydroxyl group of silica particle in solution. The organic chains react with the curing agents and form the crosslinked structures on the film surface. These reaction mechanisms were shown simply in Figure 2.13 [33].

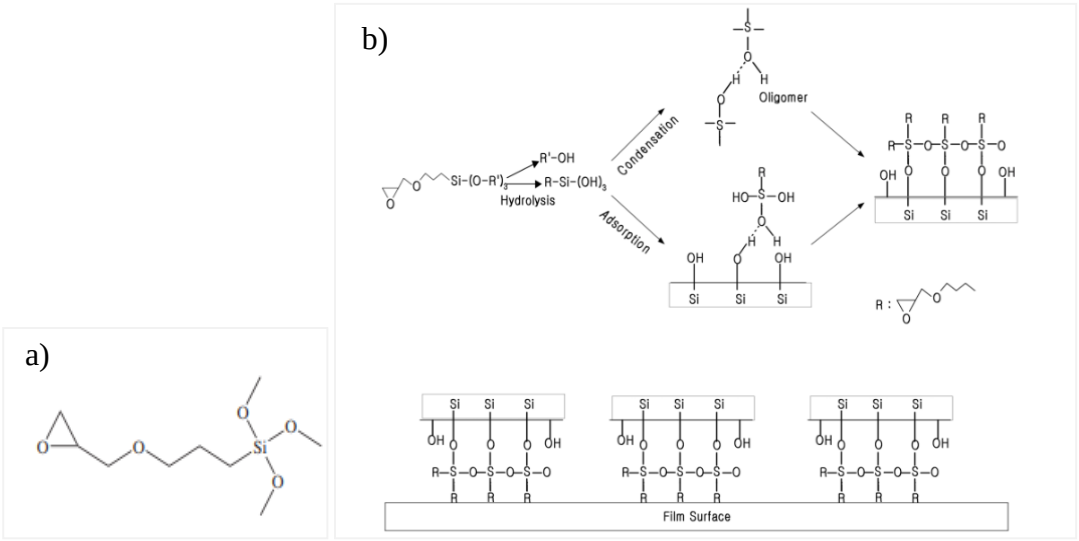
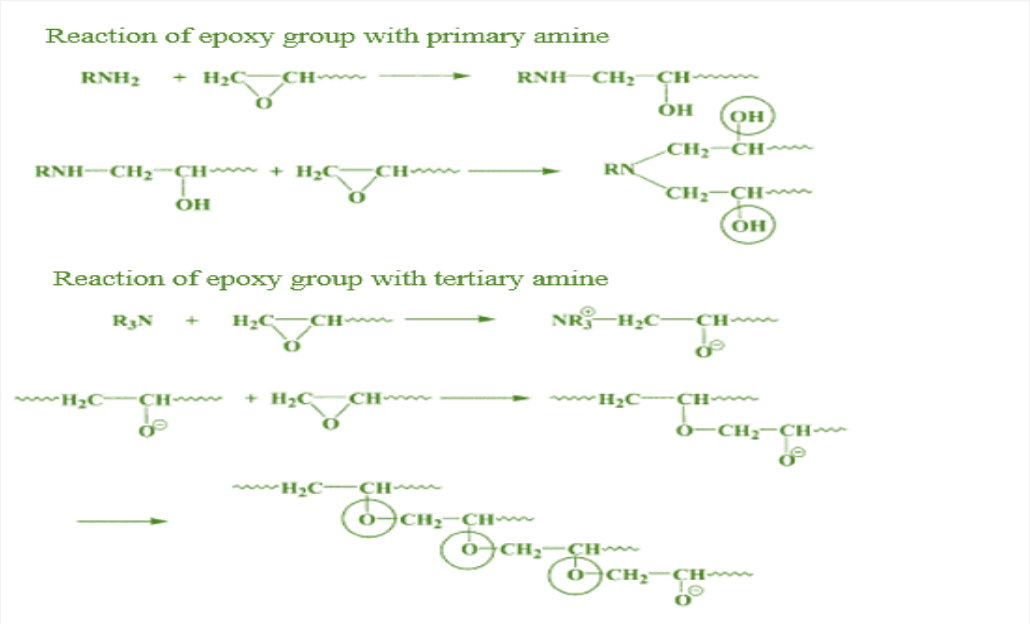


Figure 2.13 (a) Structure of 3-glycidoxypropylmethoxytriethoxysilane (GPS), $C_9H_{20}O_5Si$. (b) Its reaction mechanism of sol-gel method.

GPS/SiO_2 provide the best mechanical properties without decreasing the unique optical properties of inorganic materials. GPS addition improved coating abrasion resistance. The addition of GPS bonds particles together and fills the pores. These microstructural changes should enhance coating hardness and make the coating more resistant to abrasive penetration. Since the adsorption on the surface of silica particle was faster than condensation reaction at acid, GPS was adsorbed on the surface initially and then combined with GPS each other. The epoxy groups on the surface of the silica particle were large and the adhesive properties of the silica particles were better at strong acid, because the amount of GPS on the surface at strong acid was larger. Daniels and Francis reported GPS-modified colloidal silica coatings based on the addition of GPS to a

commercial acidic silica sol [11]. The GPS/silica weight ratio is crucial to both the critical cracking thickness and the abrasion resistance. The critical cracking thickness of the coatings increased dramatically when the weight ratio of GPS/Silica surpassed 0.4. Better abrasion resistance was obtained at a GPS/silica weight ratio of 0.5. Excess GPS content deteriorated the abrasion resistance of the coatings. The silica colloid composites ($GPSiO_2$) provide the best mechanical properties without decreasing the unique optical properties of inorganic materials. Furthermore, according to the amino groups of APTES molecules are able to react with the epoxide rings, forming secondary and then tertiary amines. Since only a portion of epoxide groups has to be functionalized with the aminosilane molecules, the tertiary amines can further react with the epoxide groups allowing the homopolymerization reaction to occur.



Scheme 2.2 Possible reactions of epoxy groups with amines (primary, secondary and tertiary).

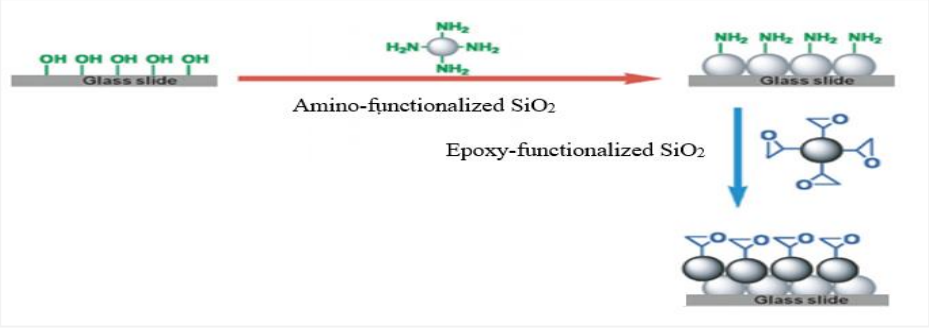


Figure 2.14 Schematic illustration of preparation of superhydrophobic surfaces on glass surfaces.

