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Study on Improvement of Self-cleaning TiO_2 based coatings on different building materials

A Thesis

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By

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بسم الله الرحمن الرحيم

وَيَسْـَٔلُونَكَ عَنِ ٱلرُّوحِۖ قُلِ
ٱلرُّوحُ مِنْ أَمْرِ رَبِّي وَمَآ أُوتِيتُم
مِّنَ ٱلْعِلْمِ إِلَّا قَلِيلًا ٨٥

صدق الله العلي العظيم

سورة الاسراء آية (85)

The Certificate of Supervisors

I certify that this thesis entitled " **Study on Improvement of Self-cleaning TiO_2 based coatings on different building materials** " was Prepared by (**Fatima Shaker Moder Abbas**) under our supervision at the Department of ceramic and building Materials / College of Materials Engineering / University of Babylon in partial fulfillment of the requirements for the degree of Master in ceramic.

Signature:

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Date :   /   / 2022

Dedication

To my Family for their endless love ,Support and encouragement

Fatima

2022

Acknowledgments

First of all, profusely all thanks be for ***ALLAH*** Lord of all creations who enable me to achieve this work.

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Abstract

In recent few years, there is an increment in study into the application of nano-titanium dioxide coatings due to its distinguished properties in various environmental applications and energy conservation such as engineering surface of self-cleaning. This study is an attempt to improve the mechanical and self-cleaning properties of brick, cement mortar and thermostone surfaces by using spin coating technique, composite coatings containing titanium dioxide with ceramic additives such as bauxite, calcite $CaCO_3$ and Teflon addition.

Polystyrene (PS) has been used dissolved with N,N-Dimethylmethanamide (DMF) was used as a basis material in different concentrations (0.01,0.05,0.1,0.15,and 0.2 g/mL) with different proportions of titania (0.001,0.002,0.004,and 0.006 g/mL).The coating was done with conditions (2000 rpm for 15 sec) and the coated surfaces were treated in an oven at 100C^{o} for 24 hours.

Tests were used to characterize the additives and to evaluate the structure, surfaces and physical and mechanical properties of the coatings such as X-ray diffraction, scanning electron microscopy, hardness test, contact angle, adhesion test, thickness test, roughness test and topographic test using atomic force microscope.

In general, the results proved obtaining porous and uniform self-cleaning composite coatings of thickness , hydrophobic and self-cleaning in terms of contact angle . generally , the values of hardness and contact angle improved after adding bauxite (1g) and calcite (1g) with titania and the addition of calcite was effective in improving the angle, while adding bauxite was effective in improving the surface hardness. The best results for contact

angle was observed in brick surfaces and for hardness, it has been observed on cement mortar surfaces.

The addition of Teflon did not achieve the expected results due to the surface topography, which was characterized by irregularity and the appearance of lumps of additives on the surface. The results proved the success of the research in protecting the surfaces of bricks, cement and thermostone with self-cleaning composite coatings of good hardness, which will maintain their environmental cleanliness and aesthetics and contribute to protecting them from scratching and external weather conditions.

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Table of Abbreviation or Symbols

Abbreviation or Symbol	***Meaning***
TiO_2	Titanium dioxide
$CaCO_3$	Calcium carbonate
PTFE	Polytetrafluoroethylene
PS	Polystyrene
DMF	N,N-Dimethylmethanamide
XRD	X-ray diffraction
SEM	Scanning electron microscope
AFM	Atomic force microscope
FTIR	Fourier-transform infrared spectroscopy
CA	Contact angle

1-1: *Preface* :

Engineers and nanotechnology have recently become more interested in hydrophobic surface treatments as a means of obtaining materials with improved qualities over their basic components.In nature, there are various forms of superhydrophobic surfaces, such as the lotus leaf and the desert beetle, that have minimal adhesion qualities. A substance's hydrophobic quality is its ability to repel water. It describes a distaste for water and also a propensity to reject or not absorb it.Hydrophobic molecules are a type of non-polar molecule that tends to stick together.Oils and fats have a feature known as hydrophobicity.Hydrophobic substances rarely dissolve in the water and any other solution that is primarily aquatic [1] .

Hydrophobic materials are often employed in chemical separation operations to isolate oil from water, manage oil spills, and separate non-polar chemicals off polar compounds. Hydrophobic surfaces are employed in corrosion resistance because they reduce corrosion rates.Hydrophilic, or water-loving, is the polar opposite of hydrophobic.On the same molecule, surface-active chemicals have both hydrophilic and hydrophobic groups.Hydrophobicity is another term for hydrophobic [1]

The capacity of these surfaces to keep water from spreading out when in touch with them is the foundation for superhydrophobic self-cleaning.A water contact angle of about 180 degrees reflects this **[1]**.

Our research focuses on creating hydrophobic coatings that are almost natural in appearance and have the desired qualities.

1-2:Surface engineering of building materials :

Surface engineering is among the most important ways to distinguish engineering products in terms of quality, performance, and life-cycle cost. Engineering materials' surface qualities have a huge impact on component workability and life, thus they can't be disregarded in design [1,2].

Some disasters and tragedies have occurred in buildings, factories, cars, skyscrapers, and other items as a result of faults related to wetness, corrosion, fouling layer contamination, water entering for electronics equipment, fog, and UV light.However, because no one substance has the capability to gain the influence of physical attributes, such difficulties must be corrected and overcome.As a result, coating materials with mixing and composite materials can provide a variety of capabilities to meet the ideal requirements for a self-cleaning item coating material [1,2] .

Researchers have taken into account the unique qualities of hydrophobic coating to solve problems with a variety of ceramic building materials, including (brick ,cement mortar ,thermostone).Coating was used to create hydrophobic, self-cleaning, mechanical properties. This type of treatment aids in corrosion resistance, anti-wetting, and self-cleaning. **[1,2]**.

Concrete, brick, and thermostone are the most often used building materials in Iraq, where they have been utilized to construct building walls and roofs in recent decades due to their great compressive strength as well as other excellent properties [2].

1-3: Objectives of the present study :

In view of the issues and challenges mentioned above ,this research is aimed at improving of TiO_2-based self-cleaning coatings on building materials using modification powders ($CaCO_3$, Bauxite , PTFE). And because of the above reasons, the substrates (brick ,cement mortar ,thermostone) has been chosen. These objectives are to be accomplished through the following procedures :-

1- Preparation of composite coatings solution to be coated on the substrates surfaces (brick, mortar and thermostone) .
2- Manufacture of self-cleaning hydrophobic coating contain polystyrene and nano-TiO_2 and the additives ($CaCO_3$, Bauxite ,PTFE).
3- Examining the coated samples by different tests; contact angle, thickness measurement, hardness, pull-off, roughness ,AFM and SEM.

2-1 : Surface Engineering:

Surface engineering refers to a wide range of technologies designed to modify the surface properties of metallic and nonmetallic components for decorative/or functional purposes. These surfaces are used to enhance the functionality and life of an engineering component. They can also offer distinct properties depending on the techniques being used.[3]

A general strategy to improve the performance of an engineering component is to use engineering surfaces.Engineering surfaces can be used to increase corrosion, wear resistance, and oxidation resistance. They can also help to maintain the electrical and thermal conductivity of an engineering component.[3]

The method of surface engineering are separated into two categories: surface preparation methods, which include the preparation of surface ingredients with cleaning; and surface treatment methods, which involve the treatment of surfaces to achieve the desired qualities. Surface modification can be accomplished through a variety of processes that alter several aspects of the surface, including charge, biocompatibility, reactivity, surface energy, hydrophilicity, and roughness [4-5].

Surface engineering has a huge impact on our daily lives, since it has resulted in:

- the ability to make tools, machine components, and entire appliances out of materials with lesser properties, which are usually less expensive, and improve their surface characteristics.

- Durability of work of equipment, machine parts, and appliances is improved, and breakdowns are reduced.
- Reduce the frequency with which utilized equipment and machine elements are replaced, and also the regularity with which service improvements are performed.
- Enhance the material's tribological life.
- Air degradation is reduced, mostly as a result of reduced energy consumption[3].

The classification of coatings by manner of production is shown in Figure (2-1)

Coating is a type of surface engineering that involves overlaying the surface of the material, also known as the substrate.The coating can be applied for ornamental, practical, or both purposes [6].

Painting and applying organic (plastic and rubber) coatings and linings are two from the most used surface engineering techniques.There are many different types of paints or linings that operate as a protective layer to insulate the substrate from the surroundings.Sheet linings, which are often made of the vinyl or vinylidene chloride family, are one type of covering that can be attached to a covered surface or floated as a bag within a tank [7].

Paints, are liquid-applied (typically by brush, roller, or spray) coating and lining materials, are the most commonly used organic materials .[7-8]

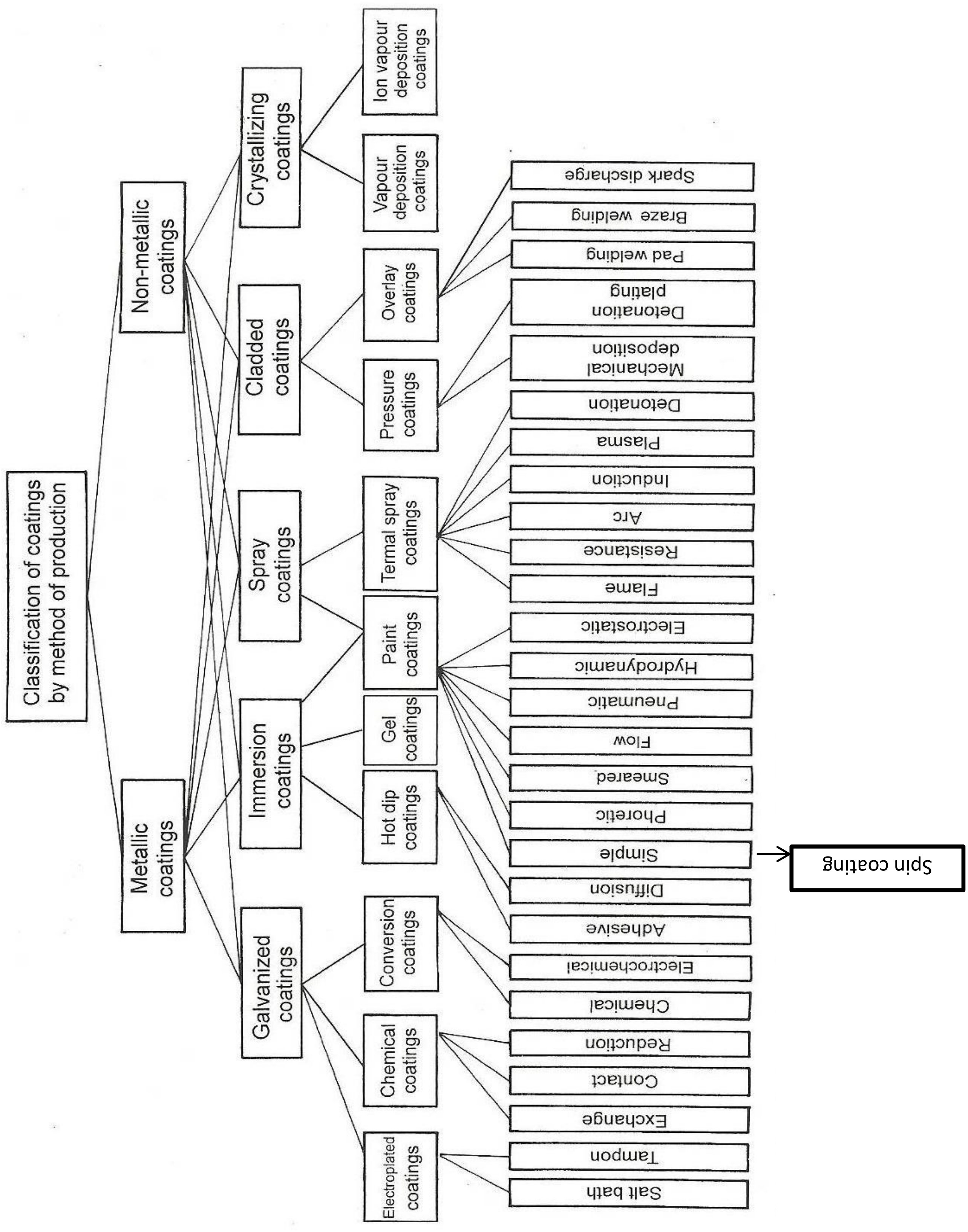


Figure (2-1): The classification of coatings by manner of production[6]

A resin, a solvent, pigments, and other extraneous substances are the four basic components of liquid-applied surface coatings.The resins, often known as binders, are classified according to their molecular kind .based on the structure of the organic compound that makes up the resin.Water or an organic solvent can be used as the solvent [8-9].

Figure (2-2) shows the classification of coating method according to the physical state of the coating material.

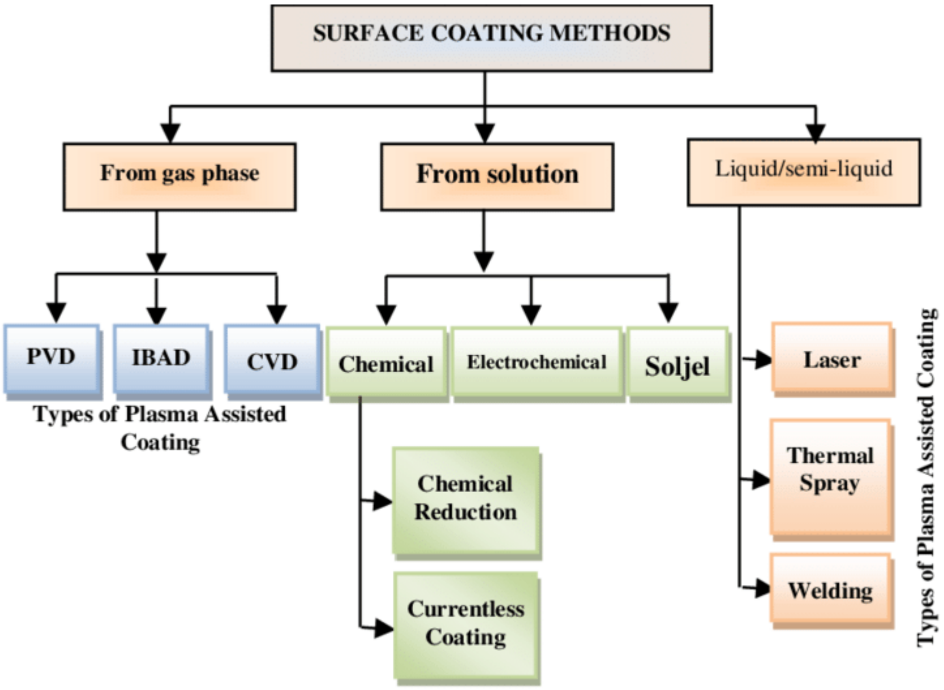


Figure (2-2): Coating categorization based on physical qualities of the substance to be coated.[7]

2-2 : Self-cleaning surfaces:

Any surface that can easily remove dirt or bacteria is referred to as a self-cleaning surface. This ensures that when it rains, for example, the rainwater automatically clean the glass windows without any need for external assistance. Super hydrophilic and super hydrophobic surfaces are the two types of self-cleaning surfaces [10].

2-2-1 : Self-cleaning through super hydrophilicity

Water spreads entirely across the super hydrophilic surface, generating a very thin layer of water.The term is most commonly applied to surfaces having water contact angles of less than 5 degrees.Whenever a thin sheet of water rolls off the surface, it cleans it by mopping up any loose particles.Combining hydrophilic surface characteristics with surface roughness is one technique for creating super hydrophilic surfaces [11]. the differences between hydrophobic and hydrophilic coatings are shown in table (2-1).

2-2-2 : Self-cleaning through super hydrophobicity

High water contact angles are used to produce superhydrophobic, self-cleaning surfaces.On the surface, a drop of water is practically spherical and easily rolls away, carrying dirt with it. The combination of hydrophobic surface composition and surface roughness results in super hydrophobicity. Super hydrophobic surfaces have water contact angles greater than 150 degrees and minimal contact angle hysteresis [12].

Table(2-1):the differences between hydrophobic and hydrophilic coatings [13]

Hydrophobic Coatings	Hydrophilic Coatings
Repel water molecules	Attract water molecules
Nonpolar	Polar
High contact angle >90°+	Low contact angle <10°
Can also repel oil	Can be washed away with water

2-3: Surface Wettability :

Surface wettability refers to a solid surface's ability to bond or (connect) with a liquid, allowing it to flow freely and fully across it. Surface wettability is a key property of substrate-coating adhesion; for example, high wettability leads to better substrate-coating adhesion [14]. In generally, it has contact angles for various forms, as shown in Figure (2-3), which depicts the geometry of four surfaces, and the engineering balance among these four surfaces is given by Young equation [15]:

$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$ ……………..….. (2-1)

Where γ_{LV} , γ_{SV} , and γ_{SL} indicate the(liquid-vapor, solid-vapor, and solid-liquid) interfacial tensions, respectively, and where (90o) represents wettability and (>90^o) represents hydrophobicity, (S, L, V) denotes (vapor, liquid, and solid) accordingly, and (θ) indicates the contact angle [15].

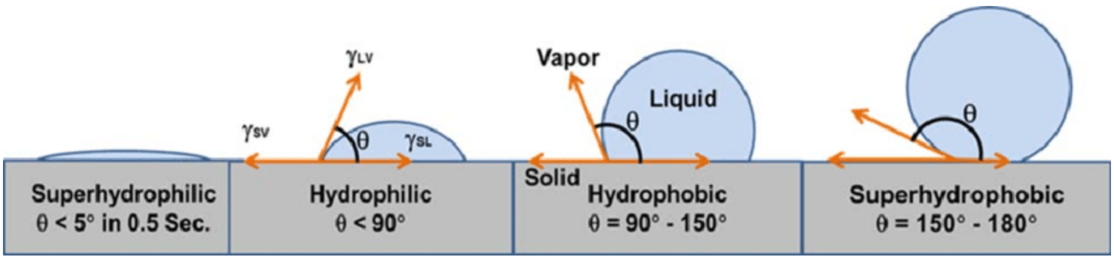


Figure (2-3) : Contact angle sections and ranges.[16]

2-4: Hydrophobic coatings:

The expression "hydrophobic substance" comes from archaic Greek and means "having a fear of water." It is made up of the words Hydro "water" and Phobicity "fear," and describes the physical qualities of a material that can resist a certain quantity of water [17].

Water resistant is an inaccurate term for hydrophobic coatings because water molecules are hydrophobic. Coating is faintly engaged, rather than repelling by coating [18]. The hydrophobicity of a solid surface is a critical quality for a variety of commercial uses, and it is determined by both the chemical composition of the surface and the geometrical structure of solid surfaces. Reduced dirt retention, self-cleanability, enhances humidity and oxidation resistance, and increased coating and substrate life expectancy are all advantages [19].

2-4-1:Coatings methods:

As indicated in table(2-2) [19], there are many different types of hydrophobic coating manufacturing procedures, including sol-gel, spray, dip, electrospinning, and electrospray. [20-21].

Table (2-2): Other hydrophobic coating techniques. [19]

Method	*Properties*	*Condition*
Sol-gel	Could combine different properties at one step; Easy to operate; Homogeneity of product at molecular level	Shrinkage during curing; Instruments should suitable for alcohol; Lack of durability; Impact handle property; Degradation of the carrier
Sputtering	Fast deposition; Take place at low temperature	Poor adhesion as no chemical bonds.
Hydrothermal	Same as sol-gel method	Same as sol-gel, method More energy consumption
Dipping	Easy to prepare , fast , low cost , less tools	Viscosity and the rheology of the paint , Rate of evaporation of the solvents, Immersion rate and shape of the parts.