Vacuum-deposited aluminium or glass-like SiO_x films are traditional barrier layers [48]. Currently, there is a trend toward chilled and possibly modified atmosphere packaging. Consumers also demand high product visibility, as in food packaging. This requires a coating layer with good and sometimes selective barrier properties in combination with high transparency, good print quality, etc. Unfortunately, an aluminim layer is opaque and unsuitable for microwave heating. It also requires high energy during production. The SiO_x films are transparent or semi-transparent, retortable, and microwaveable, but have limited flexibility and crack resistance.

CHAPTER THREE METHODOLOGY

3.1 Materials and Methods

Silica nanoparticles (10-25nm) were obtained from sky spring nanomaterials, zinc acetate dehydrate were obtained from Lobal chemicals and 3-glycidoxypropyltrimethoxysilane (GPS) was obtained from chemo scientific. Acetone, n-hexane and methanol (97%) obtained from Lobal chemicals. Ammonia solution (30%), HCl acid (34.5%), deionized water and ethanol were used in this research. Commercial microscope glass slides of 25.4 × 76.2 × 1.2 mm was used as the substrate, and adhesive tape (PVC) was used for peel test characterization.

The synthesis of thin films on glass substrate involves the following three key steps: (i) substrate pre-treatment for good quality of films, (ii) preparation of coating solution for SH-silica, Nanosilica-zinc hybrid coating solution, and nanocomposite coating solution of nanosilica-zinc with GPS, and (iii) dipping and drawing the substrates in the prepared coating solution.

The microscope glass slides washed with detergent solution and ultrasonicated at 50^{o}C for 30min, then wash with deionized water, ethanol and acetone, then dried in oven at 80^{o}C for 20min. Solution of HCl acid, deionized water, ethanol and acetone were poured into a beaker containing cleaned glass slides which were ultrasonicaed at 50^{o}C for 30min, then dried in oven for 30min. The ultrasonic cleaner is presented in figure 3.1.

Figure 3.1. Ultrasonic cleaner.

3.2. Experimental Procedures

3.2.1 Preparation of SH-silica Suspensions

Weight of 0.5405g modified silicon dioxide particles with amino group were dissolved in 40ml of n-hexane for 60min at room temperature, and a few drop of HCl acid added into the solution, there were change in pH from 5 to 3. The Cleaned glass slides immersed in the prepared coating solutions for 15sec. After dip coating, the glass slides were dried in oven for 1hr at 100°C and finally the coated glass slides annealed at 400°C for 1hr.

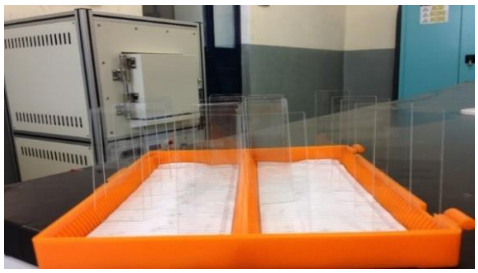
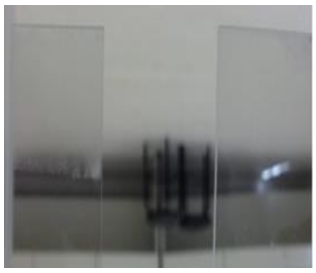
(a)  (b)  (c) 

Figure 3.2. (a) Pictures of cleaned glass slides, and (b) coating solution, and (c) coated glass slides.

3.2.2 Synthesis of Nanosilica-zinc Solution

40ml of n-hexane were used to dissolve 0.4695g of modified silicon dioxide particles with amino group for 60min at room temperature. On the other beaker, 0.086g of zinc acetate dehydrate dissolved in 5ml of methanol for 30min at room temperature. Dissolved zinc-methanol solution was mixed with Nanosilica suspension slowly for one hour under constant stirring, then few drops of HCl acid was added. Nanosilica-zinc solution were formed. Cleaned glass substrates were immersed in the solution for 15sec, and the microscope glass slides were dried at 60°C, and annealed at 300-400°C for 1hr.

3.2.3 Formation of Nanocomposite Coating Solution of Nanosilica-zinc with GPS

A multilayer approach was used to form nanocomposite thin films on glass slides, and functional groups of amino and epoxy with SH-silica, nanosilica-zinc and GPS brings a type of smart coating on glass surfaces.

20ml of n-hexane were used to dissolve 0.2512g of modified silicon dioxide particles with amino group (pH 5) for 45min at room temperature. On the other side, 0.2537g of silica

nanoparticles were functionalized with 0.5ml of GPS and 20ml of n-hexane over ultrasonication for 20min at 32°C. GPS having the low surface tension, have treated the surface of porous silica nanoparticles during ultrasonication. On the other beaker, 0.088g of zinc acetate dehydrate dissolve in 5ml of methanol for 30min at room temperature. GPS treated SiO_2 ($GPSiO_2$) solution were poured in SH-silica suspension, then it mixed with zinc-sol just after 25min. it took almost one hour to made perfect mixture of Nanosilica-zinc solution, then 0.5ml of GPS and 0.1ml of HCl acid were added. Silica nanoparticles with amino groups, silica nanoparticles functionalized by GPS, nanosiilica-zinc solutions with GPS altogether were formed nanocomposite. Thus, amino-functionalized SiO_2 and epoxy-functionalized SiO_2 were remained on glass substrates after dip-coating. Glass slides were cleaned by acetone, ethanol and distilled water respectively, and dried at 60°C for 30min. First, glass slides were coated by GPS using flow coating technique, then GPS coated glass slides stayed in vacuum oven overnight at 60°C. GPS coated glass slides were immersed in the solution of superhydrophobic silica-zinc with GPS for 15 sec, and the microscope glass slides dried at 60°C, and finally the coated glass slides annealed at 300-400°C for 1hr.

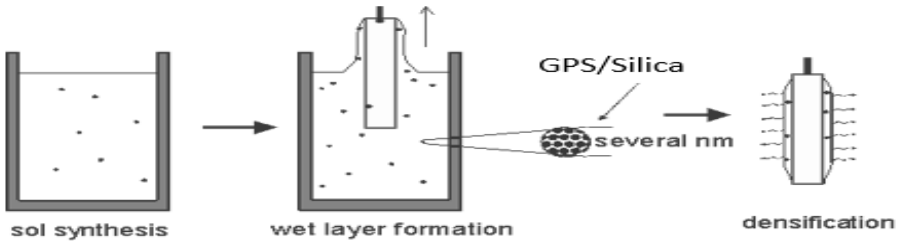


Figure 3.3. Sol synthesis and formation of thin film on glass slides.

The photographic images of superhydrophobic coating solution on stirrer, nanosilica-zinc hybrid solution before and during mixing, and after an hour of stirring; and nanocomposited coating solution ($GPSiO_2$ solution and 0.5ml of GPS) on stirrer are presented in figure 3.4.

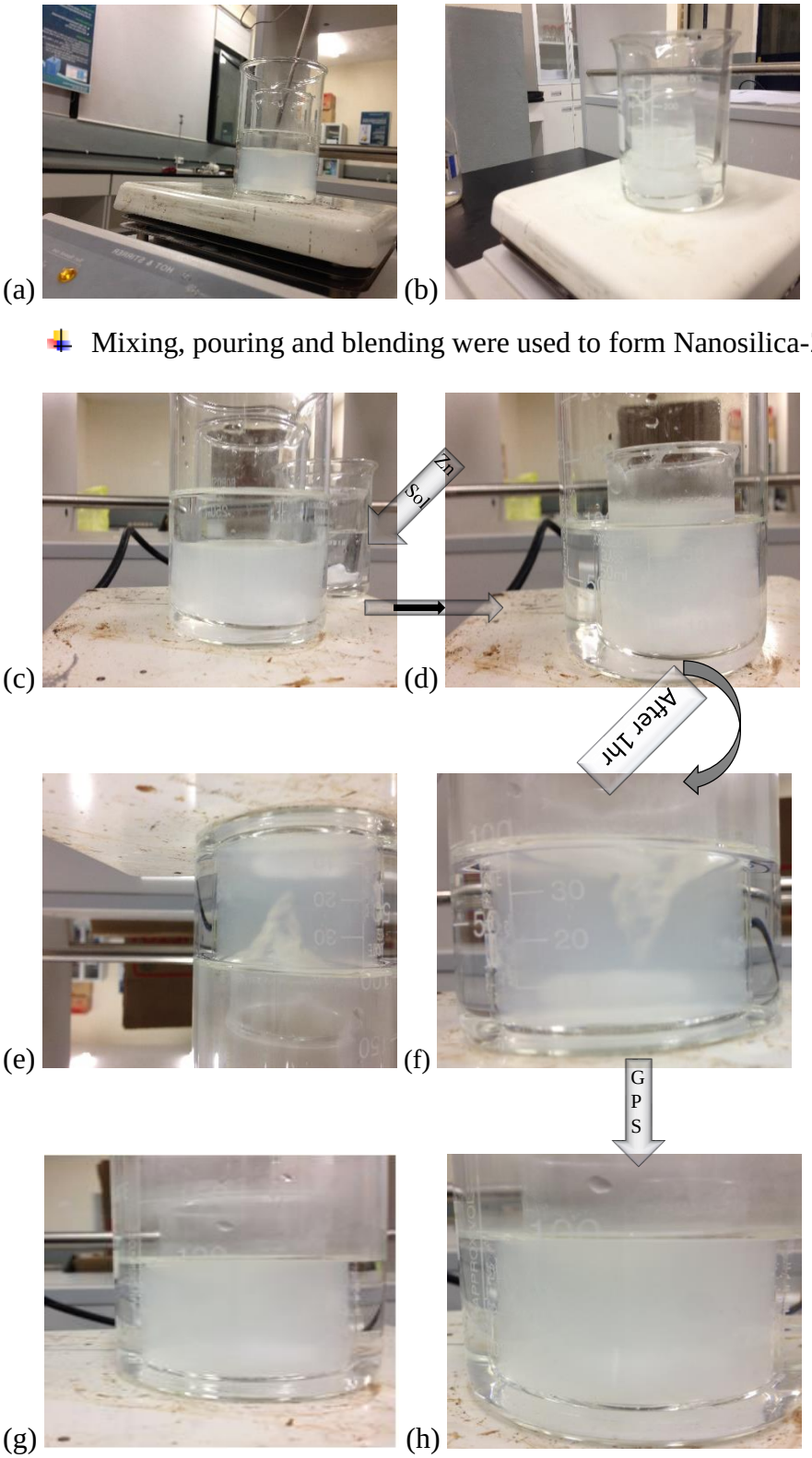


Figure 3.4. Shows pictures which were taken during synthesis in experimental session; (a-c) SH-silica sol preparation; (d-f) Nanosilica-Zn sol; (g,h) Nanocomposite suspension.

3.3 Characterization

Optical microscope were used to see the surface of SH-silica, Nanosilica-Zn hybrids, and Nanocomposited films on glass substrates. The optical transparencies of the coated substrates were measured by UV-Vis absorption spectrometer. Fourier transform infrared (FTIR) spectra of silica, SH-silica powders, and Nanosilica-zinc and Nanocomposites were measured on spectrum 65 FTIR Perkin Elmer in range 4000-400cm^{-1} using KBr pellets. The FTIR spectra were performed in order to confirm whether or not bonds were formed between the substrate and the formation of the coating on the substrate. Thermal analysis was performed by DTG-60H analyzer, Shimadzu Corporation, South Korea. The weight loss and thermal stability of SH-silica, Nanosilica-Zn, and Nanocomposited coating was checked by DTG-60H, heated to 700°C at 10°C/min in nitrogen atmosphere. XRD-7000S, Shimadzu Corporation, South Korea. X-ray target of Cu and 2Theta angle with continuous scan mode range of 10-80° at speed of 3°/min were performed to see changes in the structure of the bare substrate, substrate with the coatings like SH-silica, Nanosilica-Zn, and Nanocomposited.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Surface Morphology

Optical microscope was used to see the surface of films on glass substrates, and to see surface morphology. The optical micrographs of SH-silica, Nanosilica-Zn hybrids, and Nanocomposited films on glass substrates are shown in figure 4.1.