2-4-1-1: Spin coating technique:

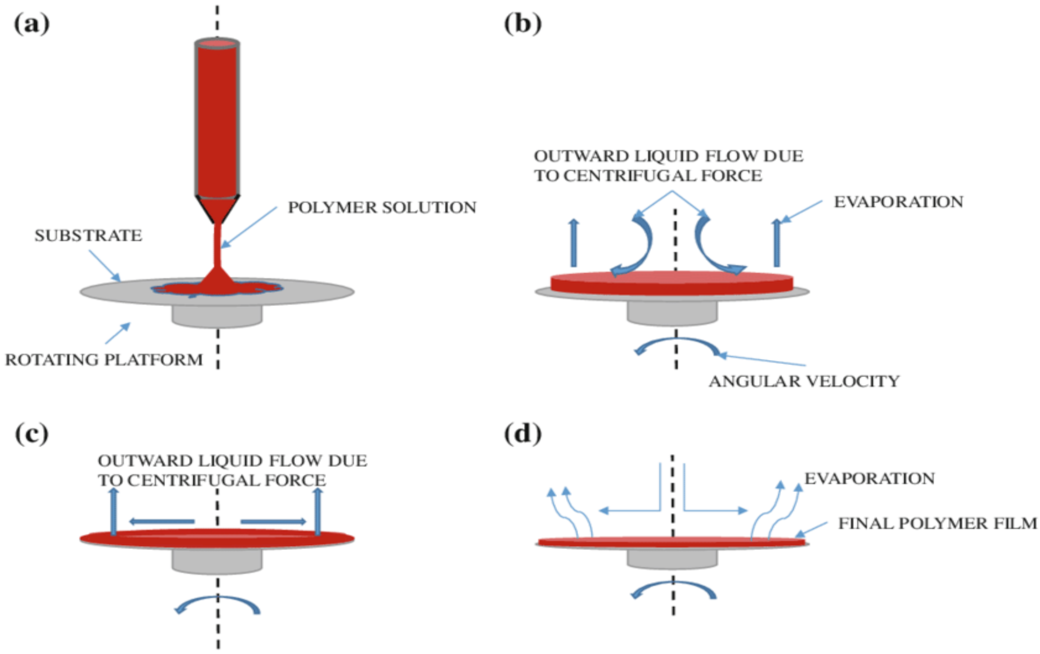
Spin coating was used for the creation of thin film coating layer for many years. Placing a tiny quantity of liquid resin in the center of a surface and spinning it at a high speed (typically around 3000 rpm) is a fundamental procedure[22]. Because of centripetal acceleration, the resin will spread to and eventually above the edges of the substrate, leaving a thin film of resin on top of the surface.The final film thickness and other parameters are affected by the nature of resin (drying time, viscosity, surface tension, percent solids, etc.) and the spin process variables[23].

Maximum rotating velocity, acceleration, and fume emission are all factors that influence the quality of coated films. repeatability is one of the most main components of spin coating .Alterations in the spin process's parameters could cause considerable changes in the coated films. [24].

Figure (2-2) depicts the spin coating process, with (a) denoting the deposition stage, (b) depicting the spin-up stage, (c) depicting the spin-off stage, and (d) depicting the ultimate evaporation stage.

2-4-1-1-1:Spin Coating Process Description:

A typical spin process includes a dispensing stage where the resin fluid is sprayed to the material's surface, a high-speed spin step to reduce the liquid, and a drying step to extract any residual solvents from the resultant film[25]. The two most common methods of dispensing are static and dynamic. All that is required for static dispensing is also a little droplet of fluid on or close to the substrate middle.This can range from around 1 cc to 10 cc depending on the fluid viscosity and the size of the surface to be covered. Larger droplets are sometimes required for greater viscosity and/or larger substrates to provide full coverage of the substrates as during high-speed spin stage.[26]



Figure(2-4): stages of spin coating process(a) denoting the deposition stage, (b) depicting the spin-up stage, (c) depicting the spin-off stage, and (d) depicting the ultimate evaporation stage.[26]

Dynamic dispense is a process that involves applying a thin film of fluid to a certain surface at a low speed. This method works by evenly distributing the fluid all the way through the sub-system. It can also help in reducing the amount of resin waste that's produced by the process. This method is especially beneficial when the liquid or the substrate has weak wetting properties. After the dispensing stage, it is usually a high speed that's used to thin the film to the desired thickness. Based on the solvent and substrate characteristics, spin speeds for this stage usually vary from 1500 to 6000 rpm.It could take anywhere between a few seconds to a few minutes to complete this procedure.The combination of rotation velocity and duration utilized in this step defines the resultant film thickness. Generally , thinner films result from greater spin speed and longer spin durations. Because there are so many variables in the spin technique that tend to cancel out and average out over time, it's best to allow it adequate time.A separate drying process is sometimes included.To dry the film even further without considerably thinning it following the high-speed spin step . This is especially useful for thick films, as long drying times may be required to improve the film's physical stability before handling.[26]

Without the drying process, problems such as the substrate running out the side after being removed from the spin dish can develop. In this situation, a moderate spin speed of around 25% of the quick rotation speed would usually adequate to assist dry the film without affecting its thickness considerably.On a Cee spin coater, each program can have up to 10 different process steps.While most spin processes only require two or three, this provides the greatest alternatives for complex spin coating needs.[26]

2-4-1-1-2: Parameters affecting spin process

1- Spin Speed

One of the most important factors that affects the performance of a spin coating is its spin speed. This is because the amount of radial force that is supplied to the liquid resin and the speed at which the air flows through it are both influenced by the substrate's speed. The ultimate film thickness is mainly determined by the spin step's high-speed spin. Even slight variations in the speed of 50 rpm can lead to a 10 percent difference in the film's overall thickness.[26]

The force that is required to push the liquid resin toward the substrate's edge and the drying rate are some of the factors that can affect the film's overall thickness. When the resin's viscosity increases, the effect of the spin process no longer feels on the surface. This means that the film's overall thickness can still be maintained even after the spin step has been raised. All of the spin coating techniques are designed to be used at 5 rpm are guaranteed to be reproducible.[26]

The ideal spin speed for a given material is usually set at 1 rpm. In order to monitor and adjust the spin speed, all of the necessary steps can be performed at a single resolution.[26].

2-Acceleration

The substrate's acceleration to the final spin speed may have an impact on the coated film's quality.Because the resin begins to cure during the spin cycle's early stages, accurate acceleration control is essential.During the first few seconds of different treatments, evaporation consumes up to half of the solvents in the resin.Acceleration has an impact on the coat properties of patterned substrates.[26]

Due to the substrate may have topographical components from earlier treatments, it's critical to equally coat the resin through and out of these flaws.The spin process provides a radial (external) force to the resin, but it is the acceleration that causes it to twist.This twisting helps the resin disperse over topography, which would otherwise prohibit the fluid from reaching particular areas of the substrate.Cee spinners' acceleration may be controlled with a 1 rpm/second resolution.The spin machine accelerates (or depreciates) along a linear ramp to reach the desired spin speed when in operation.[26].

3-Fume Exhaust

The nature of the resin fluid (volatility of the various solvents used) and the air around the substrate during the spin process affect the rate of evaporation of the resin liquid during the spin process.On a quick, dry day, a damp materials may dry faster than in humid weather, and the resin may dry according to the surrounding conditions.[26]

It is well known that air temperature and relative humidity have a significant impact on the characteristics of coating films.During the spin process, it's also necessary to keep airflow and related roughness directly above the substrate to a minimum, if not constant.The "closed bowl" design is found on all Cee spin coaters. While the exhaust cap is not completely airtight, it allows for very minimal emissions during the spinning operation.The exhaust lid works as a system to prevent undesirable random turbulence when paired that with bottom exhaust pipe under the spin chuck.With this procedure, the fluid glue dries more slowly and is less susceptible to change in ambient humidity.The enhanced film thickness homogeneity from across surfaces is due to the slower drying rate. As it gets near to the substrate's edge, the liquid dries out during spin process. Because the viscosity of the liquid increases with displacement from the substrate's center, radial thickness discrepancies may occur. By delaying the drying process, the viscosity can be maintained more constant over the substrate. The rate of drying and, as a result, the final film thickness are influenced by ambient humidity.[26]

Even minor changes in relative humidity might result in large layer thickness changes.The vapors of the resin's solvents are trapped in the bowl, and they tend to outweigh the effects of minor humidity variations while spinning in a closed bowl.[26]

Because the solvent vapors are contained and removed when the cover is lifted to remove the material at the end of the spin operation.Another benefit of this "closed bowl" form is that the spinning substrate is less vulnerable to variations in air flow around it.[26]

The properties of this air flow are influenced by a number of things. Because of the intense air flow, turbulence and eddy currents are widespread. Variations can cause a significant alteration in downward airflow. Variations and turbulence generated by the existence of workers and other equipment are eliminated from the spin process by enclosing the bowl with a flat lid surface. [26].

2-5: Spin Coating Solutions:

Usually, polymeric, plastic materials are used as a basis for coating on the surfaces of materials using the spin coating method, such as epoxy, polystyrene, silicone rubber, and others.[27] In this study, polystyrene is used as a matrix for the coating solution.

2-5-1: Polystyrene:

Polystyrene is a thermoplastic material with good formability produced from the aromatic monomer styrene. It is an inert, tasteless, rigid substance that is transparent due to its amorphous state (linear polymer) and low thermal conductivity. Polystyrene has a contact angle of 150° [28].

Polystyrene is widely utilized in automobiles, computer / electronic connector systems, structures, the food sector, packaging, and transportation [29] [30]. Figure (2-5) shows the molecular structure

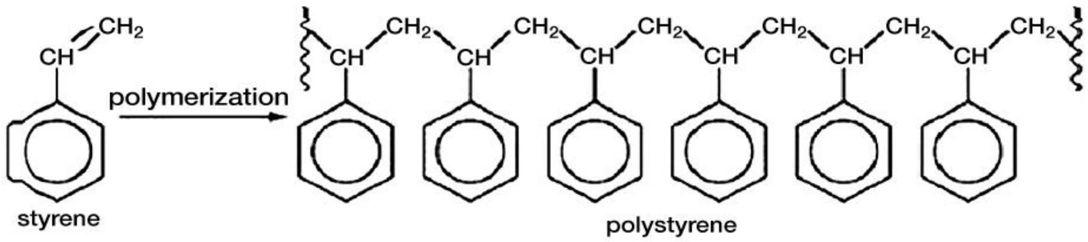


Figure (2-5): Molecular Structure of Polystyrene [29]

Polystyrene is divided into three categories :

•Transparent and brittle general purpose polystyrene (GPPS).

• High impact polystyrene (IPS or HIPS), a white, non-shiny, and somewhat flexible material.

• The third kind is expanding or foam polystyrene (EPS).[29]

2-5-2 : Additives:

2-5-2-1: Titanium Dioxide:

Titanium dioxide (TiO_2) called titania, is a naturally occurring titanium oxide. It's a versatile substance that's typically used as nanoparticles suspended in water for superior catalytic region and activity [31].

It is also been employed as a photocatalyst because of its nontoxicity and excellent stability. TiO_2 is used in a variety of industries, including aircraft, sports, paint (to provide a glossy finish, rich depth of color, and to substitute metal lead), and food (to extend the shelf life UV protection in sunscreens and other goods) and cosmetics [32].

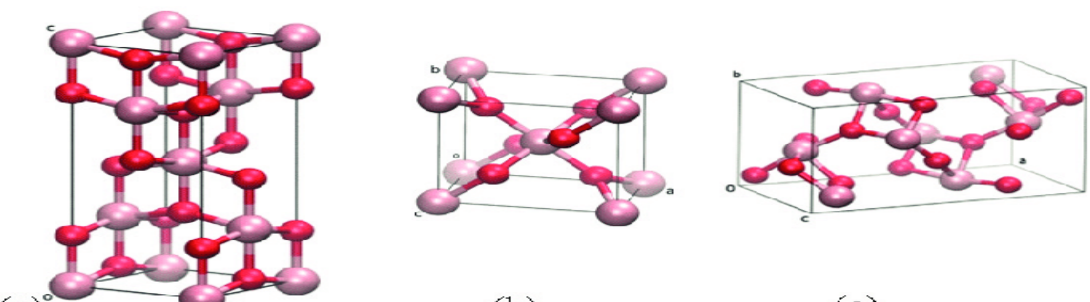
Titanium oxide nanoparticles are utilized as a white pigment in outstanding reflective coatings, or used to paints to boost brightness, as well as cement and windows for their sterilizing characteristics.[33]

When titanium dioxide is applied on outdoor surfaces, it reduces air pollution by breaking down organic contaminants, volatile organic compounds, and bacterial membrane through potent photo catalytic processes [33].

It has three separate phases in nature. Rutile, anatase, and brookite are these phases, which have low absorption and dispersion in the visible and near-infrared spectrum bands, as well as strong chemical and thermal stability [34].

Titanium dioxide polymorphs include :

- Anatase is a one of the three crystalline phases of titanium dioxide. It's a tetragonal mineral with an octahedral habit that is always discovered as small, isolated, and sharply developed crystals. Due of its increased photo activity, the anatase phase of TiO_2 looks to be a really effective catalyst than rutile. The unit cell for anatase is shown in Figure (2-6a).
- Rutile is a tetragonal material with titanium atoms in the corners and the center. An approximately octahedron of oxygen molecules surrounds each titanium atom, so each oxygen atom is encircled by an almost right - angled triangle of titanium particles.The rutile unit cell is seen in Figure (2-6b).
- Brookite is an orthorhombic material with tabular, elongated, and striated crystals that run parallel to the length of the material. Brookite, like all orthorhombic minerals, is doubly refracting and biaxial (+).Refractive indices are quite high, exceeding 2.5, even surpassing diamond at 2.42.The unit cell of brookite is shown in Figure(2-6c) [35].



(a) (b) (c)

Figure (2-6):Crystal structures of TiO_2 : (a) anatase, (b) rutile, and (c) brookite [35]

2-5-2-1-1: General mechanism of photocatalytic activity of TiO_2:

In chemistry, photo-catalysis describes the amplification of a photoreaction in presence of catalysts [36]. As a photocatalyst, many semiconductors such as TiO_2, ZnO, and others have been employed. In photocatalysis, the electrical structure of a semiconductor is crucial.[37]

The band gap, that has an energy below 3.5 eV, is the variation in energy between the Valance Band (VB) and the Conduction Band (CB) in a semiconductor.The electrons and holes are in the valence band when there is no excitation.When a semiconductor layer is exposed to light, electrons absorb specific wavelengths and move from the VB to the CB, leaving a hole (h+) inside the valence band, generating electron–hole pairs.[37]

Electrons and holes flow to the semiconductor's surface, where they can decrease and oxidize the reactants adsorbed mostly by semiconductor, respectively.The photo-induced (electrons / holes) have a substantially larger reduction and oxidation capability than hydrogen and ozone in both. As a result, these electron–hole pairs form a powerful redox system.By oxidizing OH and H_2O molecules, photo-produced holes produce hydroxyl radicals, that are absorbed on TiO_2 surfaces.[37]

At about the same time, electrons in the conduction band may help reduce O_2 molecules on TiO_2 surfaces, resulting in the creation of peroxyl radicals.Photosynthesis produces hydroxyl and peroxyl radicals, which oxidizes and degrade organic and inorganic materials. The major mechanism of hydrogen generation and photocatalytic water/air filtration, respectively, are reduction and oxidation reactions.Figure 1 shows a schematic illustration (2-7).

In a relatively short period, the photo-generated electrons and holes may recombine in the bulk or on the surface of the semiconductor, energy is released as heat or photons [37].

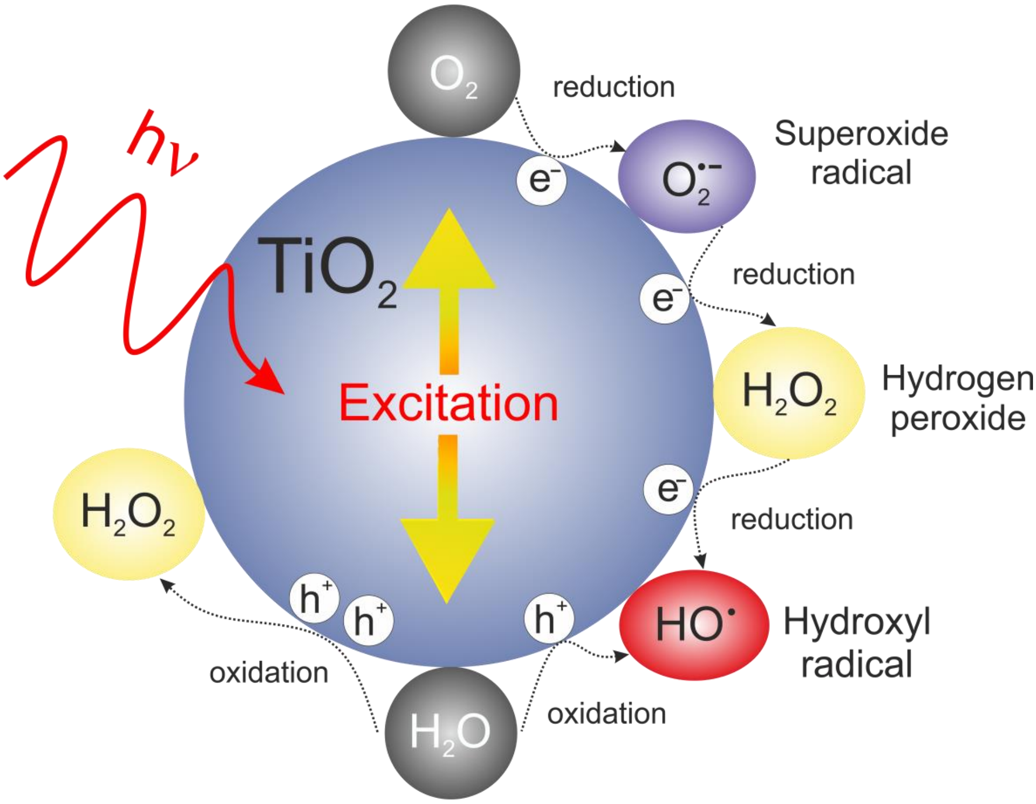


Figure (2-7): Mechanism of photocatalysis [38]

TiO_2 is a low-cost, stable, and environmentally friendly material. Photo catalytic water splitting [39-40], photo catalytic self-cleaning [41], wastewater purification [42], photo-induced superhydrophilicity[43],photovoltaic[42],antibacterial/antimicrol [38], and Gap before photosynthesis are just a few of the many fields where TiO_2 nanoparticles' photo catalytic activity has been investigated.[44]

The photo degradation of a wide range of environmental contaminants, also including difficult and complicated organic compounds and inorganic material, into CO_2 and innocuous inorganic anions is the most promising field of TiO_2 photocatalysis [41-37] TiO_2 has showed considerable promise as a photocatalyst for wastewater purification and remediation.TiO_2 nanoparticles can also be suspended freely. During the decontamination process, contaminants might be found in wastewater or coated on substrates [45-46].

2-5-2-2: Modification Additives:

2-5-2-2-1:Calcium Carbonate:

Calcium carbonate, is a chemical substance with the formula CaCO3. It is found in abundance in pearls, shellfish bones, gastropod shells, and eggshells. It can also be found in rocks as the mineral calcite or aragonite, most famously as limestone, a sedimentary rock largely made of calcite. $CaCO_3$, the active ingredient in agricultural lime, is generated when calcium ions in hard water combine with carbonate ions to form limescale. [47].

The thermodynamically configuration of $CaCO_3$ is hexagonal (β-$CaCO_3$) under normal circumstances (the mineral calcite). Other forms can be made, including the denser (2.83 g/cm3) orthorhombic (λ-$CaCO_3$) (the mineral aragonite) and hexagonal (μ-$CaCO_3$) (the mineral vaterite).The aragonite form is produced by precipitation at temperatures above (85°C), while the vaterite form is formed by precipitation at temperatures below (60°C). Calcite has six oxygen atoms coordinated with calcium atoms, while aragonite has nine oxygen atoms [48]. Vaterite's structure is still a mystery. [49].