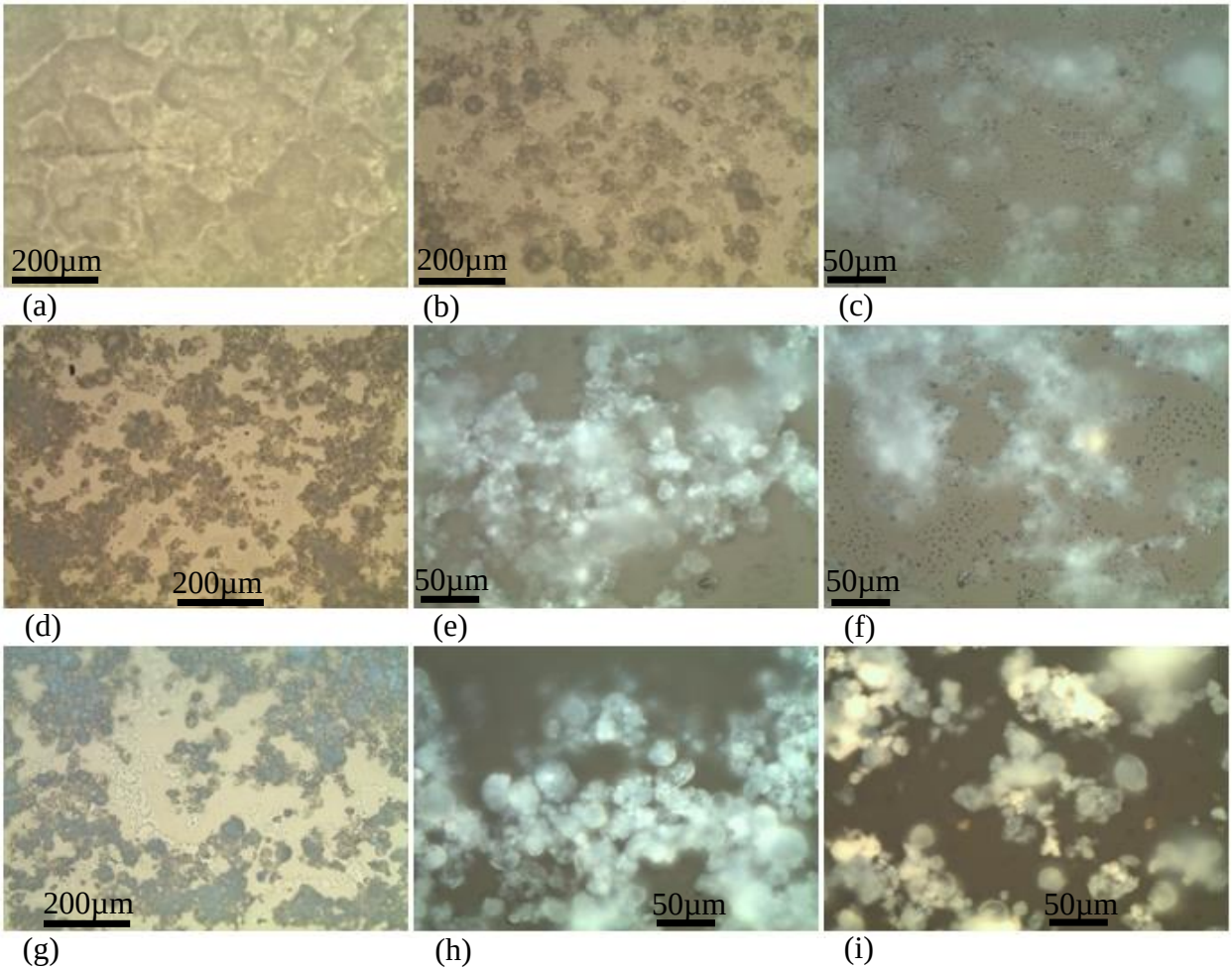


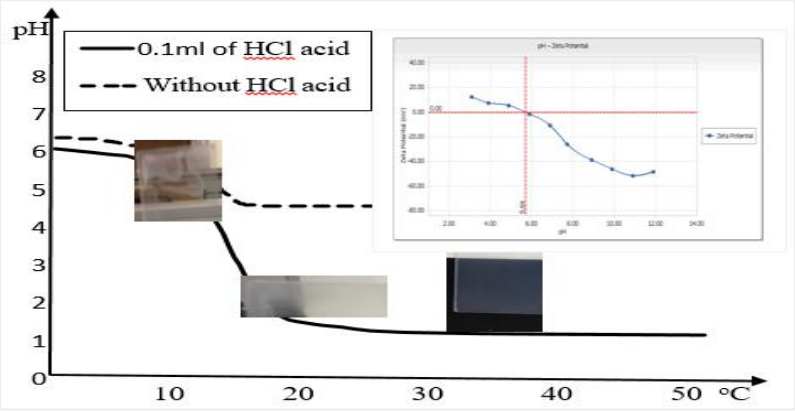
Figure 4.1 Optical micrographs of bare glass (a); SH-silica (b, c); Nanosilica-Zn hybrids (d-f); and Nanocomposited films on glass substrates (g-i).

The optical micrographs in figure 4.1 (b-i) show that there were small dots which indicates the agglomerated silica nanoparticles, and the nanoparticles easily caused aggregation on the

surface of coated glass slides. We have used two different magnifications (200µm and 50µm) to see surface and morphologies of SH-silica, Nanosilica-Zn, and nanocomposited films on different glass slides. The bare glass have an amorphous structure on the surface, but the morphology and the surface of the bare glass slides are changed to hierarchical structures because of the films formed by SH- silica nanoparticles, and their aggregation. Nanosilica-Zn was provided a high yield and more distribution of uniform structures, branched like structure and network like structure were formed. When glass slides have been coated with a multilayer approach by GPS and Nanosilica-Zn with GPS, nanocomposited films formed on glass surface, the functional groups were incorporated behind glass slides and Nanosilica-zinc molecules which keeps its steric hindrance all together and formed shiny surface with a nice looking collection of spherical shaped molecules and their aggregates. The presence of additional reactive groups allows the nanoparticles to be cross linked to provide increased stability or durability to the cured coating, and silica nanoparticles in the powder state aggregate due to their large surface areas.

4.2 Attachment of thin films on glass slides and interfacial region of thin films

In this work, zinc acetate were used to form a hybrid solution with silica. Solvated zinc were interacted with SH-silica when solvated zinc mixed with silica suspension, and nanosilica-zinc solution were formed after one hour of stirring, then Nanosilica-Zn films were remained on glass substrates after dip-coating. Thin film were formed a hierarchical structure on glass. The functional groups formed on glass substrates had a role of coupling agent; that is, they allow grafting of further molecules or groups which are initially incompatible with silica surfaces [49].



Scheme 4.1 Diagram of shift in pH varies the attachment of thin film on glass substrate vs temperature (^{o}C); inset shows the pH versus zeta potential values of silica nanoparticles.

Addition of 0.1ml of HCl acid in the coating solution caused more attachment on the glass surface when glass substrates were coated by dip-coating. HCl acid dissociated the molecules, and protons and hydroxyl ions could adsorb specifically, so HCl acid suppressed the formation of thin films on glass surface, and maintained deposition temperature could enhance to form a uniform hierarchical thin films on glass surface.

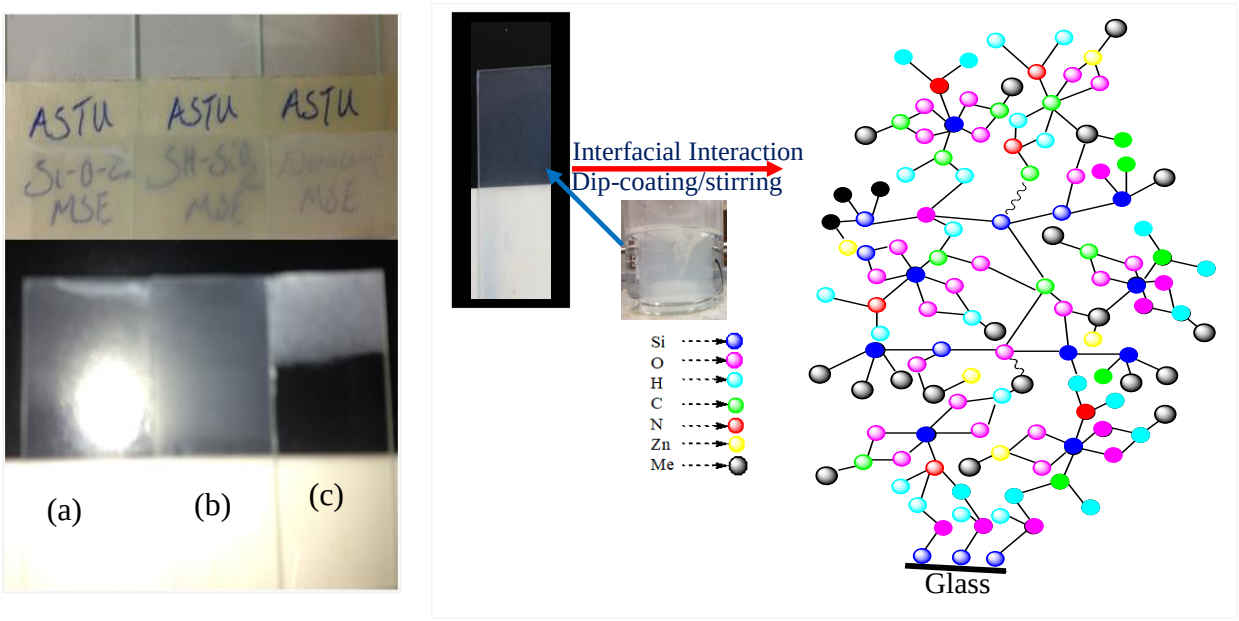


Figure 4.2. Nanosilica-zinc (a), (b) SH-silica and (c) Nanocomposited films formed on glass slides.

Scheme 4.2 The expected molecular model on the thin film.

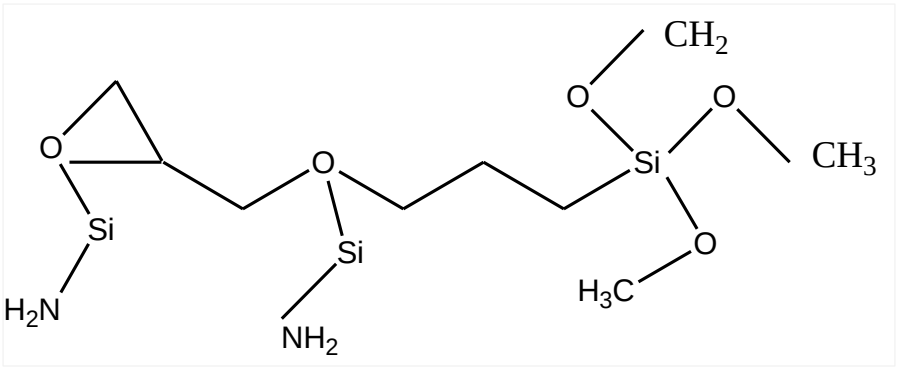


Figure 4.3 The skeleton or the structure of GPS with amino groups.

We were used FTIR to confirm the existence of functional groups and bonds or linkage formed between silanol groups, hydroxyl groups, zinc, siloxane and other functional groups.

4.3 Infrared Analysis Results

FTIR enhanced visualization of chemical information on functional groups present in the coatings. The FTIR spectra of the silica nanoparticles and the functionalized silica nanoparticles were recorded in the range of 400-4000cm^{-1} in KBr matrix. The FTIR spectra shown in Figure 4.4 consist of bands related to the stretching, vibrations, bending and deformation of both inorganic and organic structural units. The existence of amino and epoxy groups on the silica surface is also confirmed by FTIR spectra (Figure 4.5). The FTIR spectra of coatings were obtained by powders and detached films and spectra were recorded in transmission mode. Several characteristic peaks obtained within the range 400-4000cm^{-1} were arbitrarily plotted along the transmission axis and wavenumber axis.

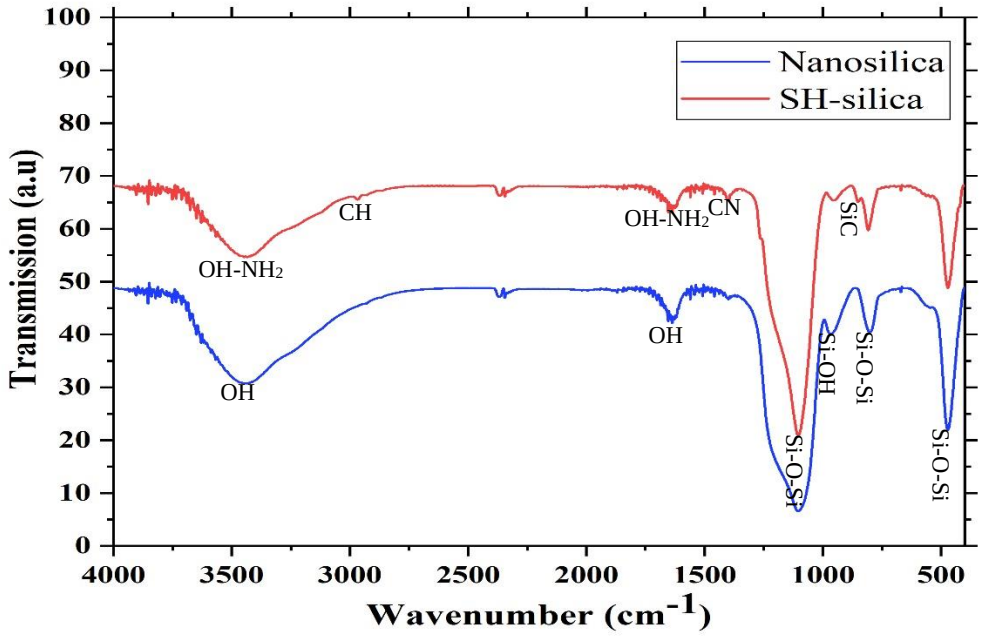


Figure 4.4. FTIR spectroscopy of Nanosilica and superhydrophobic silica particles.

As shown in figure 4.4, the presence of characteristic peaks of amorphous silica is observed. These peaks are found at 956cm^{-1} for Si-OH stretching, 1120cm^{-1} for Si-O-Si asymmetric stretching, 475cm^{-1} for Si-O-Si bending and 805cm^{-1} for Si-O-Si symmetric stretching. The absorption band around 3450cm^{-1} is a broad peak attributed to the O-H stretching vibration, it corresponds to stretching vibrations of surface O-H groups of the silica nanoparticles.

Furthermore, another absorption peak was observed at 1630cm^{-1}, attributed to the stretching vibrations of the hydroxyl group, this result confirms the existence of hydroxyl groups on the silica surface. The silanol group on silica surface allow to bond covalently with trialkoxyorganosilanes, and it was functionalized by amine and epoxy groups. The appearance of the new absorption peak at 2960cm^{-1} for C-H stretching, and Si-C at 856cm^{-1} and 1257cm^{-1}, cause reducing of the hydroxyl stretching vibration by OH-NH_2 at 3450cm^{-1} and residual amino group at 1630cm^{-1} form linkage with hydroxyl group which confirm the successful grafting on the surface of silica nanoparticles. The number of hydroxyl on surface is decreased because the surface of silica nanoparticles functionalized with amino group and other functional groups, such as C-H, SiC and CN stretching at 1396cm^{-1} [49]. Since the surface-to-volume ratio of nanoparticles is dramatically increased compared to bulk materials, the actual number of amino functional groups in the modified silica samples would be reasonably high enough. Due to the feature of amino group as a weak base and the possible aggregation.

The Si-OH groups formed during the hydrolyzing reactions would get covalently bonded with the glass substrate by the formation of Si-O-Si bonds. The Si-O-Si peak was observed in Figure 4.5, which indicated that the covalent bonds were formed between the glass substrate and the interfacial region. All films (SH-silica, Nanosilica–Zn and Nanocomposited) show the presence of Si–O–Si originated bands at 1120, 805 and 475cm^{-1} along with a peak at 856cm^{-1} for Si–C. During the decomposition of zinc acetate, it reacts with some of the residual silanol (Si–OH) groups, and some of decomposed Zn species bonded with silica (Zn–O–Si), it is shown also in the Figure 4.5. The stretching and vibration of Si-OH, Si-O-Si, and Si-O in IR region of 1000-800cm^{-1} caused for the formation of Si-O-Zn at 946cm^{-1}. The existence of bands near 1460 and 1384cm^{-1} associated with the C=O stretching vibration originated from the acetate group, silanol groups on silica nanoparticles have been consumed by acetate groups on zinc acetate [50].