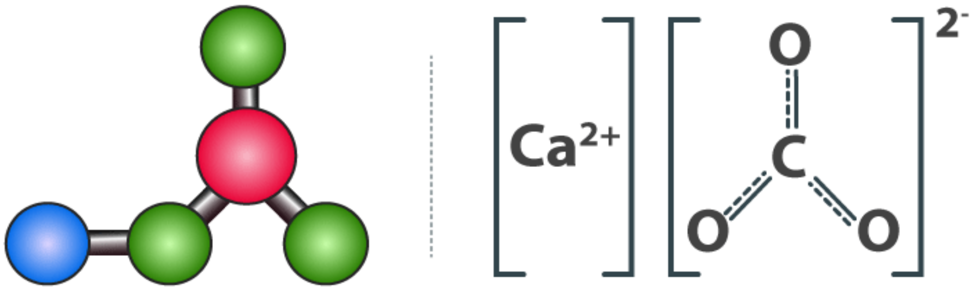


Figure (2-8):Structure of Calcium Carbonate[49]

The applications of $CaCO_3$ are

- $CaCO_3$ is widely used in the pulp and paper industry.It has the potential to be utilized as both a filtration and a pigment, resulting in a whiter, higher-quality pigment than some other minerals.
- In the building industry, calcium carbonate is used as a filler in concrete to increase its durability and aesthetics, as well as to clean metals used in construction.
- $CaCO_3$ is also found in fertilizers, where it is utilized to provide calcium to plants while simultaneously maintaining soil pH stability.
- $CaCO_3$ can also be utilized as a vitamin supplement and a food element for both cattle and humans.
- In water - treatment plants, $CaCO_3$ is used to reduce acidity and contaminants.[50]

2-5-2-2-2: Bauxite:

Bauxite is a mineral composite made up of gibbsite, boehmite, kaolinite, hematite, anatase, and quartz that are used in the Bayer process to make alumina. Gibbsite ($Al(OH)_3$), boehmite (Û- $AlO(OH)$), and kaolinite ($Al_2[Si_2O_5](OH)_4$) are the most common hydroxides among these minerals. In aspects of aluminum class, mineralogy, reactivity silica, and other impurity concentrations, bauxite has a wide range of attributes [52].

Bauxite is an aluminum resource made up of over a hundred distinct minerals, the most important of which being aluminum, iron, silica, titanium, and calcium.Aluminum is mostly found in hydrated oxides in bauxite, such as hydrargillite (gibbsite)- Al_2O_3 $.3H_2O$, boehmite-AlOOH, and diaspore-AlOOH.[53]

Aside from these minerals, aluminum can also be found in bauxite as in form of corundum (Al_2O_3) and other aluminosilicates, the most common of which is kaolinite ($Al_2O_3.{}_2SiO_2.2H_2O$).Bauxite contains silicon in the form of free or bound oxide.Free oxide minerals, such as quartz, quartzite, chalcedony, and amorphous SiO_2-opal, are crystal forms of SiO_2 that can be found in bauxite.SiO_2 is the most common free oxide present in the formation of quartz mineral.Silicon is most commonly found as just a bonded oxide in the mineral kaolinite ($Al_2O_3.2SiO_2.2H_2O$).[53]

In general, Hematite and magnetite, both dehydrated and hydrated oxides, are present in bauxites .Bauxites are classified as hydrargillite (gibbsite), boehmite, diaspore, and mixed (hydrargillite-boehmite and boehmite-diaspore) depending on the mineral form of the existing aluminum as the base mineral.The following components make up the chemical makeup of bauxite: Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO, and the loss on combustion at 1075°C.The SRPS B.G8.512 standard is used to conduct a standard method for chemical analysis of aluminum in bauxites [53].

Bauxite is a pisolitic rock with a low specific gravity and a delicate white to grayish to reddish brown color (specific gravity : 2.0- 2.5).Bauxite is a heterogeneous material made mostly of one or more aluminum hydroxide minerals, with tiny or trace amounts of silica, iron oxide, titania, aluminosilicate, and other inclusions [54]. It is found naturally in Al- Anbar and the western desert of Iraq.

The Bauxite Uses are

- The ideal and only source for manufacturing aluminum is bauxite.
- After they have been removed, aluminum and aluminum-based alloys are extensively used in electronics, construction, automobiles, and even cutlery.
- Chemical, refractory, abrasive, cement, steel, and gasoline are just a few of the sectors that use bauxite.
- Aluminum compounds are made from bauxite and alumina in the chemical industry.
- It is used as a raw ingredient in the production of refractory materials.
- Bauxite is used in the aerospace, electric, and dental cement industries as a desiccant, adsorbent, and catalyst.

- Lateritic bauxite is typically used when no other building materials are available.
- To avoid accidents, construction companies use calcined bauxite as an anti-skid road material in defined areas.
- Papermaking, water filtration, and petroleum refineries, and also rubber, plastic, paint, and cosmetics, are all businesses that use bauxite tooling for the mechanical and civil engineering sectors.[55-56]

2-5-2-2-3:Polytetrafluoroethylene (PTFE):

A tetrafluoroethylene synthetic fluoropolymer had a wide range of uses. Teflon by Laboratories, a DuPont spin-off, is the most well-known brand name for PTFE-based formulations. The compound was first developed in 1938 by DuPont.[57]

Polytetrafluoroethylene is a fluorocarbon solid because it is a high-molecular-weight polymer comprised completely of carbon and fluorine (at room temp). Because of its high electronegativity, fluorocarbons have reduced London dispersion forces, making PTFE hydrophobic: neither water nor water-containing substances wet it. PTFE has one of the lowest coefficients of friction of any material.[57]

Non-stick coatings for dishes and other cookware are made of polytetrafluoroethylene. Carbon–fluorine bonding is extensively utilized in containers and pipes for reactive and corrosive compounds due to its non-reactive nature. PTFE lowers friction, wear, and power consumption in equipment when used as a lubricant. As an allograft, it is commonly used in medical treatments. It is also used to coat catheters to prevent bacteria and other viral infections from clinging to them and causing hospital-acquired infections. [57].

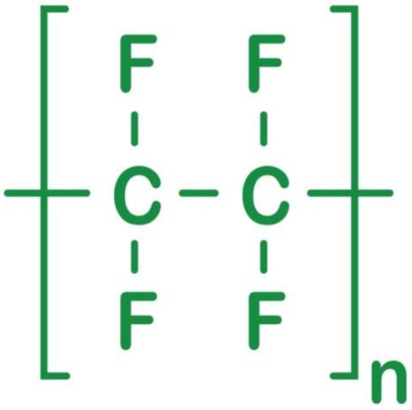


Figure (2-9): Polytetrafluoroethylene structure[57]

The PTFE Applications are

- Teflon, that can be used to produce non-stick cookware, is perhaps the most well-known PTFE variant.
- The dentistry profession has employed PTFE's non-stick characteristics to maintain fillings from sticking to neighboring teeth.
- Because of it is anti-corrosive and non-reactive, Teflon is also utilized to build containers and pipes.
- This is important for laboratories that need to store extremely corrosive compounds in glass containers.
- Teflon also has increased tensile strength due to its carbon-fluorine bonding.
- Teflon may be used as a machine lubricant.

- When used in this manner, Friction, energy consumption, and equipment wear are all reduced with PTFE.Lubricant for bicycle chains is an example of this.
- With its heat resistance and strength, Teflon is also used to produce gaskets.It's used as a plumbing thread

- Teflon is utilized to protect cables and connector components because of its outstanding electrical insulation qualities. It's perfect for connection wire, coaxial cable, and printed circuit boards because of this.
- Consumer products containing teflon include outdoor clothing, school uniforms, footwear, and insoles. seal tape.[58]

2-6: Literature review :

A literature review was discussed in this chapter in order to compare the current work to the work of previous scholars.

- In (2005) Hinczewski, D. Saygın, *et al*, showed Optical filters are made from SiO_2 and TiO_2 multilayers using the spin coating process. By coating the films evenly on both sides of the glass substrates, they generated two types of three-layer anti-reflection (AR) filters for the near–infrared range, as well as a nine-layer reflective filter for the near–UV region. They developed a basic theoretical model for all of these filters, which includes the densification of sol–gel films during the coating process, and matched it to real-world data to extract properties of distinct layers inside the coatings.[59]
- In (2008) Kang, Minsung, *et al*, studied Under electrospinnable circumstances, the ability of N,N-dimethylformamide (DMF) to dissolves polystyrene (PS) of (35 wt percent) was

maximized. The electrospun fibrous films were superhydrophobic, with a wettability of 154.2± 0.7°, according to contact angle measurements.[60]

- In (2010) Lu, Qh., *et al,* studied TiO_2/bauxite-tailings (TiO_2/BTs) composites produced by chemical liquid deposition were analyzed using X-ray diffractometry (XRD), scanning electron microscopy (SEM), and N 2 adsorption studies.UV photocatalytic activity of TiO_2/BTs.The photocatalytic efficiency of TiO_2/BTs composites was investigated in terms of calcination temperature, pH, and cycles.The photocatalytic performance of the compounds carbonized at 500 and 600 °C is the best, with phenol decomposition ratios reaching 35 and 78 percent under the same conditions after 40 and 160 minutes, respectively, which is higher than the Degussa P25's 29 and 76 percent (TiO_2).The ability of TiO_2/BTs500 composites to breakdown phenol increases as pH drops (BTs500 refers to carbonized bauxite tails at 500°C). [61]
- In (2011) Suciu, Ramona-Crina, *et al*, studied The hydrolytic sol-gel process was used to create and analyze TiO_2 films, which were then spun onto glass substrates. The titania nanocoatings on indium tin oxide were made in an aqueous solution using the titanium diethanolamine complex as a precursor using the sol-gel process. FT-IR, UV–VIS, Raman spectroscopy, and X-ray diffraction were used to evaluate the physical and chemical changes that occurred all through the sol-gel process, and the properties of the TiO_2 powder precursor .[62]
- In (2011) Elfanaoui, A., *et al,* studied titanium oxide TiO_2 thin film for environmental services such as water photosplitting

.The spin coating procedure of sol precursor onto glass substrates was used to make TiO_2 thin films.The effect of the number of deposited films on the films' crystalline quality was explored. Atomic force microscopy (AFM) and scanning electron microscope were used to examine the surface morphology of the deposited layer (SEM).The film had a high transmission of roughly 90%, according to UV-Vis-NIR spectroscopy.[63]

- In (2012) GÜRBÜZ, Mevlüt, *et al*, studied Titanium dioxide (TiO_2, 25nm) and Si-modified TiO2 nanoparticles were spray sprayed onto ceramic tiles to form the photo-catalytic active surface. The samples were characterized using X-ray diffraction (XRD) and a scanning electron microscope (SEM). In photo-catalytic testing, methylene blue was used as an organic pollutant to examine the photo-catalytic activity of uncoated, unmodified TiO_2 coated, and Si-modified TiO2 coated tiles .In terms of photo-catalytic activity, the results showed that Si-modified TiO_2 coated tiles outperformed uncoated and untreated TiO_2 coated tiles. For 5-15 and 30mg/Methylene blue concentrations, about 100 percent clean ability was found for Si-modified TiO_2 coated tiles in 80, 100, and 120 minutes. On the other hand, uncoated and unaltered TiO_2 coated surfaces demonstrated no thorough cleaning. Tiles are used to illustrate all methylene blue ratios.[64]
- In (2013) Buasri, Achanai, *et al*, showed making TiO_2 nanocomposites and surface-modified TiO_2 nanoparticles out of polystyrene by compression molding (PS). 3-(methacryloxy)propyl trimethoxysilane was used to modify TiO_2 nanoparticles. The thick nanocomposite films that

resulted were compared to pure polystyrene. Because of their hydrophobic properties,TiO_2 nanoparticles were found to spread better in PS matrix. The optical band gap of PS could be reduced from 4.0 eV in pure PS to less than 3.0 eV in PS-TiO_2 nanocomposite by adding a little amount of TiO_2 nanoparticles. The effects of surface treatment and UVC irradiation on nanocomposites' physical characteristics and deterioration were studied. [65]

- In (2014) Graziani, Lorenzo, *et al*, investigated TiO_2 photocatalytic characteristics applied to clay brick surfaces during deposition and after age. Before the durability test, the nano-film morphology, wettability, and self-cleaning efficiency of TiO_2 were evaluated. During the aging test, the ability to self-clean was also assessed in order to assess its variance in long-term applications. The photoactivity of TiO_2 was shown to be steady after aging, indicating that TiO_2 had strong photocatalytic efficiency when placed to clay brick substrate.[66]
- In (2014) Huang, Jiwei, *et al*, studied The mechanical stirring of a combination of nano-TiO_2 and nano-$CaCO_3$ solutions over a substrate to create a super hydrophobic surface, followed by the alteration of a low-surface-energy oleic acid. The results reveal that nano-$CaCO_3$ surfaces are physically connected with nano-TiO_2 particles, and that once the based composites particles is added into the hydrophobic methyl, double-scale roughness structures form, increasing the contact angle degree to 162.1° and a sliding angle of 7°.[67]
- In (2016) Khirandish studied The E-Spin technique was used on PS/TiO_2 fibers with limonene as a solvent. SEM was used

to analyze the morphology of nanocomposite fibers, which revealed that there were some aggregates of nano TiO_2 particles and that increasing the number of nano TiO_2 lowered the fiber diameter of PS. The results suggest that increasing the number of nano TiO_2 in PS fibers increased UV protection. After coating with PS/TiO_2 nanocomposite, tensile strength and elastic modulus both enhanced [68].

- In (2018) Barmeh, Alireza, *et al*, studied The influence of Ni doping on the self-cleaning properties of TiO_2 thin films under visible light. A spray coating approach was used to make the TiO_2 thin films. The TiO_2 thin films were studied using grazing incidence X-ray diffraction (GIXRD), field emission scanning electron microscopy (FE-SEM), also known as Energy X-ray spectroscopy, and UV-Vis. absorbance spectroscopy. Photoactivity and wetting of TiO_2 thin films were studied. According to FE-SEM images, the Ni-doped TiO_2 thin film displays a considerably more homogenous morphology than the undoped TiO_2 thin film. Thus according UV-Vis absorbance spectra, this Ni-doped TiO_2 thin film exhibits a bigger highest absorption wavelength and a smaller band gap than the undoped TiO_2 thin film. Photo-activity and hydrophilicity were obtained under visible light. . [69]
- In (2018) Zhang, Shuai, *et al* ,studied On a stainless steel substrate, a (TiO_2-PTFE) nanocomposite coating was created using a sol-gel dip coating technique. A sub-layer of bioinspired polydopamine was first coated on the stainless steel substrate to improve adhesion and reactivity, and then TiO_2-PTFE was equally co-deposited onto the PDA sub-layer. Due to synergistic interaction with TiO_2 and PTFE, the (TiO_2-

PTFE) coated showed increased corrosion resistance in synthetic body fluids when contrasted to a solo TiO_2 coating or a PTFE coating. When evaluated with grown fibroblast cells, the (TiO_2-PTFE) coating showed excellent biocompatibility, indicating it could be a feasible alternative for resolving current concerns about metallic implants.[70]

- In(2019) M. Zeinali *et al*, studied an ex-situ produced (TiO_2+polystyrene) nanocomposite coated on quartz surfaces using the spin-coating process, with varying concentrations of TiO_2 nanoparticles. The Z-scan technique is used to investigate the nonlinear optical characteristics of (TiO_2+PS) nanocomposite films. The findings show that incorporating TiO_2 NPs into a PS polymer matrices can be a new technique to lower TiO_2 NPs' band gap toward visible light, which is of significant interest for their utilization in this area of the spectrum. The results reveal that raising the TiO_2 NP concentration in spin-coated TiO_2 PS films improves their optical nonlinearities, thereby opening up new possibilities for their own use as non - linear optical coatings in photonics.[71]

- In (2019) Hussein, Ayat, *et al*, Studied There are two types of substrate coatings available. Mixed two percents, three percents, and six percents of TiO_2 nanoparticles with cement paste to begin. Second, mortar substrates were treated with a nano TiO_2 watery solution. Techniques like as dipping and spray coating were used. A laboratory test approach was employed to analyze the effectiveness of the produced photoactive specimens. The specimens were exposed to NO gas and their ability to remove the gas over time was measured.

When using spray and dip processes, the efficiency of titanium dioxide covering construction materials was proved by the elimination of gaseous pollutants such as nitric oxide reaching 98.85 percent. When nano titanium was mixed with 3%, it was also successful in removing nitric oxides, with a 97 percent clearance rate. It had been The spray method was discovered to be the most practical method. [72]

- In (2020) Syafiq, A.,*et al*, studied Organic Polydimethylsiloxane polymer with inorganic nano-Calcium carbonate ($CaCO_3$) filler are used to make transparent self-cleaning coatings that are sprayed onto glass panels. After four months of external exposure, the self-cleaning and stability of nano-$CaCO_3$ surface coatings were examined. The transmission of 0.8 wt% nano-$CaCO_3$ coated substrate was marginally deteriorated by 7% as a result, demonstrating that it has an excellent self-cleaning effect. The water hammer pressure of rainfall impact and mist have deteriorated as the loading ratio of nano-$CaCO_3$ had increased, resulting in higher capillary pressure and air-pockets. As a result, the coating system's Water Contact Angle was only lowered by 2%, and it had excellent anti-fog properties.[73]

2-6-1: Summery:

The literature contains details on the many procedures and materials used to achieve hydrophobicity ,hardness and surface finish on the exterior walls of commercial and residential structures and in this study, hydrophobicity and hardness were obtained with additives ($CaCO_3$,bauxite,PTFE) that were not previously used as coating materials with nano-titanium dioxide.

Author/year	Ref.	Summery
Hinczewski,D. Saygın,*et al.(*2005)	[59]	Optical filters are made from SiO_2 and TiO_2 multilayers using the spin coating process.They developed three types of near-infrared anti-reflection (AR) filters, as well as a nine-layer reflective filter for the near-UV band.
Kang, Minsung, *et al*.(2008)	[60]	Electrospun fibrous films have been developed that are superhydrophobic, with a wettability of 154.2± 0.7°, according to contact angle measurements. Under electrospinnable circumstances, the ability of N,N-dimethylformamide (DMF) to dissolves polystyrene was maximized.
Lu, Qh., *et al* (2010)	[61]	TiO_2/bauxite-tailings composites prepared by chemical liquid deposition. Composites carbonized at 500 and 600°C is the best for photocatalytic performance. Phenol decomposition ratios responding for 40 and 160 minutes reach 35 and 78 percent.
Suciu, Ramona-Crina, *et al.(*2011)	[62]	The titania nanocoatings on indium tin oxide were created in an aqueous solution utilizing a titanium diethanolamine complex as a precursor and the sol-gel technique.TiO_2 films were coated on glass substrates using the spin coating method.
Elfanaoui, A., *et al*. (2011)	[63]	The spin coating procedure of sol precursor onto glass substrates was used to make TiO_2 thin films. The film has a high transmission of roughly 90%, according to UV-Vis-NIR spectroscopy. It could be used for environmental services such as water photosplitting.
GÜRBÜZ, Mevlüt,*et al* (2012)	[64]	Methylene blue was utilized as an organic pollutant in tests to assess the photocatalytic activity of tiles coated with titanium dioxide (TiO_2,25nm) and Si-modified TiO_2 nanoparticles. It was found that for 5-15 and 30mg/L methylene blue concentrations, about 100 percent cleanability was observed in 80, 100, and 120 minutes for Si- modified TiO_2 coated tiles.
Buasri, Achanai, *et al*. (2013)	[65]	Methacryloxyethylpropyl trimethoxysilane was used to modify TiO_2 nanoparticles. The thick nanocomposite films that resulted were compared to pure polystyrene. Nanocomposites' optical bandgap could be lowered from 4.0 eV in pure PS to less

		than 3.0eV in (PS-TiO_2) nanocomposite.
Huang, Jiwei, *et al*.(2014)	[66]	Nano-$CaCO_3$ surfaces are physically connected with nano-TiO_2 particles, and that once the based composites is added into the hydrophobic methyl, double-scale roughness structures form. The contact angle degree is 162.1° and a sliding angle of 7°.
Graziani, Lorenzo, *et al*. (2014)	[67]	TiO_2 photocatalytic characteristics applied to clay brick surfaces during deposition and after age. During the aging test, the ability to self-clean was also assessed. The photoactivity of TiO_2 is shown to be steady after aging, indicating that it has strong photocatalysis efficiency.
Khirandish .(2016)	[68]	The E-Spin technique was used on PS/TiO_2 fibers with limonene as a solvent. Increasing the number of nano TiO_2 in PS fibers increased UV protection. After coating with nanocomposite, tensile strength and elastic modulus both enhanced.
Barmeh, Alireza, *et al* (2018)	[69]	The TiO_2 thin films' photoactivity and wetting were tested. Under visible light, the effect of Ni doping on the self-cleaning characteristics was also examined. Grazingincidence X-ray diffraction, field emission scanning electron microscopy, and UV-Vis absorption spectroscopy were used.
Zhang, Shuai, *et al*. (2018)	[70]	TiO_2-PTFE nanocomposite coating shows enhanced corrosion resistance in synthetic bodily fluids as compared to the solitary TiO_2 coating or the PTFE coating. The coating additionally displayed exceptional biocompatibility using fibroblast cells cultured, indicating that it could be a promising technique for overcoming problems with metallic implants.
Hussein, Ayat,*et al* (2019)	[71]	Dip and spray coating techniques were used to produce photoactive specimens for use in building construction. The spray approach was found to be the most practical.
M. Zeinali *et al*.(2019)	[72]	TiO_2+polystyrene (PS) nanocomposite coated on quartz surfaces using the spin-coating process, with varying concentrations of TiO_2 nanoparticles. Z-scan technique used to investigate the nonlinear optical characteristics of (TiO_2+PS) films. Findings show there is a new technique to lower TiO_2 bandgap toward visible light.
Syafiq, A., *et*	[73]	Nano-$CaCO_3$ coatings are used to make transparent

*al.(*2020)		self-cleaning coatings that are sprayed onto glass panels. After four months of external exposure, the coating system's Water Contact Angle was only lowered by 2%, and it has excellent anti-fog properties.

3-1 : *Introduction :*

This chapter focuses on demonstrating the properties of materials utilized as well as the experimental methods, which include creating nanocomposite solutions for spin coating and then describing the tests that were used. Fig(3-1) shows the experimental procedure carried out in this study .

3-2 : *Materials and Chemicals* :

Table (3-1) shows the characteristics of the materials used in the current study

Table (3-1): characteristics of materials and chemicals used

No.	Name	Chemical formula	Purity %	Properties	Origin
1	Polystyrene	$(C_8H_8)n$	99.5	Transparent granules Molecular Weight g/mol) (104.1 Density(1.04 g/cm^3)	American polymer service Inc.
2	N,N-Dimethylformamide	C_3H_7NO	99	Colorless liquid Molecular Weight(73.09 g/mol) Density(0.94 g/cm^3)	Thomas Baker(chemicals) Pvt.Ltd
3	Titanium dioxide	TiO_2	99	White fine nano particle, with a diameter (30nm-50nm)	Hongwu International Group Ltd
4	Calcium carbonate	$CaCO_3$	99	White fine micro particle	Sinopharm chemical reagent Co.,Ltd

5	Bauxite	Mineral composite		Reddish brown powder	Iraq Geological Survey
6	Polytetrafluoroethylene	$(C_2F_4)n$	100	White fine particle with diameter (1.6 µm)	Dynamic Coatings, Inc

3-2-1 : *Bauxite:*

The bauxite powder used in this investigation was made from Iraqi bauxite rocks.The Iraq Geological Survey provided the bauxite rocks.To obtain the quasi-finished powder, manual kibbling of rocks was accomplished using mortar.The powder was cleaned and dried after that.The powder was subsequently processed for 8 hours at 350 rpm in a ball mill, and a sieve with several gradients was employed to achieve a small granular size in the ceramic laboratory at the University of Babylon's College of Material Engineering.The powder was then burned at 1400 degrees Celsius to remove moisture and impurities.

3-3 : *Preparation of substrates*:

The spin coating process was used to deposit hydrophobic nanocomposite coatings in this work.Bricks, cement mortar, and thermostone were chosen as ceramic substrates from locally available and often used construction materials.

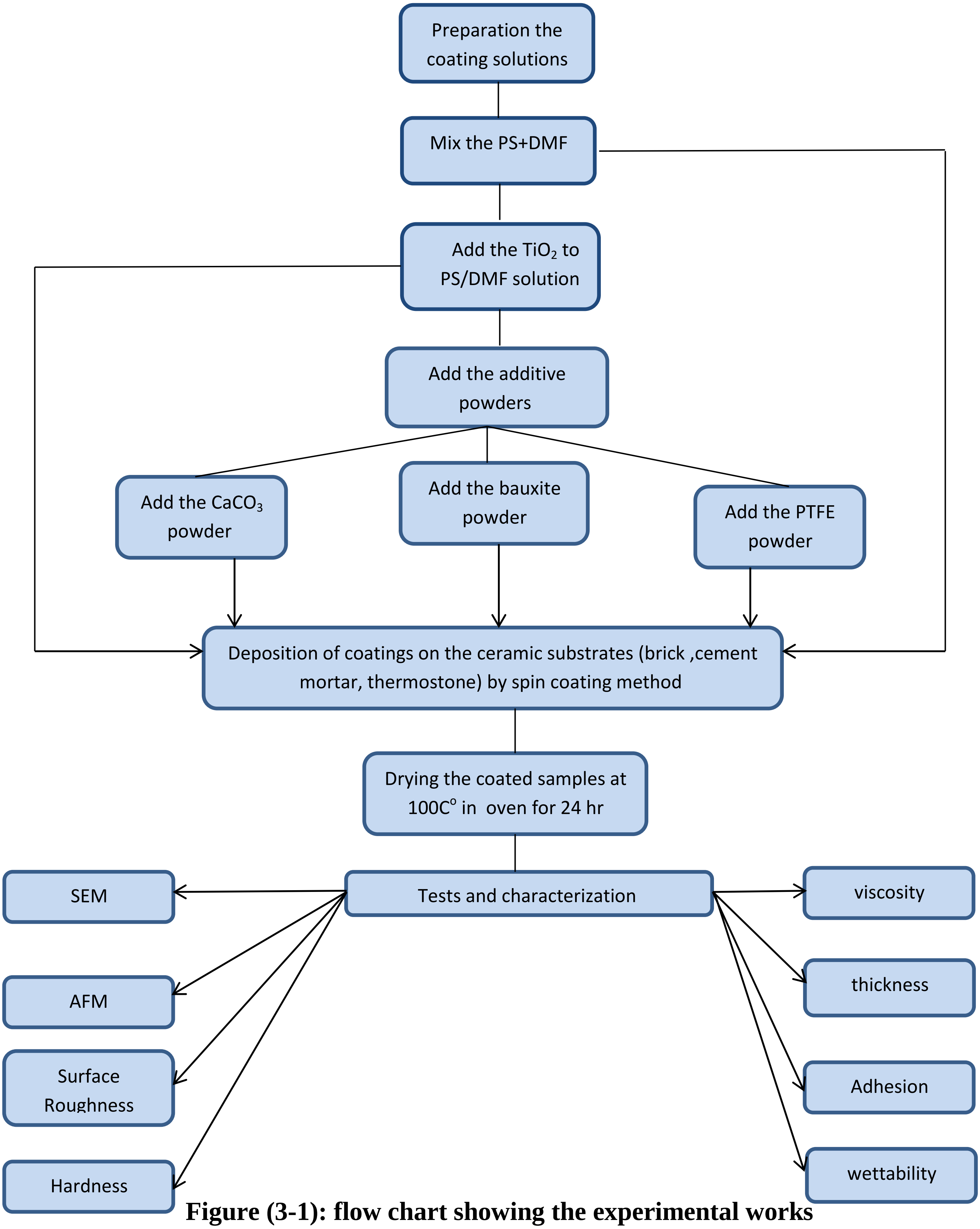


Figure (3-1): flow chart showing the experimental works

The selected substrates bricks and thermostone were cut and poished to the same dimensions (2x2x0.5 cm^3) by hand saw, washed and cleaned with distilled water and alcohol and then dried in oven at (100^oC) to achieve a smooth surface free of contamination and scratches .the cement mortar substrates was prepared using a mixture of cement, sand and water in a ratio of 1:3:1 using sand and cement tested and subject to standard specifications. The mixture was poured into molds measuring (2x2x0.5 cm^3) and left to dry at room temperature for 28 days, then dried in the oven at a temperature of 100 and washed with distilled water and alcohol figure (3-2) show preparation of surface before coating.

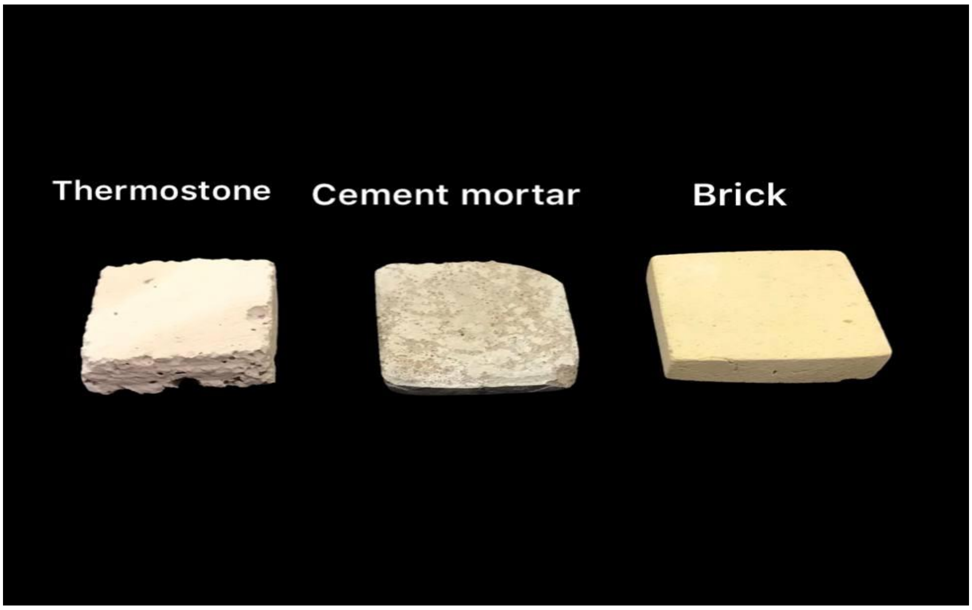


Figure (3-2) : Prepared substrates before coating .

3- 4 : *Preparation of coating solutions :*

In this study ,spin coating solutions for the hydrophobic nanocomposite coatings composed of polymer matrix reinforced with functional additives of TiO_2,$CaCO_3$,Bauxite and PTFE. These solutions were prepared as described in the followings

3-4-1 : *Preparation of polymer matrix solution :*

After several attempts in selection the polymer matrix solution (PMs),the polystyrene (PS) and N,N-Dimethylformamide (DMF) solvent were chosen to be the main components of the PMs .

Firstly, PS granules were dissolved in N,N-Dimethylformamide solvent. Ten g of (PS/DMF) polymer solution was depended for all polymer matrix solutions prepared. Different percentages of PS in the polymer matrix solutions (PS/DMF) were prepared (0.01,0.05,0.1,0.15 and0.2 g/ml).

To examine the influence of PS on the resulted coatings by means of coatings uniformity ,density stature ,consistency and contact angle for hydrophobicity properties. To achieve homogeneity, the PMs was placed on a magnetic stirrer for 6 hours.After that, a 1ml syringe pump with a spin coating mechanism was inserted to start the coatings deposition .

3-4-2: *Preparation of nanocomposite coatings solutions:*

In this step, 0.001 g/ml of TiO_2 nanoparticles was the starting ratio which added to the best PS/DMF solution that provided the coated surfaces ,with the best results to prepare the PS/DMF/TiO_2 nanocompsite coatings. Then ,the TiO_2 ratios were increased to 0.006 g/ml (0.001 ,0.002, 0.004, and 0.006 g/ml) to examine their effects on the hydrophobicity. In the same manner mentioned above ,after pointing the best TiO_2 ratio could provide the required modification in surface hydrophobicity, the addition of modification particles of $CaCO_3$, bauxite and PTFE was done gradually .Table (3-2)shows the specification of specimens .

Table (3-2) :specimens descriptions

Specimen code	Descriptions					
	PS (g)	DMF (ml)	TiO_2 (g)	$CaCO_3$ (g)	Bauxite (g)	PTFE (g)
PS1	0.1	9.9	--------	--------	--------	--------
PS5	0.5	9.5	--------	--------	--------	---------
PS10	1	9	---------	---------	---------	---------
PS15	1.5	8.5	---------	---------	---------	---------
PS20	2	8	---------	---------	---------	---------
T1	2	8	0.01	---------	---------	---------
T2	2	8	0.02	---------	---------	---------
T4	2	8	0.04	---------	---------	---------
T6	2	8	0.06	---------	---------	---------
TC1	2	8	0.06	0.5	---------	---------
TC2	2	8	0.06	1	---------	---------
TB1	2	8	0.06	----------	0.5	---------
TB2	2	8	0.06	----------	1	---------
TP1	2	8	0.06	----------	---------	0.5
TP2	2	8	0.06	----------	---------	1

To achieve nanoparticle extensive mixing with PMs, an ultrasonic mixing machine was employed for TiO_2 nanoparticles and other additives (for 10 minutes at 35 C^o).The liquid was syringe-pumped directly onto the surface to coat it.The nanoparticles utilized are suspended and attach towards the surface after being coated by evaporation of solvent; only polymers containing nanoparticles will achieve such adhesion with the substrate in question .Figure (3-3) shows magnetic stirrer and ultrasonic devices

(a) (b)

Figure (3-3) :(a) Magnetic stirrer and(b) ultrasonic devices

3-5: *Spin coating Set-Up* :

Disposition, spin up, spin off, and evaporation were the four stages of a spin coating process.Using a syringe pump, a coating solution was first cast onto the substrate.The solution was then forced outward by the centripetal force, covering the substrate's surface.The majority of the extra coating solution was discharged to the side at this point, and airflow begun to dry the film .Finally, the solvent evaporated in the final stage, leaving a thin, homogeneous layer behind. Coating solutions were injected into the spin coating equipment through a syringe pump.For 15 seconds, the spin speed was 2000 rpm . The spin coating machine that was used in this study was (Spin Coater (500-6000 rpm, 8 Max) w/ Optional Heating Cover- VTC200) and the coating process was done in University of Babylon/ Polymers engineering department. spin coating device is shown in Figure (3-4).

Figure (3-4) : spin coating device and coating stage .

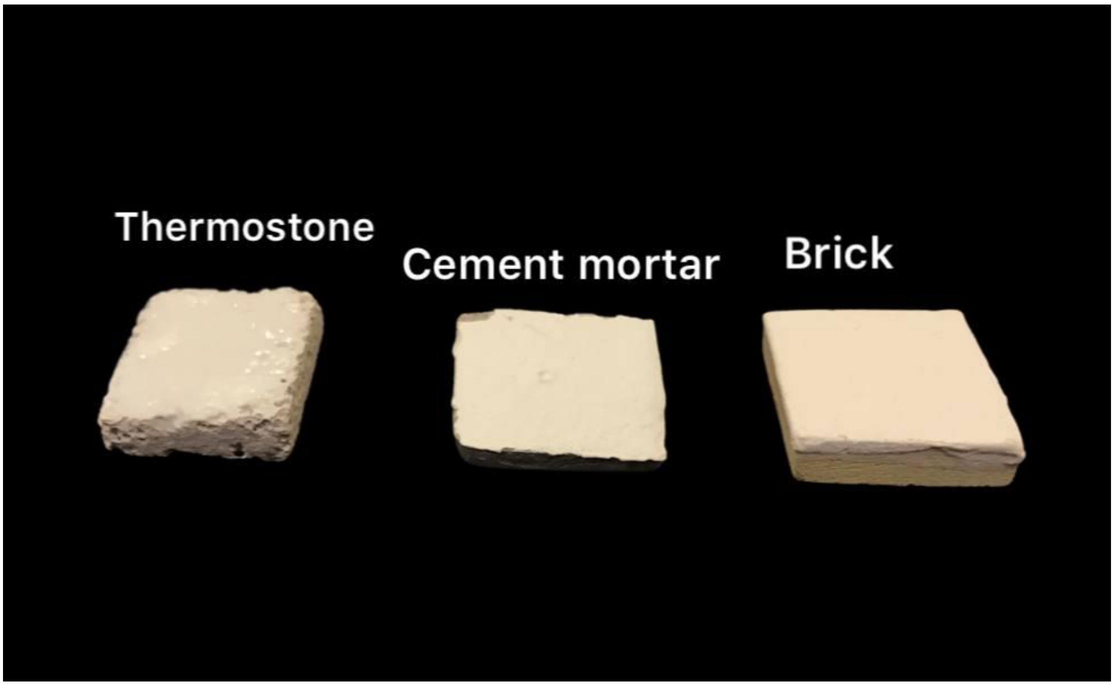


Figure (3-5):substrates surfaces after coating

3-6: *Instrumentation* :

This section contains a discussion of the physical and mechanical test instruments used in this investigation, as well as the methods of inspection for each instrument.

3-6-1 : X-Ray Diffraction (XRD):

XRD is a valuable process for characterizing the phase composition and measuring the structural properties of a material. X-ray diffractometer device (XRD 6000, Shimadzo, Japan) was used in this study and the test was done at Babylon University / College of Material Engineering at the Ceramic and building materials department , Cukα radiation (λ = 1.5405 Å) was used , and the scanning speed was about 5º/min .

3-6-2 : Fourier transforms infrared Spectrometer (FTIR):

Inorganic materials were evaluated using the FTIR device that used in this study is (Shimaduz 1800, Japan) at College of Materials engineering/ Department of Polymers Engineering at the Babylon University). The wavenumber was in the middle of the range. (500-4000 cm^{-1}).

3-6-3 : *Contact Angle Test Instrument* :

An Optical system used to measure contact angle, it manufactured in Holmarc Opto-Mechatronics Pvt. Ltd. (India) with automatic unit and software for contact angle estimation (static and dynamic). It was also suitable to calculate the surface interfacial tension. This test was done at the University of Babylon/ Polymers engineering department.

The test made by placing the surface on plate or the basic of device on which water drops are delivered by syringe pump. It record the contact angle on screen of PC.. Figure (3-6) shows a photograph for contact angle measurement and clarification image of the droplet.

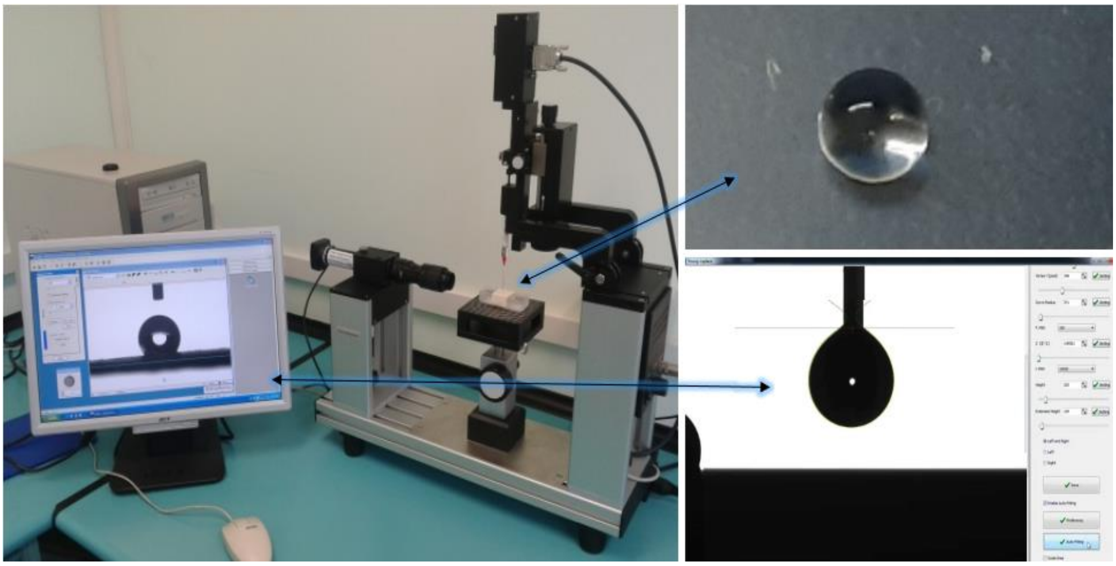


Figure (3-6) : Contact angle measurement device

3-6-4 : *Viscosity Test* :

A viscometer, also known as a viscosity meter or rheometer, is a device that measures the internal flow resistance or viscosity of a fluid. The viscosity was determined using a Digital LCD Rotary Viscometer, which was employed in this work to determine the viscosity of polymer solutions. Figure (3-7) depicts it. The experiment was carried out in the Polymers Engineering Department of the University of Babylon.