The FTIR results suggest that the surface of the silica nanoparticles is terminated with -OH groups which act as anchoring points for the formation of covalent bonds with the hydrolysable groups and form linkage with other functional groups.

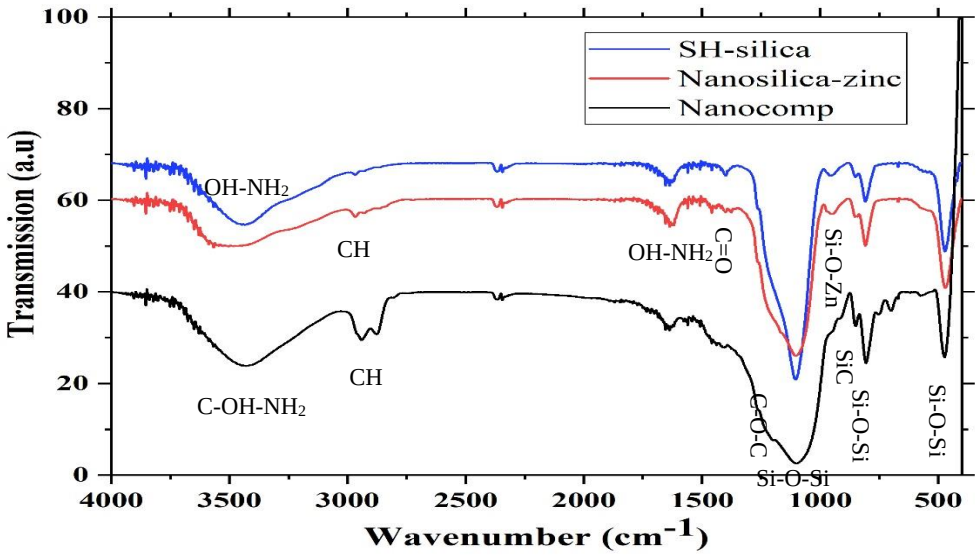


Figure 4.5 FTIR spectra of SH-silica, Nanosilica-Zn, and Nanocomposites.

Nanocomposited exhibited a very strong absorption peak at 1000–1300cm^{-1}, attributed to the stretching vibration of the Si–O–Si bond. This band overlaps between 1180 and 1240cm^{-1} corresponding to C–O–C connections. The epoxy ring appears towards 696 and 756cm^{-1}. The peaks at 2945cm^{-1} and 2870cm^{-1} which correspond to –CH stretching vibration. FTIR data also show that silanols are consumed by epoxy, amino and zinc acetate, and caused for formation of a broad absorption bands of hydroxyl groups (C-OH-NH_2) at 3427cm^{-1}. Hydroxyl groups are essential structural unit which can able to reform bonds with compounds with respect to compounds absorption bands, and form a linkage with functional groups. GPS is known as an organic binder, and caused more adsorption on silanol groups during surface functionalization. We have taken $GPSiO_2$ ratio to fill the pore space of porous silica nanoparticles by surface functionalization using ultrasonication. The increased adsorption have been observed for nanocomposited coating after drying may be related to drying-induced deposition onto the surfaces and GPS can also bind more hydroxyl groups on silica surface.

These results suggest that the amino and epoxy groups were successfully functionalized onto the surface of the silica nanoparticles (silanol), in Nanosilica-Zn, and in Nanocomposited films.

4.4 Thermal Analysis Results

The weight loss and thermal stability of SH-silica, nanosilica-Zn, and nanocomposited coating was checked by DTG–60H analysis as shown in Figure 4.6. Figure 4.6a shows the weight loss of the SH-silica when heated to 700°C at 10°C/min. The observed weight loss between 100°C and 700°C is related to organic group decomposition and silanol group dehydroxylation. There were a slight decomposition of amino groups at 500°C, the amount of weight loss is not very significant. SH-silica showed a weight loss of 5.173%. On the contrary the nanosilica–Zn shows a weight loss from 100°C onwards due to the decomposition of zinc acetate. Nanosilica-Zn showed a weight loss of 10.901% up to 700°C (Figure 4.6b). Zinc acetate decompose without any deterioration of the amino groups associated with silica. Figure 4.6c shows the thermal behavior of nanocomposited, it exhibits a three stage decomposition process. The first step of decomposition was observed below 200°C corresponding to the loss of adsorbed methoxy, ethoxy, and zinc acetate molecules, but the adsorbed molecules on the porous silica show slight decomposition because of silica's thermal stability behavior. The second decomposition was observed between 200°C and 400°C, there were further weight losses because of zinc acetate decomposition, amino groups started to decompose slightly, and also epoxy groups which causes disintegration and formation of truncated bonds like NH_2-SiO_2, Si-OH, Si-O-Si, Si-O-Zn, SiC. The endothermic peaks between 270°C and 300°C on the DTA curve indicates the decomposition for zinc acetate, amino and epoxy groups/components. The weight loss was also extends to 700°C because of disintegration, and it was observed on the third stage. Nanocomposited showed a weight loss of 32.815%. Thermal stability analysis was also observed in Figure 4.6e, as shown in the figure show the typical DTA profiles for SH-silica, nanosilica-Zn, and nanocomposited powders. Nanosilica-Zn and nanocomposited show an endothermic peak below 100°C, it indicates the presence of zinc. The DTA curve between 350-600°C shows the presence of organic groups. Above 600°C silica particles keep thermal stability of the samples, and we check out their thermal stability using muffle furnace up to 1000°C. Nanocomposited is exceptional because of disintegration happened at 270°C-300°C cause for formation of bonds like SiC. A broad exothermic peak at temperature 350°C and other small exothermic peak at temperature of 500°C indicate for the reformation of bonds after a slight decomposition of amino groups from silica surface.