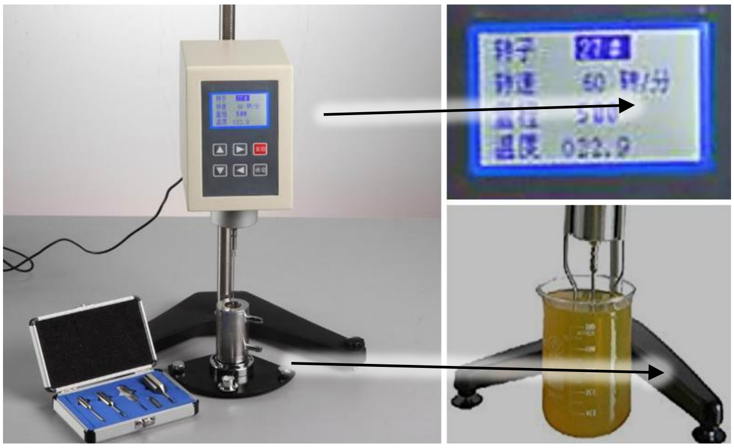


Figure (3-7) : Viscosity instrument.

3-6-5: Micro-hardness test:

At the University of Babylon, the hardness of coated specimens was examined using an HVS-1000, Laryee, Digital Micro-hardness tester figure(3-8) with a force of 4.9N and a holding duration of 15 seconds. The average of three measurements was used to calculate the HV value, which was carried out in accordance with ASTM E3841. Vickers hardness was calculated by (applied load /indentation's sloping area).

3-6-6 : Surface Roughness Test :

TIME Group Inc.'s Hand-Held Roughness TR200 roughness gauge was utilized with the Random Signal-µm technique, which was a side sign for roughness of a random type and shape.The surface roughness device is shown in Figure(3-9).

Figure (3-8) : hardness instrument

Figure (3-9) : Surface roughness instrument.

3-6-7: Measurement of Thickness:

Figure (3-10) shows a non-destructive technique for assessing the dry film thickness of coatings on substrates using a manual digital (micro Printer, TT260, China).This avoids the need for post-inspection coating repair, saving both the inspector and the contractor time.The gadget test was offered in the College of Materials Engineering / University of Babylon's Polymers and Petrochemical Industries facilities.

Figure (3-10): Thickness measurement

3-6-8 : Atomic Force Microscope Test Instrument :

AFM is a kind of scanning probe microscopy (SPM) and it was shown to have high resolution on the scale of fractions of a nanometer in order to see particle size and surface roughness. Figure (3-11) depicts an AFM created in Nanowizard using DirectOverlayTM, as well as the results of tests conducted at the University of Baghdad's Chemical Science Department and the University of Babylon's Materials Engineering College.

Figure (3-11) : AFM microscope instrument.

3-6-9 : Scanning Electron Microscope Test Instrument :

The best contact angle acquired from coating solutions provided was visualized using SEM images. SEM pictures were also taken before and after the addition of nano-sized TiO2 particles and other additives. The surface modification changes and the surface morphology following coating can be seen using a scanning electron microscope (SEM).The experiment was carried out at the University of Babylon's College of Materials Engineering.The SEM instrument utilized is shown in Figure (3-12).

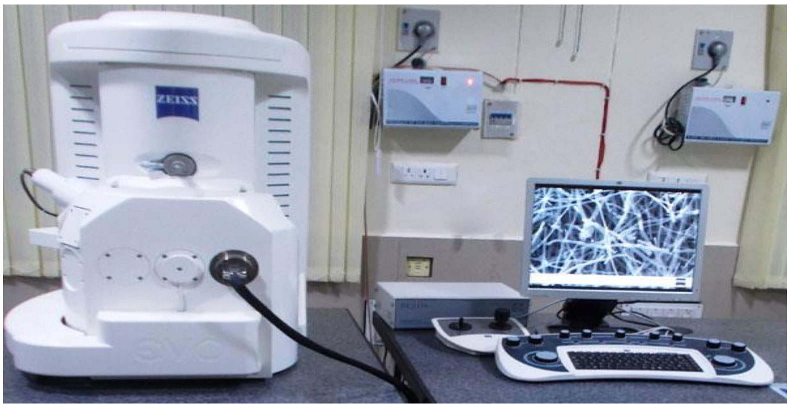


Figure (3-12) : SEM microscope instrument.

3-6-10 : Pull-off test :

The Automatic Adhesion Tester (The Positest AT-A) evaluated the force necessary to pull a particular testing range of coating away from a base using hydraulic pressure in this investigation. The pull-off pressure was automatically applied by an electrically operated hydraulic pump. This test was done in the polymer engineering department/college of materials engineering of Babylon University.

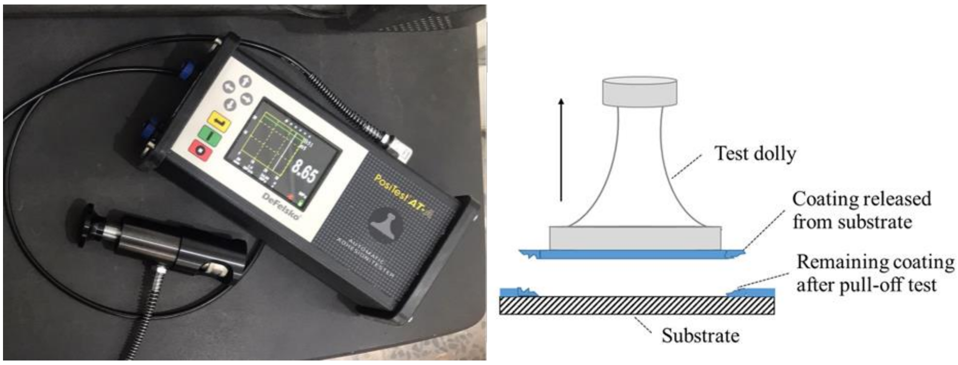


Figure (3-13): pull-off device

4-1 : *Introduction*

This chapter focuses on exhibiting and explaining all of the experimental results, including powder tests and contact angle results for all of the manufactured samples via spin coating, as well as changes in mechanical and physical properties like as (hardness, surface roughness and adhesion test).Also included are photographs of coated surfaces taken with an optical microscope , as well as SEM and AFM images of coated surfaces that achieve the best contact angle when compared to other coated specimens.

4-2: X-ray Diffraction

Figures (4-1) to (4-4) show XRD patterns of (nanoTiO_2, $CaCO_3$,bauxite,PTFE) powders respectively ,which scanned in diffraction angle (2θ) from 10^o,20^o to 60^o.The phases were identified by comparison with standard reference pattern from powder file (JCPDS cards). The patterns show the existence of phase anatase nano-TiO_2 powder approving with standard cards number (JCPDS No.01-083-2243). Results of XRD for $CaCO_3$ powder confirmed the peaks of $CaCO_3$ approving with standard cards number (JCPDS No.01-072-1937). According to conventional cards, the XRD patterns of bauxite powder revealed the AlO(OH) and $Al(OH)_3$ peaks (JCPDS No.00-021-1307) this confirms the presence of bauxite, considering that these are the basic oxides that constituent the bauxite and The XRD patterns of PTFE is (JCPDS card no. 00-047-2217) .

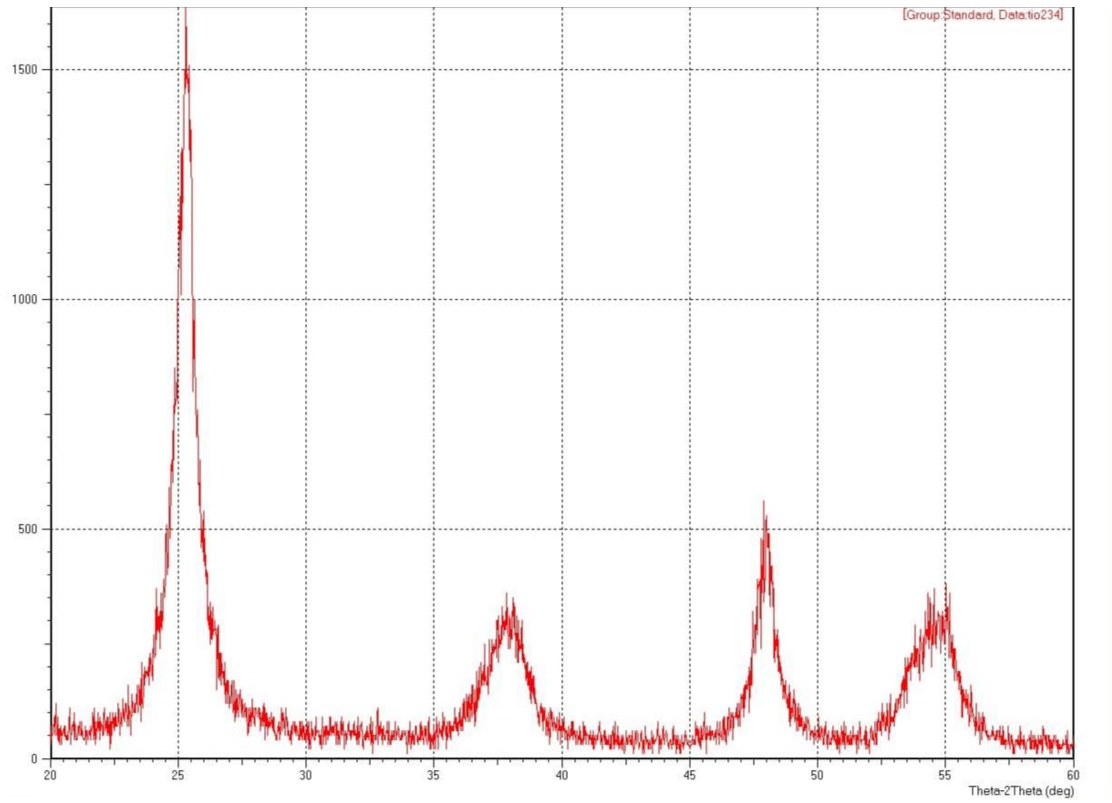


Figure (4-1): Results of XRD for anatase nano TiO_2

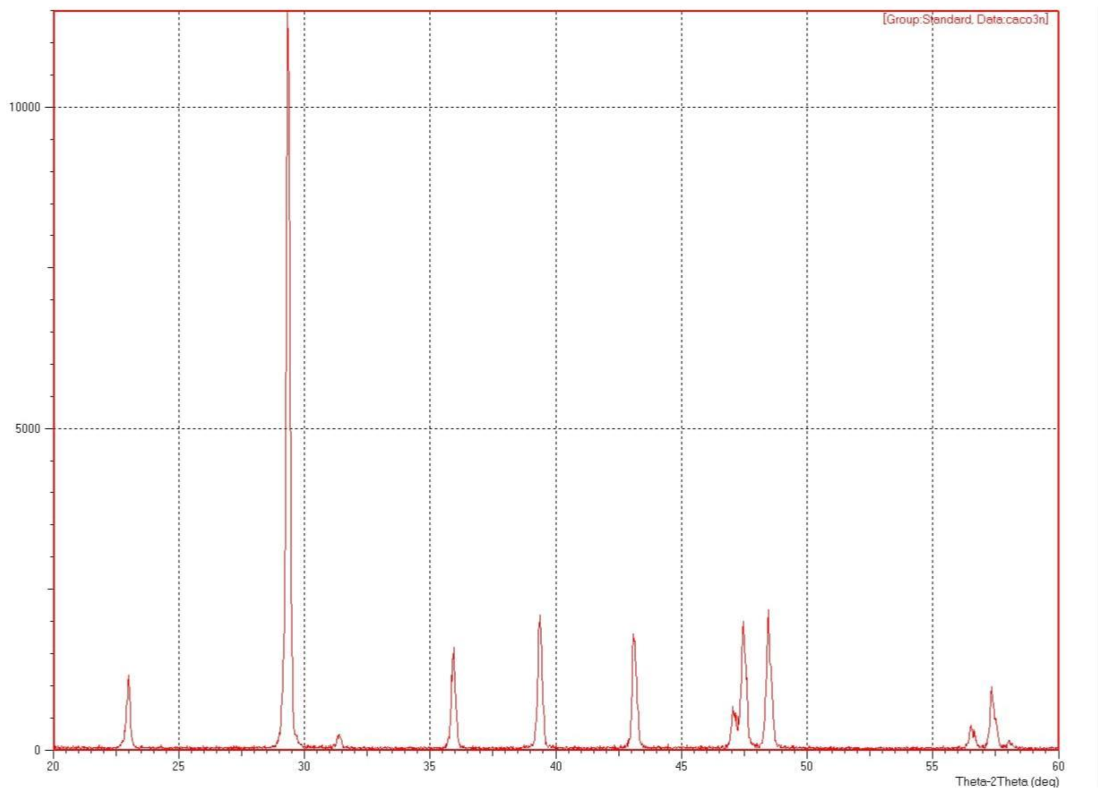


Figure (4-2): Results of XRD for $CaCO_3$

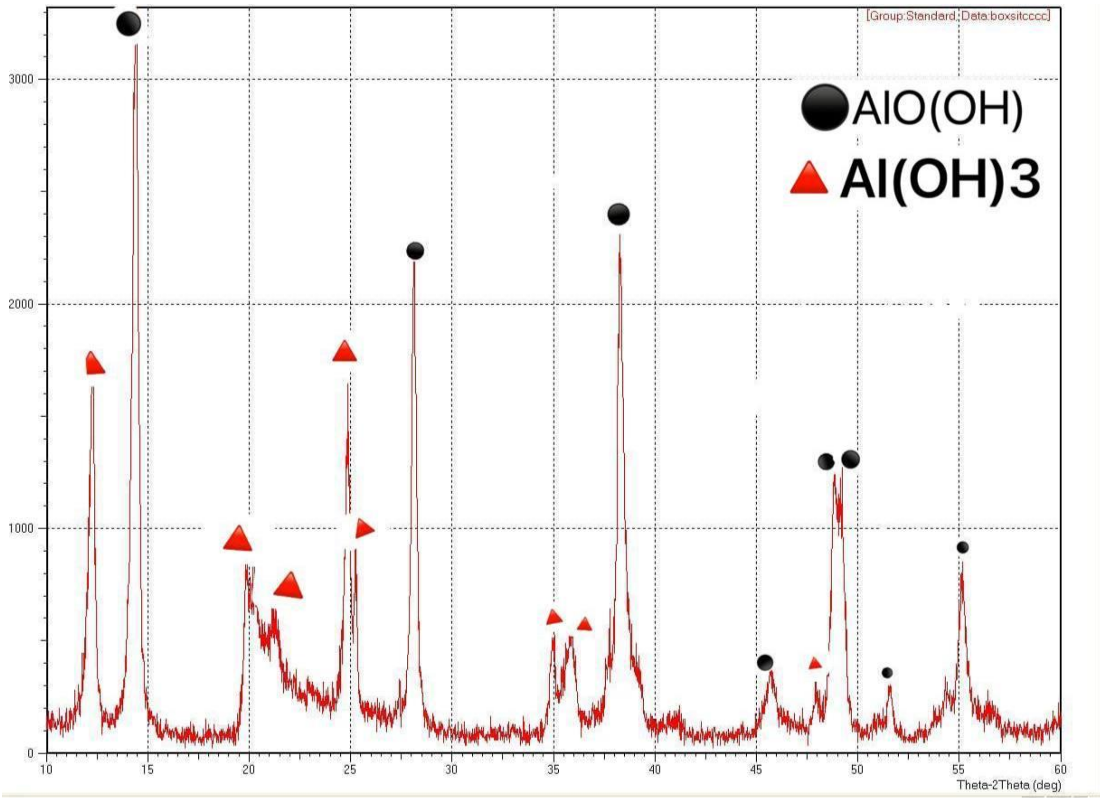


Figure (4-3): Results of XRD for bauxite

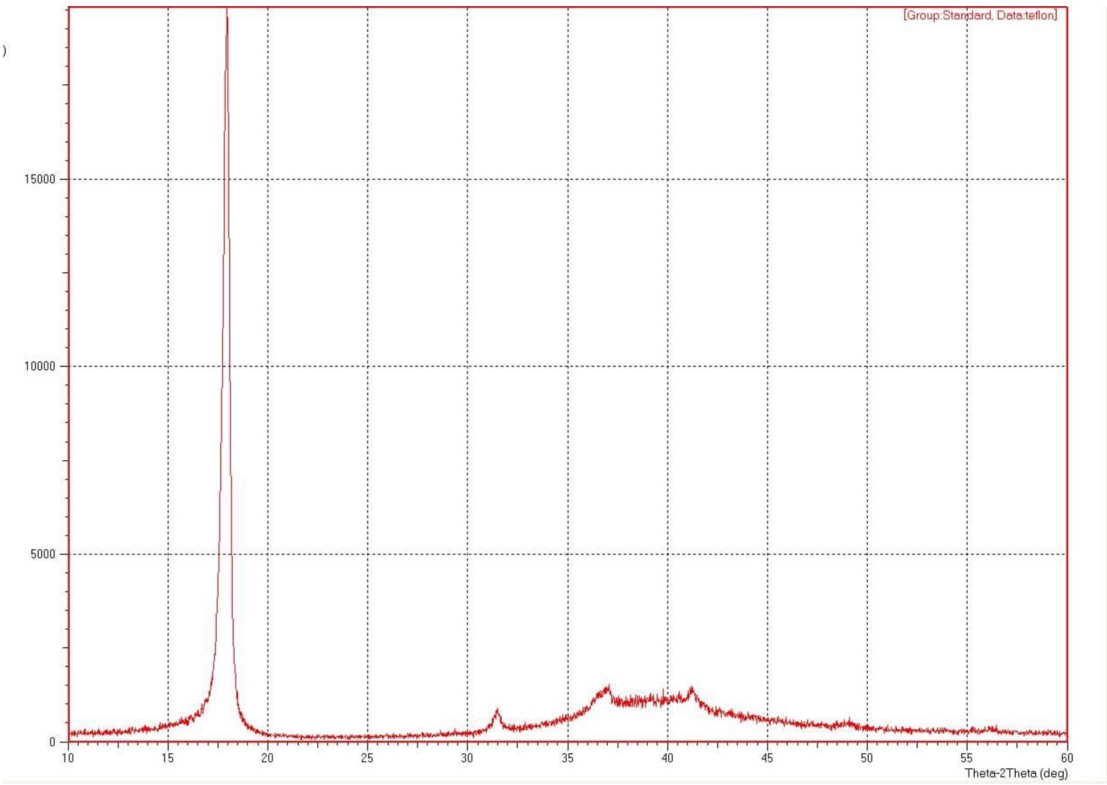


Figure (4-4): Results of XRD for PTFE

4-3: Fourier transformed infrared (FTIR)

Figures (4-5) to (4-8) show the results of FTIR analysis studied for the nano TiO_2 ,$CaCO_3$,bauxite ,PTFE, respectively. The formation characteristics of high purity product as shown in the results . The spectra of FTIR results (figure 4-5) of the TiO_2 nanoparticles indicated the peaks corresponding to TiO_2 only . The peak spotted at 455.20 cm $^{-1}$ is owning to the (Ti O O) bond vibration. The FTIR spectra (figure 4-6) of $CaCO_3$ powder shows the peaks that identical to $CaCO_3$, the peak spotte at 709.80 cm^{-1}. The (figure 4-7) shows the FTIR spectra peaks of bauxite spotted at 424.34 cm^{-1}. Also ,the PTFE spectra peaks are shown in (figure 4-8) and it is observed at 401.10 cm $^{-1}$.

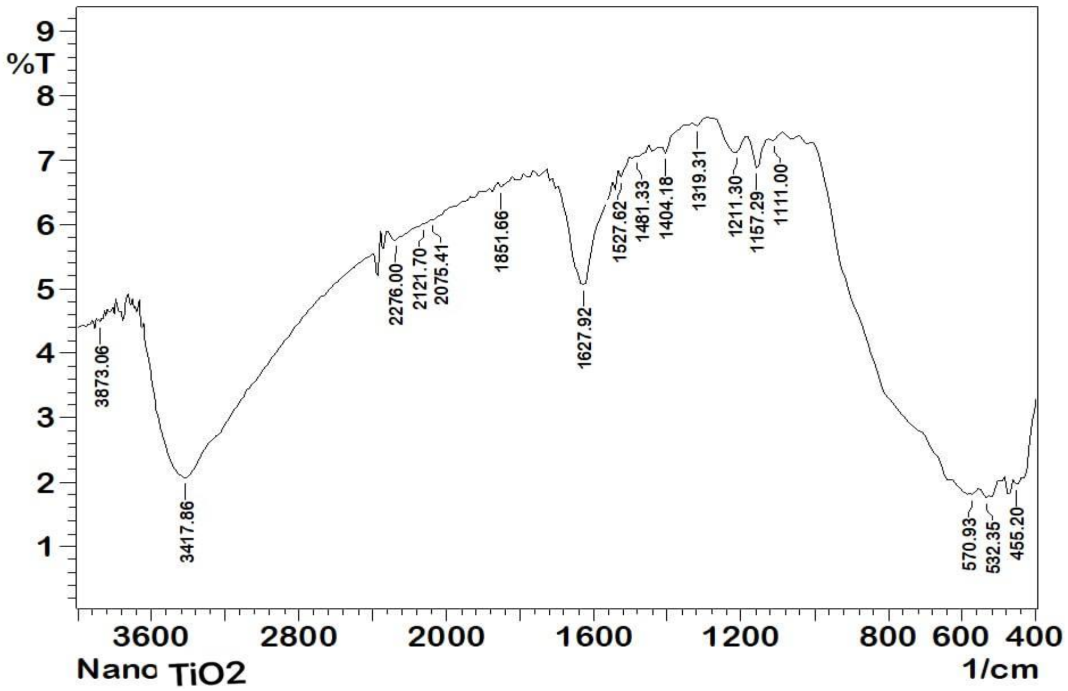


Figure (4-5): Results of FTIR for nano TiO_2

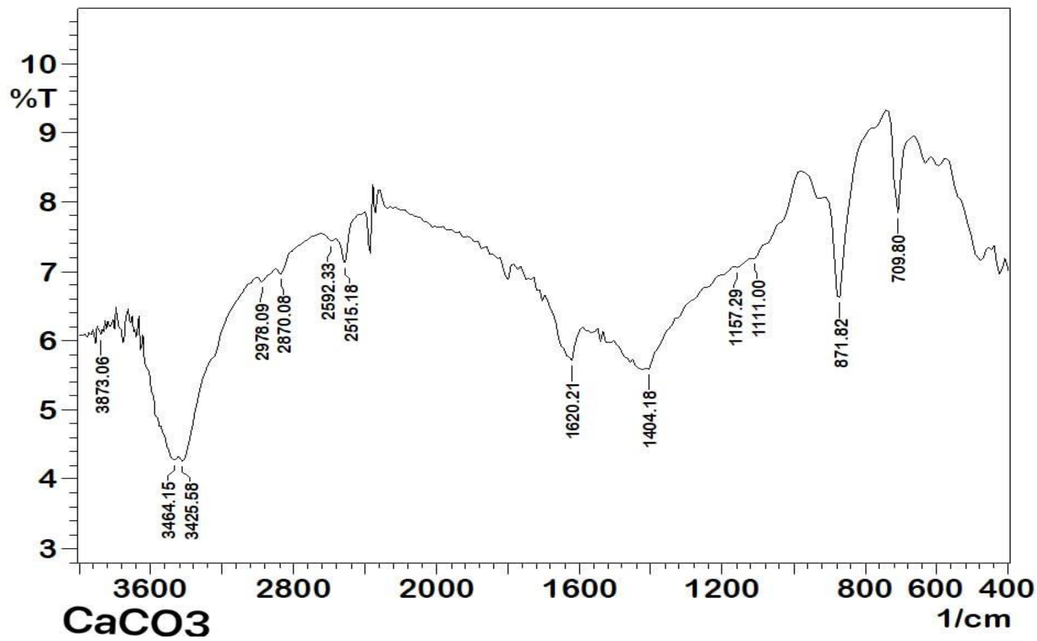


Figure (4-6): Results of FTIR for $CaCO_3$

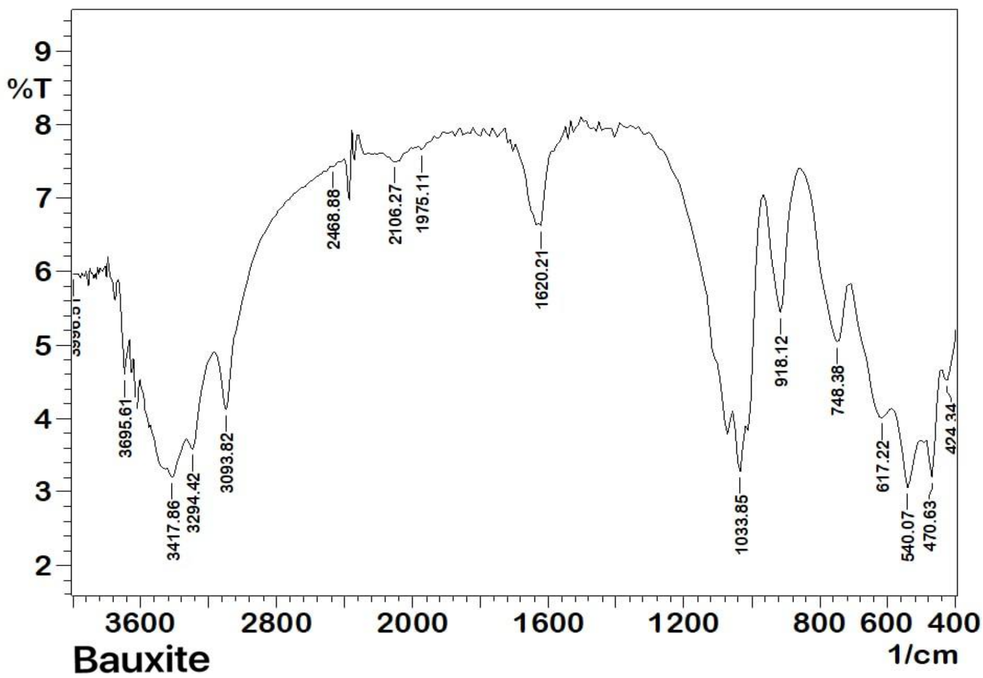


Figure (4-7): Results of FTIR for bauxite

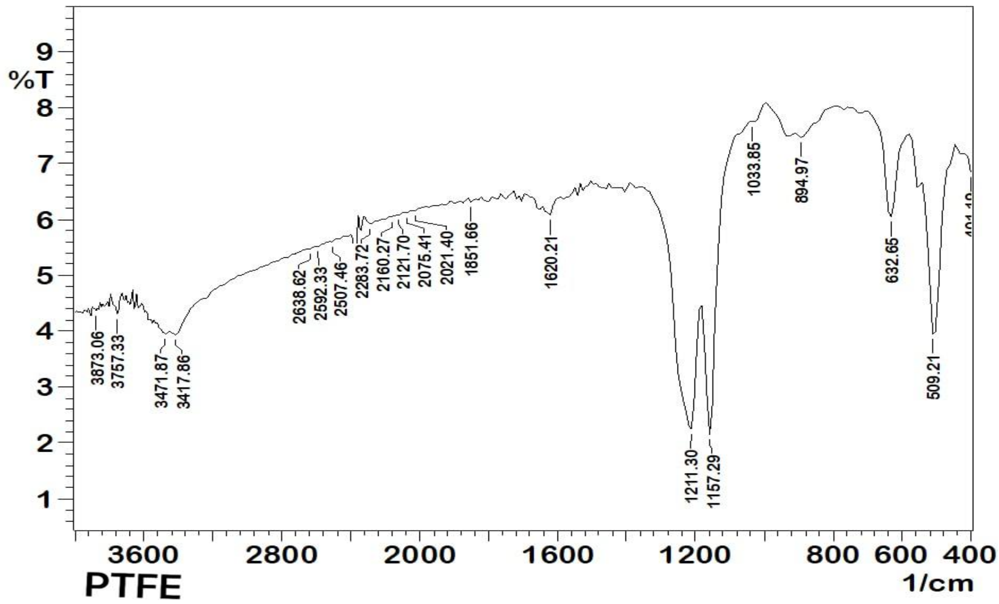


Figure (4-8) : Results of FTIR for PTFE

4-4: Viscosity Results

At the beginning the polymer matrix solution (0.2g/ml PS) had been examined before and after the addition of TiO_2 and the other additives of ($CaCO_3$, bauxite , PTFE). The results of viscosity in figure (4-9) shows that (0.2g/ml PS/DMF) polymer matrix solution owns the suitable viscosity for PS to obtain hydrophobic surface layer by spin coating, which equals to (24.57 $m^2.sec^{-1}$). Because of the nano particles of TiO_2 and a small amount added the viscosity result of (0.2g/ml PS/0.006g/ml TiO_2) not much different from (0.2 g/ml PS/DMF) polymer matrix solution viscosity result ,which equals to (25.38 $m^2.sec^{-1}$). Due to the micro particle size and the large amount added of the additives ,the viscosity results of (0.2 g/ml PS/0.006 g/ml TiO_2/(1g) $CaCO_3$), (0.2 g/ml PS/0.006 g/ml TiO_2/ (1g) bauxite)and (0.2 g/ml PS/0.6%wt TiO_2 /(1g) PTFE) shows a noticeable increase in viscosity ,which equal (59.88 $m^2.sec^{-1}$) , (76.12 $m^2.sec^{-1}$) and (47.09 $m^2.sec^{-1}$) respectively . [68]

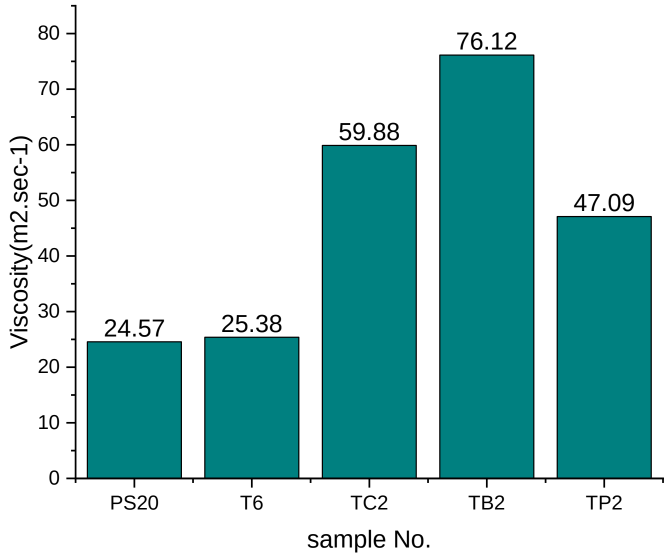


Figure (4-9): Viscosity results

4-5 : Surface Roughness Results

Surface roughness test was examined for the coated specimens. The surface roughness results depend on the use of surface in nature. Figure (4-10) to (4-12) show surface roughness results for different substrates before and after coating. The surface of ceramic has a higher roughness value in general and the surface is full of pores, such value of roughness must be lowered by coating with hydrophobic nano composite . In general, the roughness of all samples has decreased and improved after coating with different types of nanocomposite coating solutions, and that the best improvement in roughness has been observed in the surfaces of cement mortar samples compared to the surfaces of brick samples and the surfaces of thermostone samples that recorded the lowest percentage of the mentioned improvement and the reason for this is due to the porous nature for bricks and high porosity of thermostone surfaces.

Although the addition of Teflon to the coatings recorded the best improvement in the roughness, followed by TiO_2, but the surfaces of the Teflon samples did not improve their contact angle. It seems that the reason for this is due to the topography of the coating surface after the addition of Teflon, which was clarified in the AFM images . the surfaces of the coatings after adding Teflon were not uniform in density and the presence of lumps of the coating in general on the surface, which affected the values of the contact angle.

What appears from the above the values of contact angle depend on the consistency of the roughness ratio with the topographical regularity of the surface, and this is what we noticed in the AFM results for the samples added with $CaCO_3$; we also note the topographical regularity and recorded the roughness values (1.1963µm) in the brick surfaces and (0.8213µm) and then (1.1394µm) in the surfaces of the thermostat and this corresponds to the surface behavior in the lotus effect.

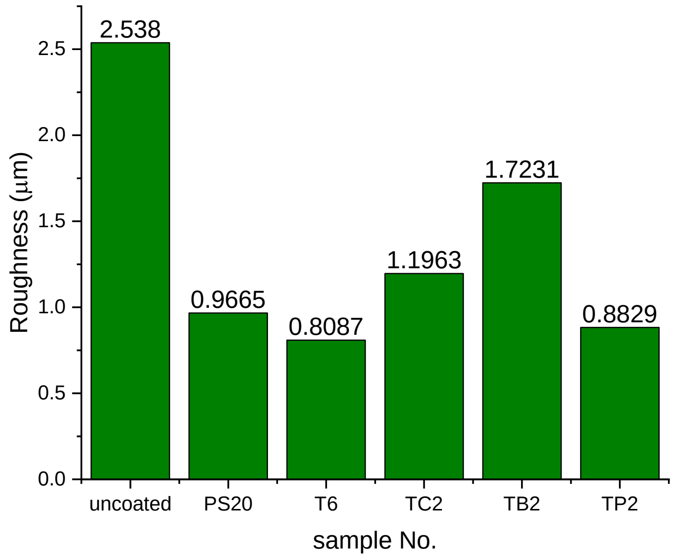


Figure (4-10): Surface roughness results for brick

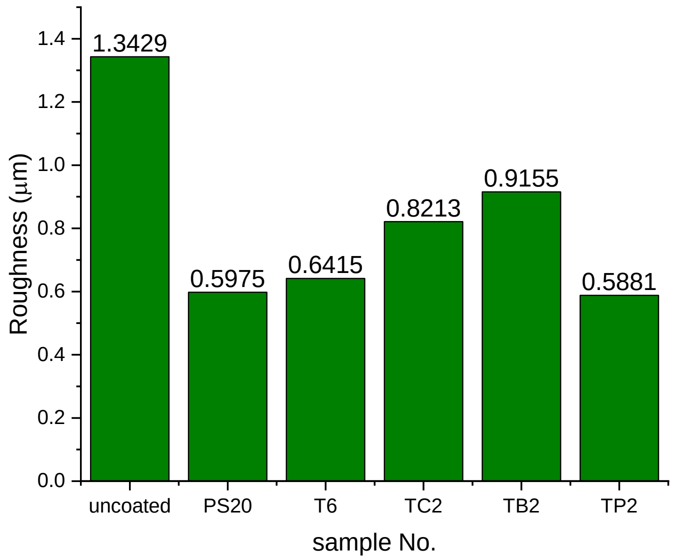


Figure (4-11): Surface roughness for cement mortar

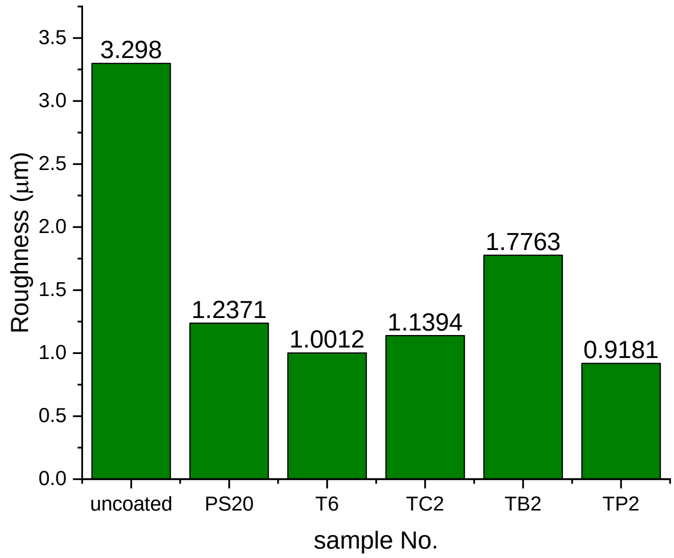
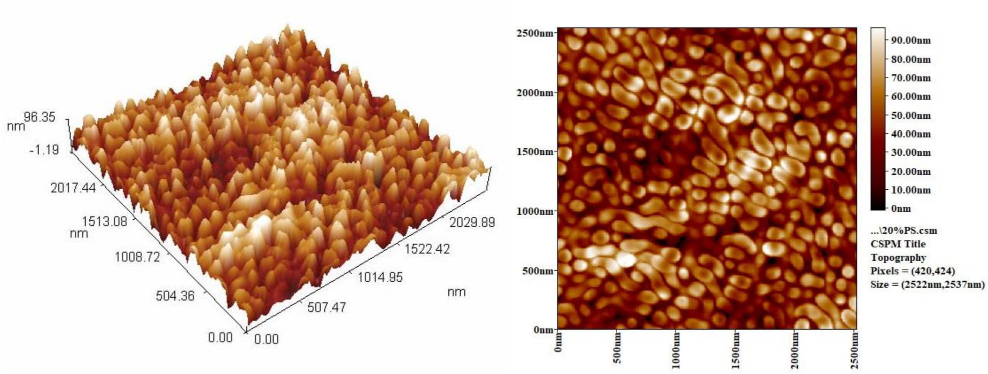


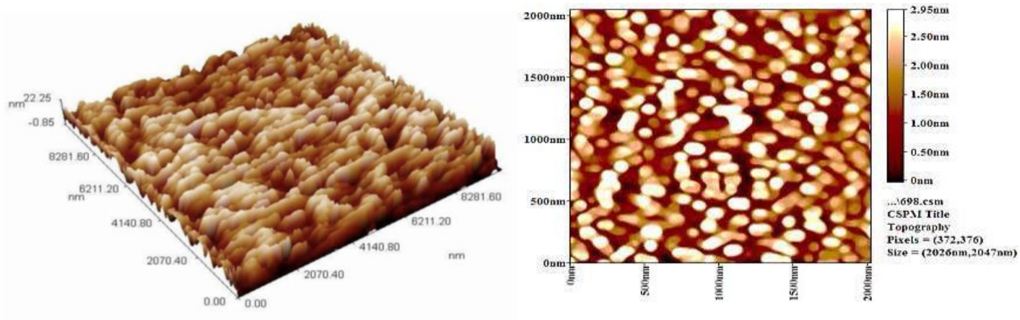
Figure (4-12): Surface roughness for Thermostone

4-6: Atomic Force Microscopy AFM

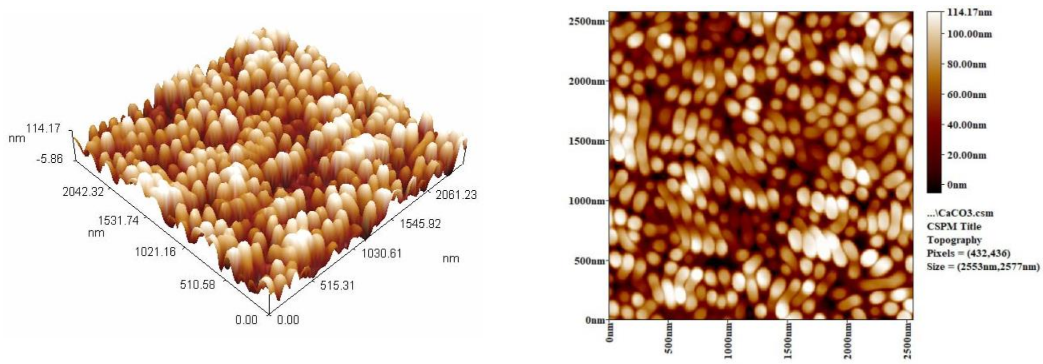
The AFM is a tool for evaluating the surface topography and morphology of produced coating samples. The AFM images reveal the form and particle size distribution of the coated layer. The goal of this study is to learn more about the surface morphology and geometry of structures for coated brick samples. The AFM results are shown in Figure (4-13). The tribology is dense and it is almost regular for all samples with uniform distribution of coatings , as illustrated in the photos . As mentioned in section 4-5 ,the more uniform distribution of the coating particles observed in the topography for the $CaCO_3$ containing coatings have its effect on providing those coatings with the highest contact angles, thereby, improving the hydrophobic properties .