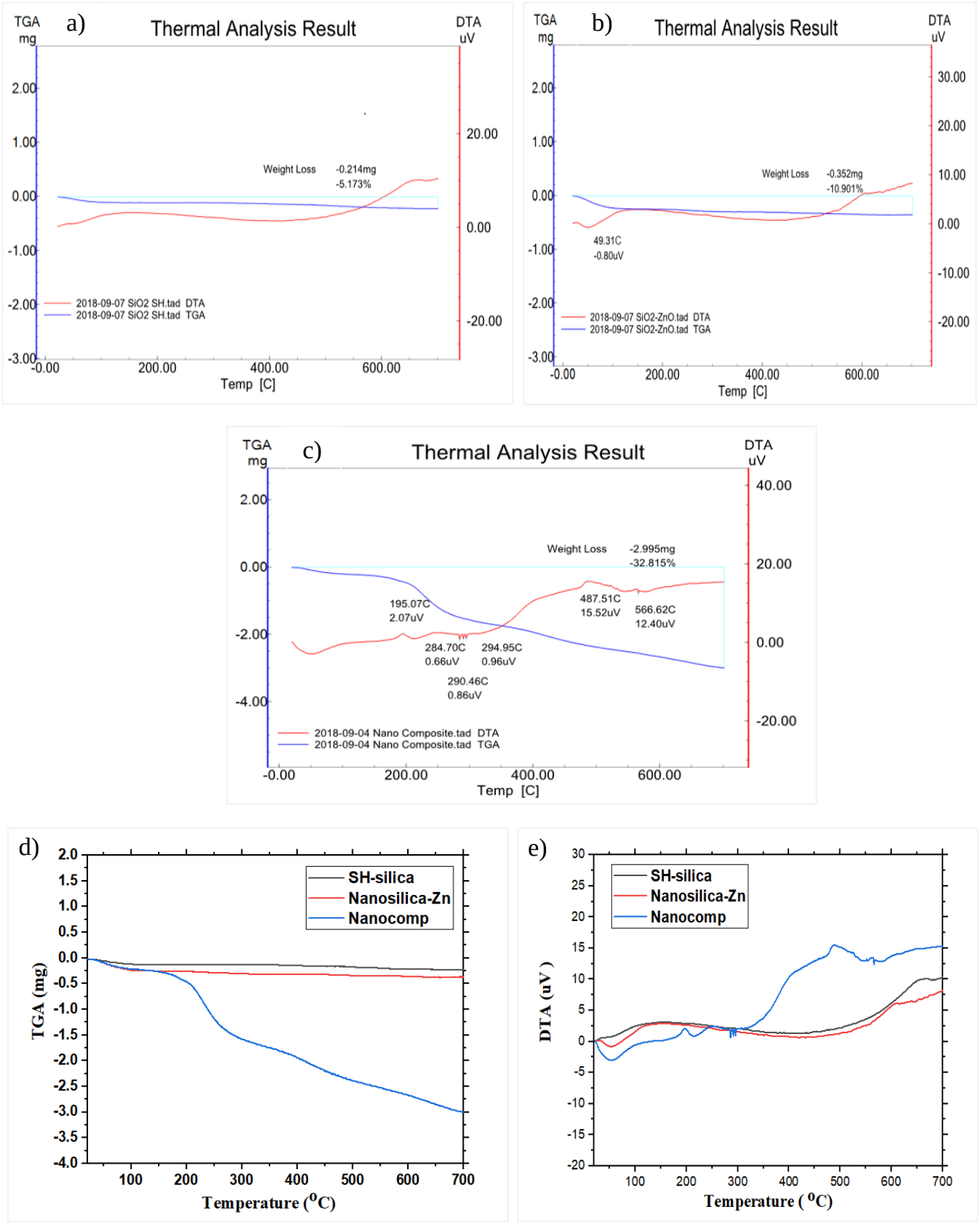


Figure 4.6. (a) TG-DTA curves of SH-silica, (b) Nanosilica-Zn, (c) Nanocomposites, (d) weight loss of SH-silica, Nanosilica-Zn and Nanocomposites, and (e) differential thermal analysis of SH-silica, Nanosilica-Zn and Nanocomposites.

4.5 X-Ray Diffraction Results

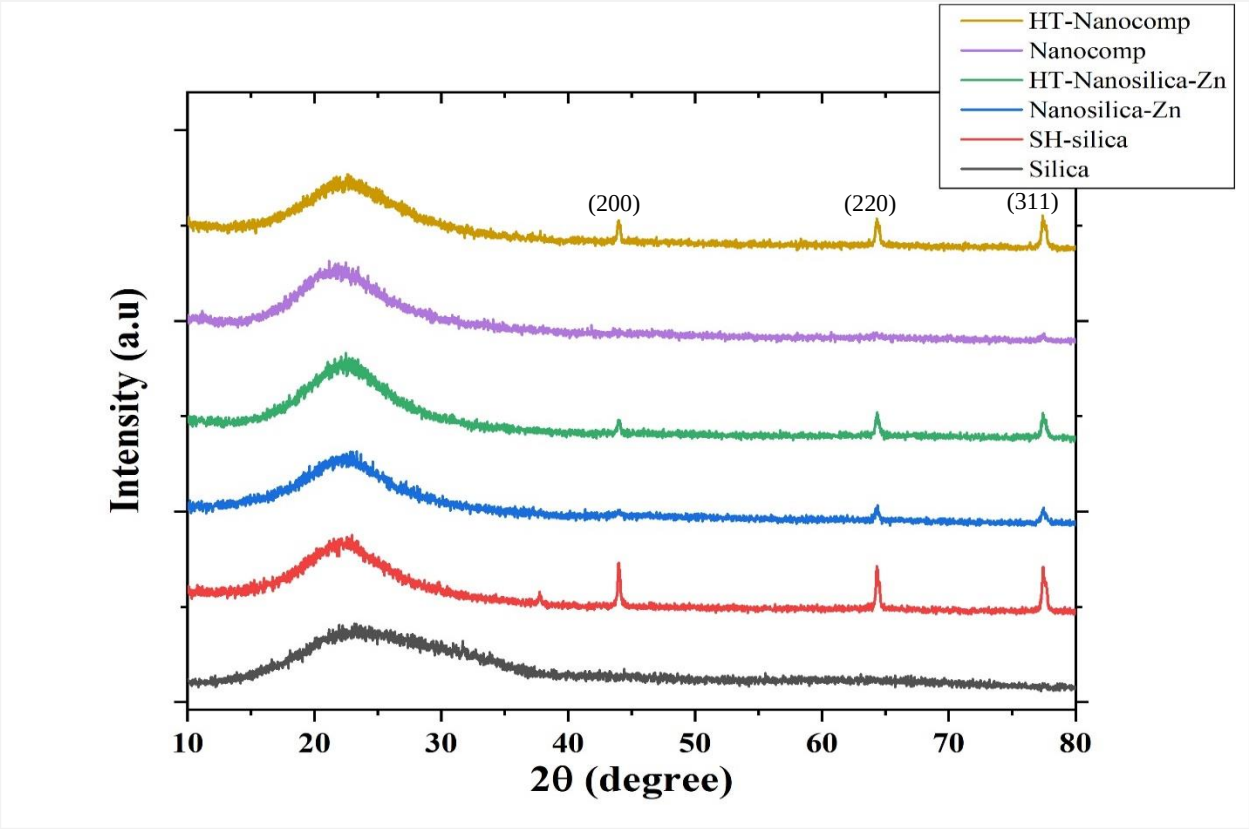


Figure 4.7. XRD diffraction patterns of silica, SH-silica, Nanosilica-Zn, Nanocomposites.

Silica particles have amorphous nature and characteristics, whereas SH-silica have surface modified silica nanoparticles with a single layer chain by an organosilanes molecules and amino group on silica surface, which forms a phase or structure of SiC (311) as shown in figure 4.7. In Nanosilica-zinc, the effect of coupling agent cause a hemispherical pointed tips (200) for surface modified zinc phosphate/silicate instead of hexagonal wurtzite structures. The Nanocomposited was also have amorphous nature because the porous silica particles were surface treated by GPS, and nanosilica-zinc solutions were also functionalized by GPS during nanocomposited formation. GPS undergoes hydrolysis reaction with its three hydrolysable groups and its epoxy ring for final ramification, and binds with silica, it gives an amorphous characteristics, but peaks are formed at (220) and (311) for SiC after annealing as shown in figure 4.7. During surface functionalization process, hydrogen bonding and covalent bonds remained inside bridge, and Si-C were formed. HCl acid was dissociated coating solution, and suppressed formation of thin films on glass slides.

4.6 Optical Transparency Result

Optical transmission properties of SH-silica, Nanosilica-Zn hybrids, and Nanocomposited films deposited on glass substrates were measured by spectrophotometer analyses over the spectral range of 300-1100 nm and compared with uncoated glass sample. Results are shown in Figure 4.8. Coated glass substrates became semi-transparent compared to bare glass, but SH-silica coatings and Nanosilica-Zn hybrid coatings have better transmittance values in visible-nir region compared to nanocomposited thin films on glass, and heat treated Nanosilica-Zn have lower transmission than not heat treated Nanosilica-Zn below 360nm. Nanocomposited coatings have lower transmission below 360nm. The effect of zinc incorporation in Nanosilica could be coming from the property of zinc oxide UV protection. Heat treated nanocomposited film have higher transmittance than nanocomposited which is not heat treated.

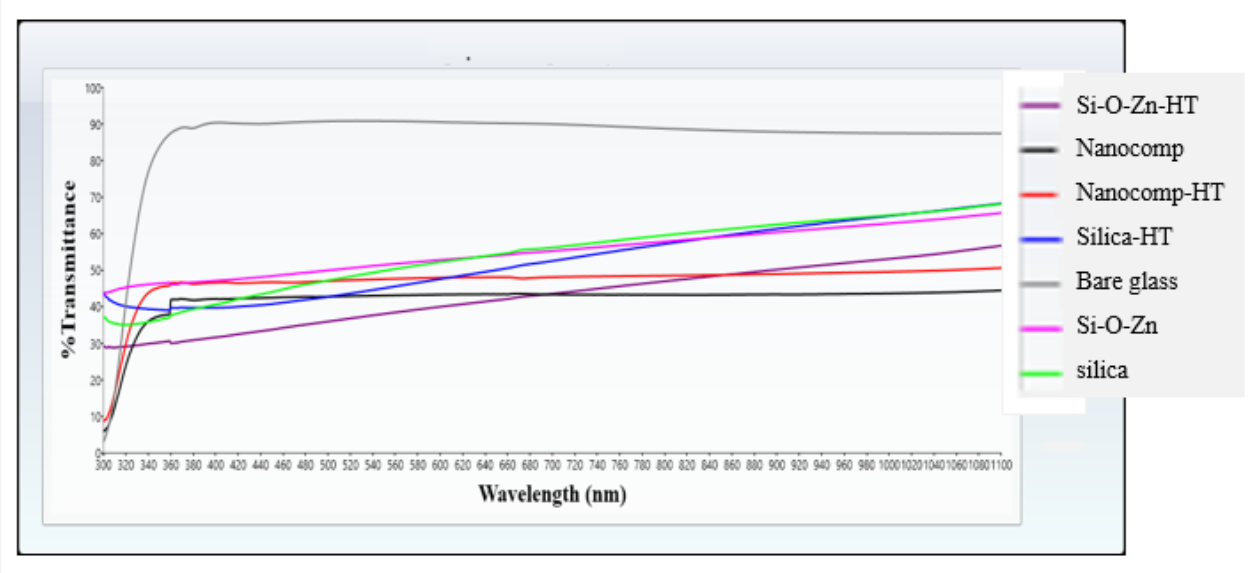


Figure 4.8. Optical Transmittance spectra values of bare glass, SH-silica, Nanosilica-Zn hybrid coating, and Nanocomposite thin films.

The hydrophobicity and optical transparency are competitive properties from viewpoint of surface roughness. The roughness induces scattering of light and decreases intensity of transmitted light.

4.7 Peel Test Result

We have used the gravitational force to carry out a peel test characterization, which is shown in figure 4.9. The obtained results are presented in figure 4.1.

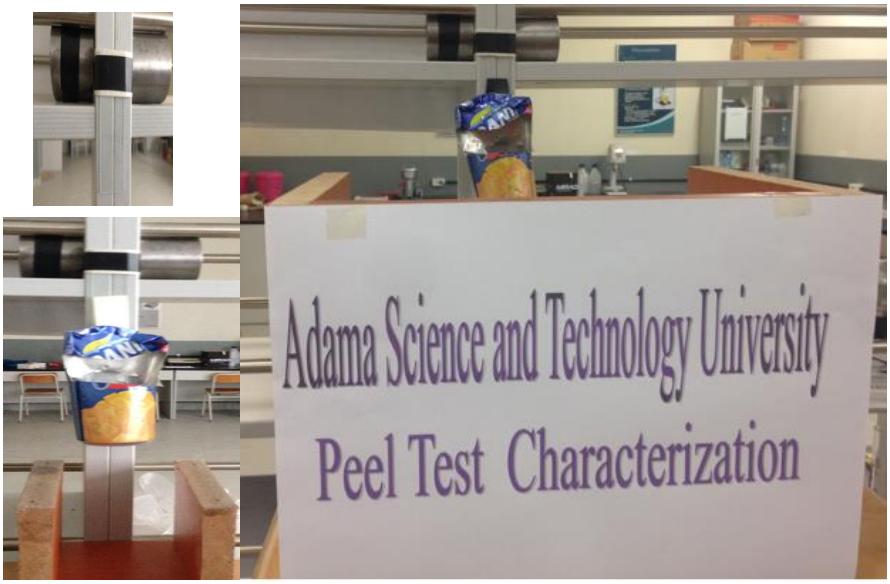


Figure 4.9 Pictures were taken during peel test characterization in ceramic lab of Materials Science and Engineering department.

Type of sample (film)	Required weight (kg) for peeling	Force (N) needed to peel films from glass slide	Weight loss (%) from glass slide
SH-silica film	0.1586	1.55	0.32
Nanosilica-Zn film	0.1711	1.67	0.15
Nanocomposite film	0.219	2.14	0.06

Table 4.1 Results obtained from Peel Test Characterization.

CHAPTER FIVE CONCLUSION

The structure of interfacial network or region by GPS coated glass substrate with SH-silica-Zn solution were form nanocomposited thin films on glass substrate by dip-coating and flow coating process. The established results show that the films were formed the desired structure with functional groups on nanosilica-zinc, and GPS formed a hierarchical homogeneous layer on glass substrates, even the samples were characterized after three months. The thin films on glass substrate were functional, and keep their structure based on reports or established results in this research.

The suspension pH, deposition temperature, and amounts of zinc acetate and GPS were critical processing parameters for controlling the coating formation on glass. Addition of GPS as an organic binder in the silica solution caused the decreasing of voids on the film surface at strong acid. GPS cause more adsorption of the organic compounds on the surface of silica particles and glass surface.

Nanosilica was provided the topography of surface roughness on the coated glass surfaces which are semi-transparent compared to bare glass. Amino and epoxy group were combined to form a multifunctional coating on glass.

The results obtained are not complete, and further experimental works and remained results are expected. To accomplish the process completely, the formed interfacial network or region on glass slide have to be etched by an organosilane solution, coupling agent like TMCS or HMDS.

GPS coated glass substrate, modified silica nanoparticles with amino groups and zinc acetate provide a clean source of coating on glass substrates, and other substrates.

In this research, we had tried to form a new material or coating on glass substrate, and it will opens up to do more research like microorganisms can grow in voids and spaces or they can live in smaller habitat for their surviving, and it makes difficult to clean and avoid microorganisms in medical centers, and affected rooms also. Infiltrating porous particles and substrates with nanocomposite coating to fill voids, and form a high gloss surface finishing. The works had done in this research may give a clue to avoid microorganisms with the antibacterial property of zinc or preventing a space for the growth of microorganisms, so it will be a good research idea.

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