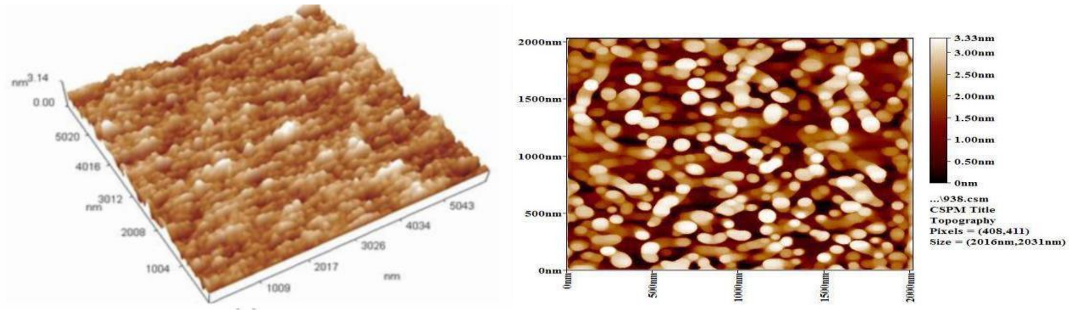
(a)AFM image of PS20



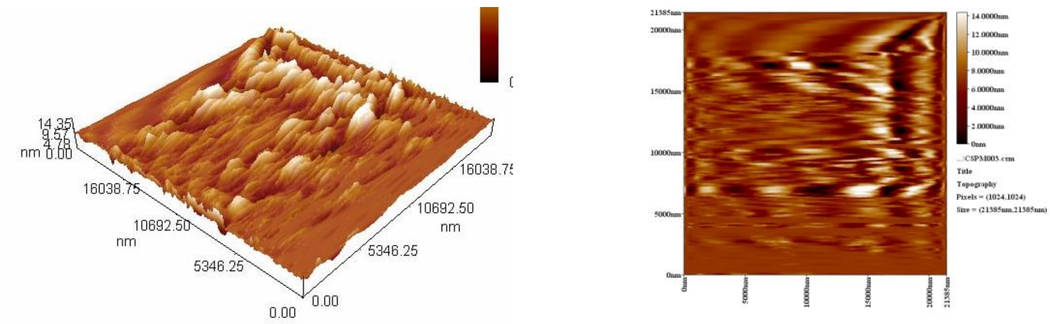
(b)AFM image of T6



(c) AFM image of TC2



(d)AFM image of TB2



(e) AFM image of TP2

Figure (4-17):AFM results of the coated brick surfaces (a)PS20,(b)T6,(c)TC2,(d)TB2,(e)TP2

4-7: Contact Angles(CA) Results

The wettability of surfaces was determined by CA test. All coated specimens were examined by CA test to evaluate the properties of surface if it is hydrophilic or hydrophobic. Table(4-1) and Figures (4-14) to (4-16) show contact angle results for coated specimens . In the beginning coating the brick ,cement mortar and thermostone surfaces with (PS) polymer matrix solution at different ratios as explained in chapter three. Meanwhile, higher contact angle was associated with hydrophobic properties were given by (0.2g/ml) of PS, it was about (94.4771^o). These percentages were considered in this research to add the nano TiO_2 in different percentage and the higher contact angle was given by 0.006g/ml TiO_2 about (154.9627^o). Then starting to add the additives to the 0.6%wt TiO_2 in different amounts until achieve higher contact angle from all additives solutions and it was given by (1g) from all ($CaCO_3$,bauxite ,PTFE),the highest contact angle in this study obtained from 0.2 g/ml PS /0.006g/ml TiO_2 /(1g) $CaCO_3$ about (167.3987^o) coated on brick. Ceramic substrates before coating owns CA of (0.000) ,due to the high porosity of brick, mortar and thermostone building materials, the water drop is absorbed by the sample surface and does not allow the formation of a drop on the surface before coating. In comparison to uncoated substrates , the ceramic substrates brick, cement mortar and thermostone coated with different composite solutions, showed a hydrophobic and super hydrophobic properties because the coating layer work on closing all the pores at the substrates surfaces and Also, because of the addition of TiO_2 and the role it plays in improving the angle of contact due to its hydrophobic properties, as well as the case when adding $CaCO_3$ due to the topography of the surface of the particles that make up the surface of the paint, it gives a super hydrophobic surface.[71]

As for the coatings containing bauxite, the contact angle decreased because the minerals that make up bauxite are hydrophilic. As for Teflon, the contact angle decreases because the atoms are not evenly distributed on the surface of the coating as shown previously in the AFM images, so it does not give the best result for the contact angle.

Table (4-1): Contact angle results

Sample No.	Substrates		
	Brick	Mortar	Thermostone
PS20	94.4771^O	92.1145^O	90.3291^O
T6	154.9627^O	153.2259^O	148.7121^O
TC2	167.3987^O	159.8512^O	150.3401^O
TB2	106.7660^O	101.9946^O	98.2297^O
TP2	110.4692^O	109.2333^O	104.5728^O

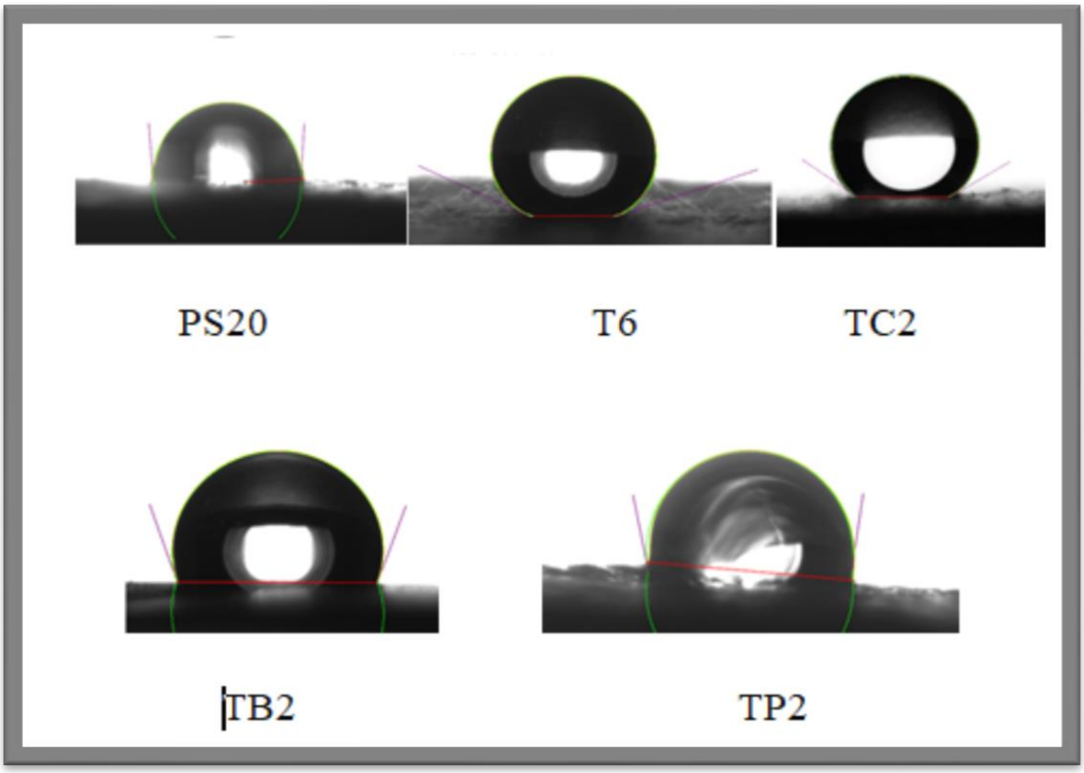


Figure (4-14): Contact angle results for brick substrate

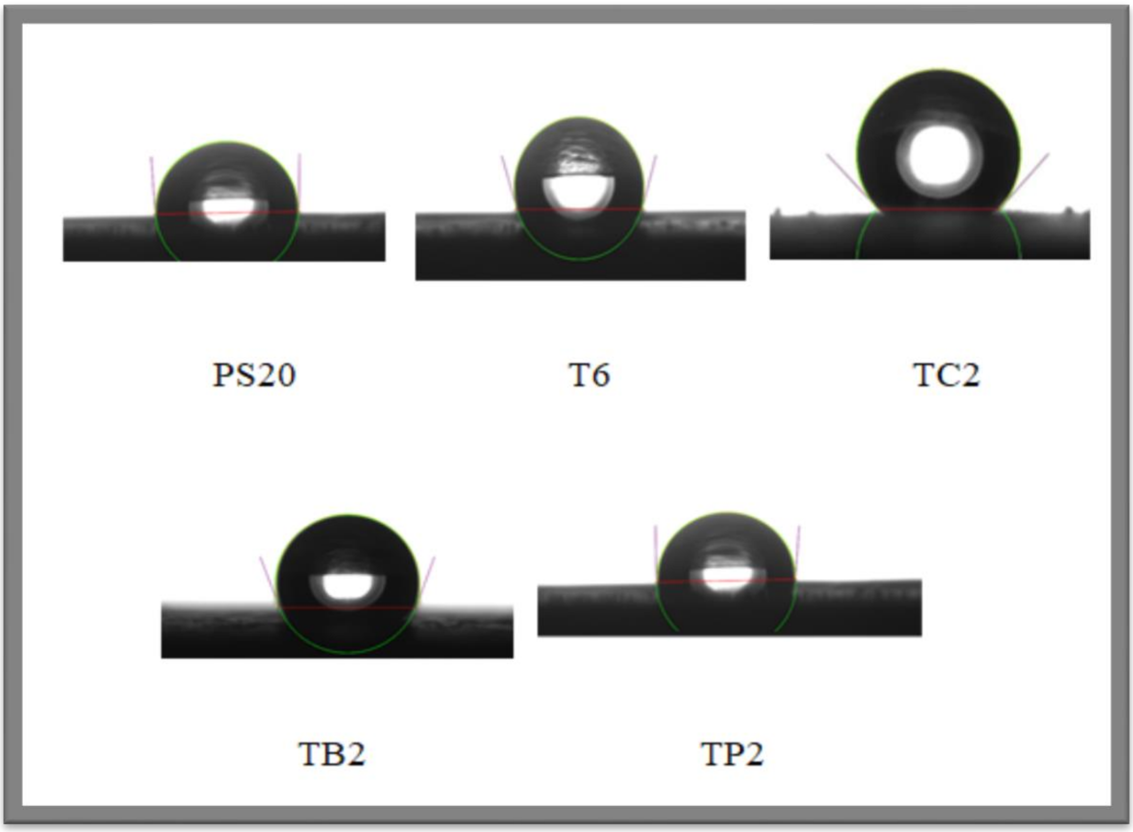


Figure (4-15) Contact angle results for cement mortar substrate

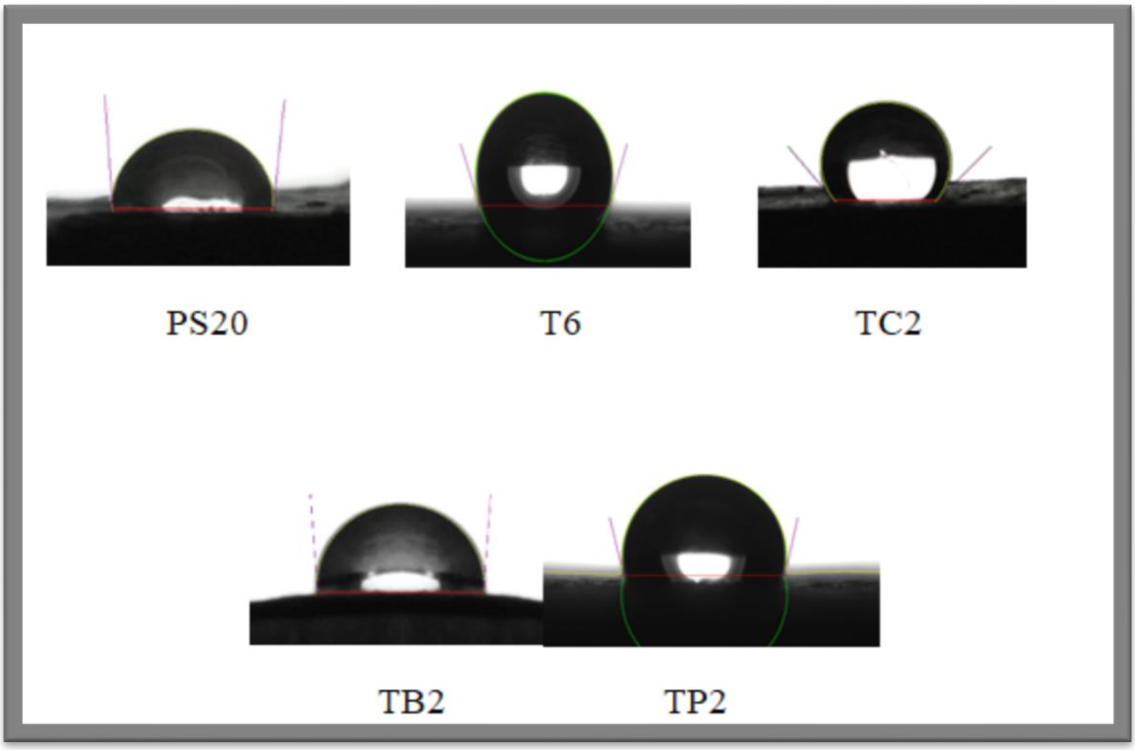


Figure (4-16): Contact angle results for Thermostone substrates

4-8: Hardness Results

Figures (4-17) to (4-19) show the hardness results. Hardness results show an increase after coating, as a result of the increase in bonding because of the particles addition which decreases the motivation of polymer molecules and tend to improve the resistance of materials to scratches.

In general , the incorporation of ceramic particles of TiO_2 ,$CaCO_3$ and bauxite in the composite coating could improve the hardness of the substrates from 60.67 Hv to about (97.75-497.8 Hv) due to the nature of those hard ceramic particles in providing the matrix material with improved mechanical properties .

In comparison to the other samples ,the substrates coated with bauxite containing coating solution had the highest hardness value because of abrasive and toughness properties. Also it can be noticed that the thermostone samples have the lowest hardness values due to the weak mechanical properties and the porous structure of the material. Also, the cement mortar samples have the highest hardness results due to its strong mechanical properties and compact structure.

The improvement of the surfaces hardness of brick, cement mortar ,and thermostone to 484.4, 497.8 and 202.49 Hv, respectively, proved the success of the present study in providing those surface with hydrophobic (CA=98.2297^{o}- 106.766^{o}) and improved hardness properties for self-cleaning and hard anti scratch conditions . As expected ,addition of PTFE to the coating could not record the highest hardness , due to its polymeric nature.

The percentage of improvement in each substrate was 7.98 for brick , 4.81 for mortar and 11.91 for thermostone.

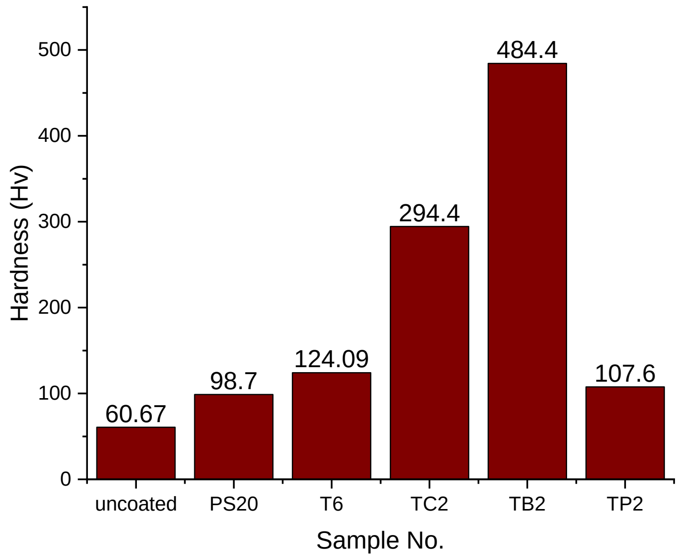


Figure (4-17): Hardness results for brick

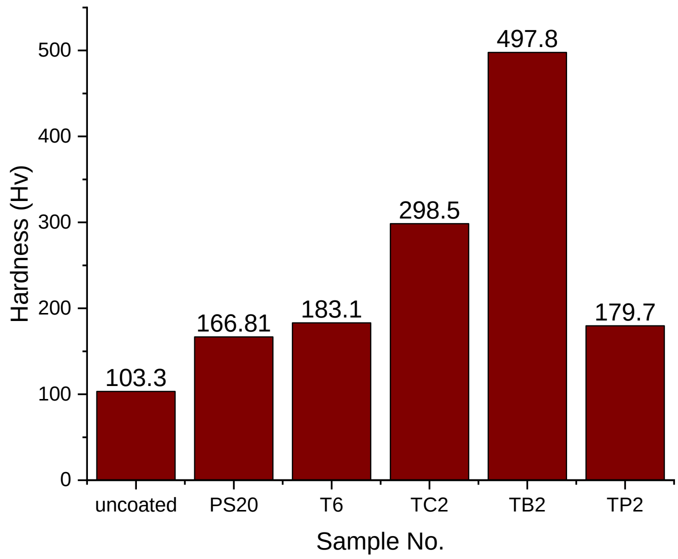


Figure (4-18): Hardness results for cement mortar

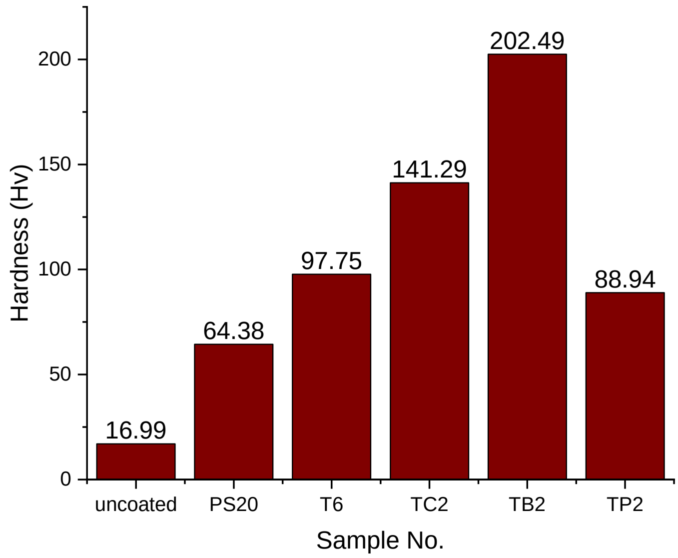


Figure (4-19): Hardness results for Thermostone

4-9: Thickness Measurement

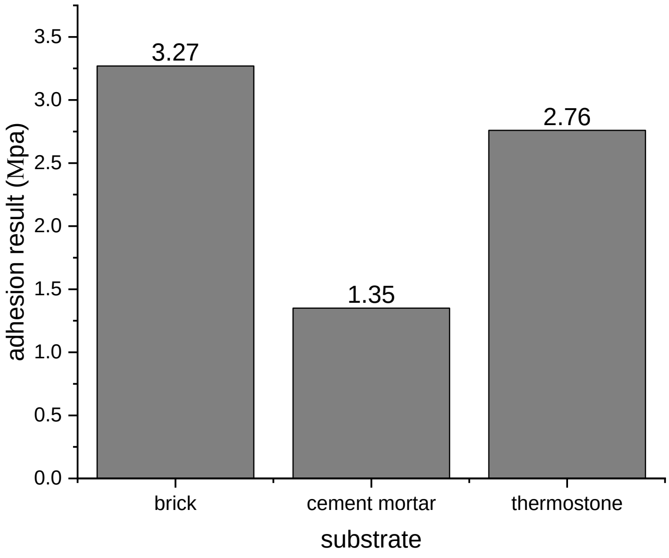
In this study, the thickness of spin coating depend on several factors such as; speed of rotation ,spinning time and amount of solution . furthermore ,because these factors are constant in this study, they don't change, so the thickness of the coating depends on the material deposited as is evident in the table (4-2). The largest thickness was obtained in the cement mortar surfaces, because it is the least porous between the substrates . Thus, the coating solution does not penetrate inside the substrate surface , but rather remains on the surface, forming a thick layer of coating. As for thermostone bricks, because of their high porosity, the coating solution enters the pores, leaving a thinner layer on the surface. Also, we note that the thickness of the coating increases when adding additives, because the additives' particles increase the viscosity of the solution and thus reduce the ability to penetrate inside the surface pores, so the layer is thicker at the surface.

Table (4-2): Thickness results for different substrates

Sample No.	Substrates thickness(mm)		
	Brick	Cement mortar	Thermostone
PS20	0.033	0.091	0.029
T6	0.042	0.097	0.031
TC2	0.068	0.13	0.052
TB2	0.093	0.19	0.078
TP2	0.081	0.16	0.071

4-10: Adhesion results :

Pull-off test was used to detect the adhesion between the coating layer and the substrate . The pull off test was done using the coated ceramic substrate (brick ,cement mortar , thermostone). This test is defined as the force required to remove the coating layer from the surface [74] . Figure (4-20) shows the results for the substrates surfaces. As shown in the diagram, the result of bricks and thermostone is better than cement mortar due to the roughness of the surface and the presence of pores that improve the overlap between the coating layer and the surface, which leads to increased adhesion and the failure happened in the substrate because of the brittleness of the brick and thermostone , which means that it is a cohesive failure for both brick and thermostone . As for the mortar ,because of its toughness and high mechanical properties the failure occurred between the coating layer and the substrate surface so the mode of failure is adhesive failure .



(a) pull off results

(b) mortar sample **(c) brick sample**

Figure (4-20): Adhesion results(a) pull off results

, (b) mortar sample , (c) brick sample

4-11: Scanning Electron Microscope (SEM) Images

Figures (4-21) to (4-25) show the scanning electron microscope images of the coated brick samples. These results show the porous structure of the coating layer and the particles distribution of the additives through the coating layer ,in figure (4-21) due to the small coating thickness, the cracks in the brick surface are not completely covered by the coating material, and also because of the low viscosity of the coating solution made it is easy to absorb by the pores on the surface. As for figure (4-22) for samples with nano TiO_2 added, the nanoparticles of TiO_2 and the porous structure of the coating layer as well, and the cracks have decreased. As for the figure (4-23) for the samples with $CaCO_3$ added, the best surface coverage and crack coverage with the presence of $CaCO_3$ particles that act as a binder that increases the density of the coating solution and prevents the surface pores from absorbing the solution as well as in figure (4-24) for the sample to which bauxite is added, where the large microparticles of bauxite through the matrix due to the thickness of the coating higher than The rest of the mixtures are approximately. As for the figure (4-25) for the samples that have Teflon added, the porosity is the highest compared to the rest of the additives, and the topography of the porous surface can be attributed to the nature of the polystyrene material, as well as the heat treatment that was carried out after the coating process to dry the coating on the surface of the samples.[71]

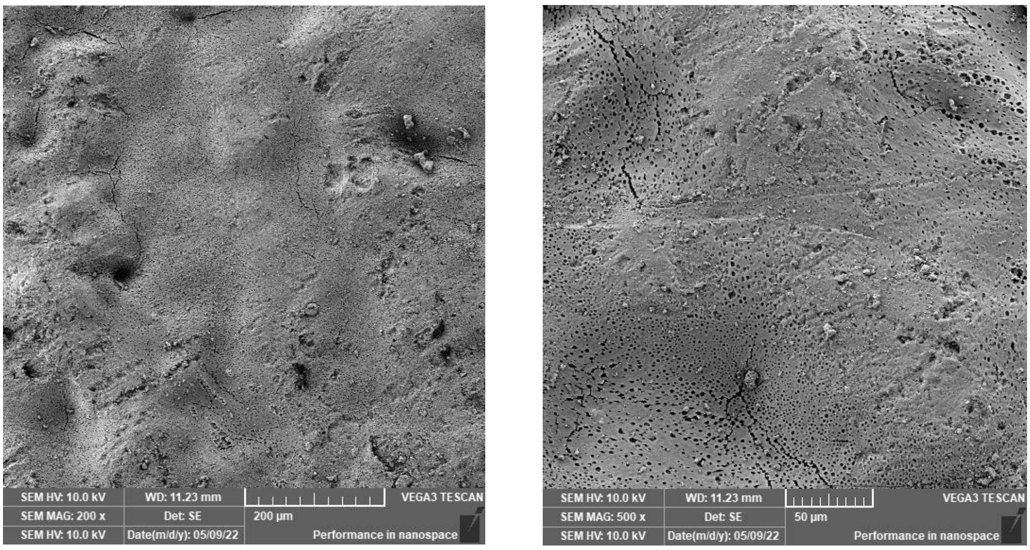


Figure (4-21): SEM results for PS20 for brick

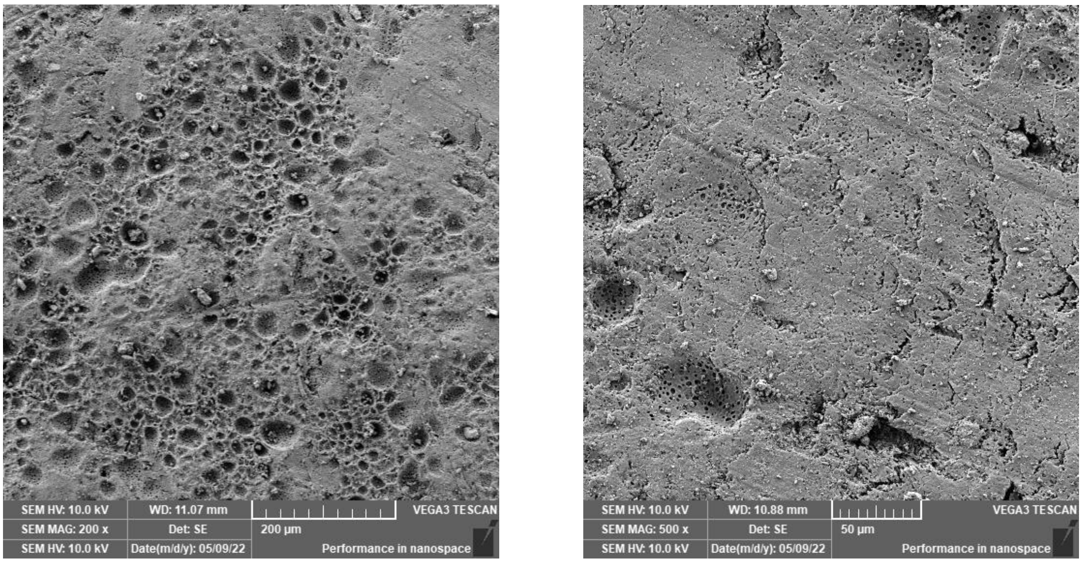


Figure (4-22): Results of SEM for T6 for brick

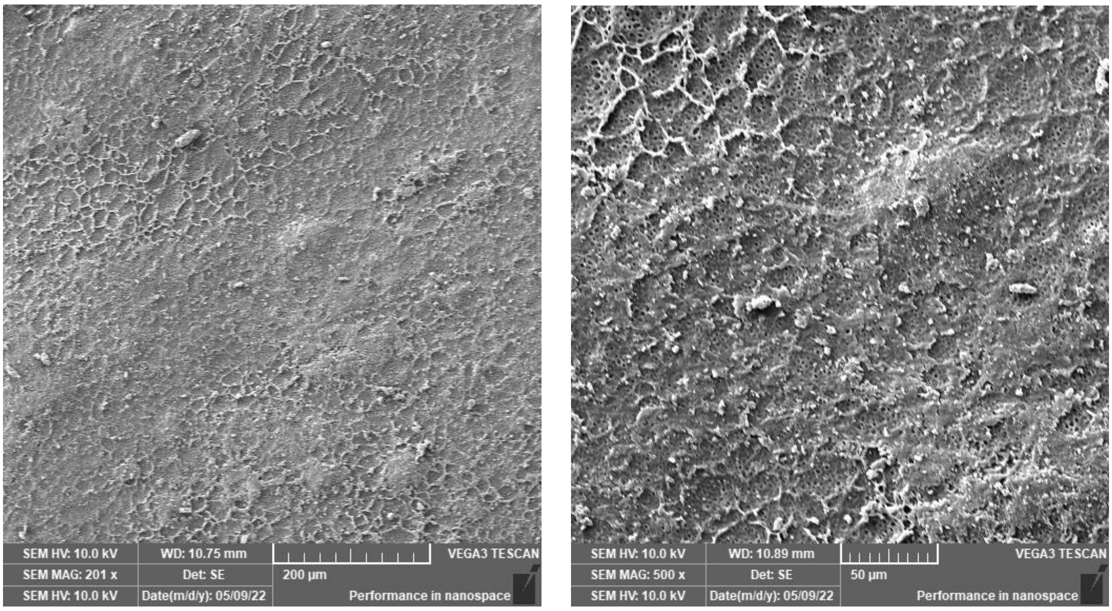


Figure (4-23): Results of SEM for TC2 for brick

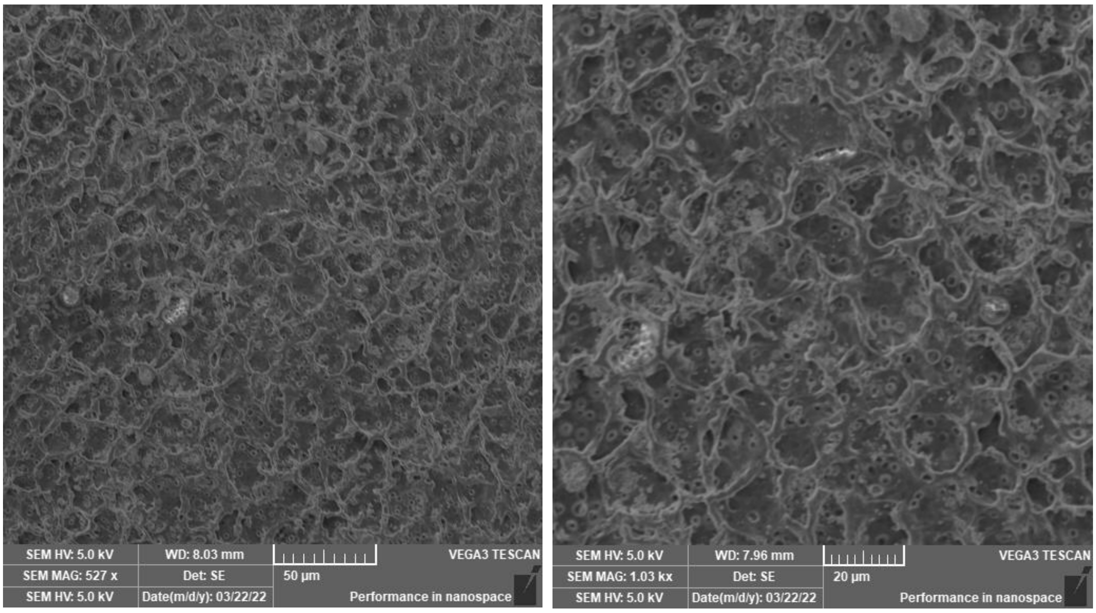


Figure (4-24): Results of SEM for TB2 for brick

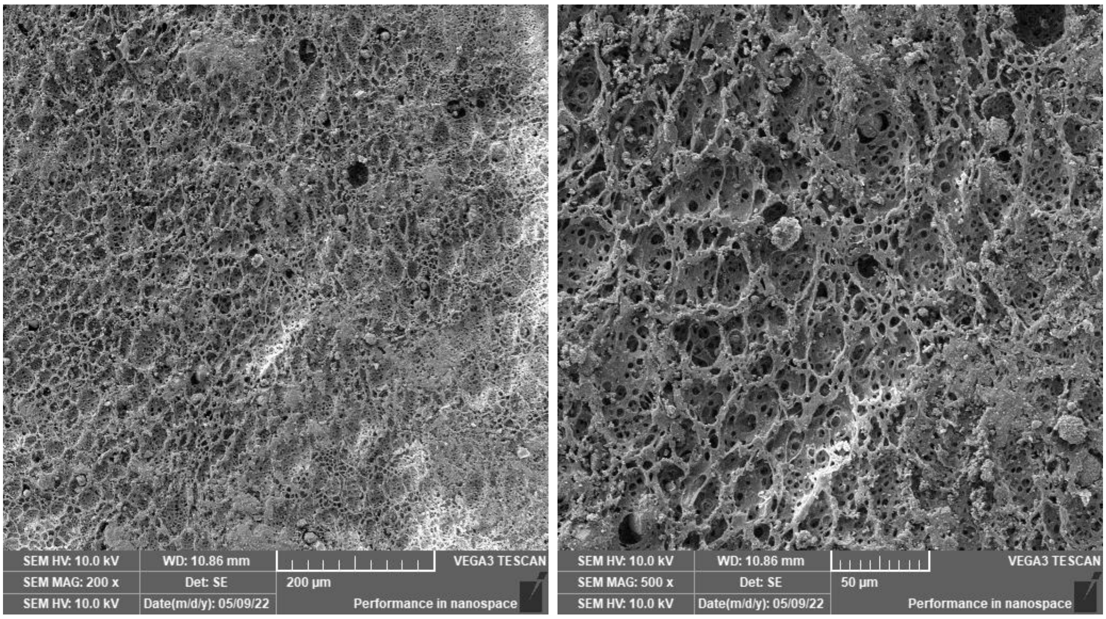


Figure (4-25): Results of SEM for TP2 for brick

5-1 : *Conclusions* :

1- The current study success in deposition of hard ,hydrophobic and super hydrophobic nano composites coatings by spin coating technique using Polystyrene PS matrix material with the addition of nano TiO_2 particles and natural ceramic additives of ($CaCO_3$ and bauxite) and Teflon additives .

2- The results shows that porous and uniform self-cleaning composite coatings of thickness (29-190 µm), hydrophobic and self-cleaning in terms of contact angle enhanced to (167.3987^o-104.4692^o),hardness(124.09-497.8Hv), roughness (0.8087-1.7763Ra), and Adhesion results showed that the brick samples had the higher adhesion values and could be obtained (1.35-3.27MPa) for cement mortar and brick sample respectively .

3- The best contact angle for coating with PS substrate without additives is (94.4771^o) and hardness (166.8Hv), which improved to (154.9^o) and hardness (183.1Hv) after adding (0.006 g/ml TiO_2).
.

4- Generally , the hardness and contact angle values improved after adding bauxite (1g) and calcite (1g) to TiO_2, with the addition of calcite enhancing the angle and the addition of bauxite boosting the surface hardness.

5- The best findings for contact angle were found on brick surfaces, whereas the greatest results for hardness were found on cement mortar surfaces.

6- Due to the surface topography, which was characterized by irregularity and the formation of lumps of additives on the surface, the addition of Teflon did not produce the desired effects.

7- The results showed that the research was successful in protecting the surfaces of bricks, cement mortar , and thermostone with self-cleaning composite coatings of sufficient hardness, which will help to maintain environmental cleanliness and aesthetics while also protecting them from scratching and external weather conditions.

8- The morphology of the coated surfaces showed porous morphology for all surfaces characterized by clear distribution of the nano TiO2 particles and larger particles of $CaCO_3$ and bauxite, with accumulations of Teflon particles .

5-2 : *Suggestions for Future Work* :

1- Fabrication of super hydrophobic coating of silicon rubber modified with nano TiO_2 using other method.

2- Using another oxides as a reinforcement like nano SiO_2, Zr_2O_3 ,ZnO.

3- Using another coating technique such as electrospray method.

4- Manufacturing of super hydrophobic coating of PS with nano TiO_2 on glass and porcelain surfaces.

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الخلاصة

ازدادت في السنوات الأخيرة البحوث الخاصة باستخدام الطلاءات الحاوية على أوكسيد التيتانيوم النانوي TiO_2 لما له من خصائص متميزة في مختلف التطبيقات البيئية وحفظ الطاقة مثل هندسة السطوح ذاتية التنظيف.هذه الدراسة هي محاولة لتحسين الخواص الميكانيكية وذاتية التنظيف لسطوح الطابوق والاسمنت والثرموستون باستخدام الطلاء بتقنية الغزل الحاوية على ثاني أوكسيد التيتانيوم مع إضافات سيراميكية مثل البوكسايت والكالسايت $CaCO_3$ واضافة التفلون.

تم استخدام البوليستايرين (PS) المذاب بمادة ثنائي ميثيل فورماميد (DMF)كمادة أساس وتراكيز مختلفة (0.01,0.05,0.1,0.15,and 0.2g/mL) مع تراكيز مختلفة من التيتانيا النانوية (0.001,0.002,0.004, and 0.006g/mL)تم الطلاء بظروف(2000 دورة/ دقيقة لمدة 15ثانية) والسطوح المطلية تم معاملتها بالفرن بدرجة حرارة100 مئوية لمدة 24 ساعة .

تم استخدام فحوصات لتوصيف المضافات ولتقييم البنية والسطوح والخواص الفيزيائية والميكانيكية للطلاءات مثل فحص حيود الاشعة السينية ، الفحوصات المجهرية باستخدام المجهر الإلكتروني الماسح، فحوصات الصلادة ،زاوية التماس ،فحص الالتصاقيه ، فحص السمك ،فحص الخشونة وفحوصات الطبوغرافية باستخدام المجهرالقوة الذرية .

بصورة عامة اثبتت النتائج الحصول على طلاءات مركبة ذاتية التنظيف مسامية ومنتظمة السمك و كارهة للماء وذاتية التنظيف بدلالة زاوية التماس. بصورة عامة قد تحسنت قيم الصلادة وزاوية التماس بعد اضافة البوكسايت (1g) والكالسايت (1g)مع التيتانيا وكانت اضافة الكالسايت مؤثرة في تحسين الزاوية بينما اضافة البوكسايت كانت مؤثرة في تحسين الصلادة السطحية وان افضل نتائج لزاوية التماس قد لوحظت في سطوح الطابوق وافضل نتائج للصلادة قد لوحظت في سطوح الاسمنت.

ان اضافة التفلون لم تحقق النتائج المتوقعة منها بسبب طبوغرافية السطح التي تميزت بعدم الانتظامية وظهور تكتلات للإضافات على السطح .النتائج اثبتت نجاح البحث في حماية سطوح الطابوق والاسمنت والثرموستون بالطلاءات المركبة ذاتية التنظيف وذات صلادة جيدة والتي سوف تحافظ على نظافتها البيئية وجماليتها وتساهم في حمايتها من الخدش وظروف التعرية الجوية الخارجية.

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل

قسم السيراميك ومواد البناء

دراسة في تحسين طلاءات ذاتية التنظيف ذات الاساس TiO_2 على مواد بناء مختلفة

رسالة

مقدمة الى كلية هندسة المواد /جامعة بابل كجزء من متطلبات نيل درجة الماجستير في هندسة المواد /السيراميك

من قبل

فاطمة شاكر مضر عباس

إشراف

أ . د .

سمير حامد عواد

1444هـ **2022 م**