**Republic of Iraq**
**Ministry of Higher Education and Scientific Research**
**University of Babylon**
**College of Materials Engineering**
**Department of Ceramic and Building Materials Engineering**

***A Graduation Project***

# *Manufacturing bricks with self-cleaning, scratch-resistant and heat-reflecting surfaces to save energy and protect the environment*

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جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بابل
كلية هندسة المواد
قسم هندسة السيراميك ومواد البناء

# *تصنيع طابوق ذات سطوح ذاتية التنظيف مقاومة للخدش وعاكسة للحرارة لتوفير الطاقة وحماية للبيئة*

مشروع تخرج

*مقدم الى قسم هندسة السيراميك ومواد البناء في كلية هندسة المواد - جامعة بابل كجزء من متطلبات نيل درجة البكالوريوس في علوم هندسة المواد - السيراميك* من قبل

**فاطمة حيدر عبد الحسين**

إشراف

**أ. د. سمير حامد عواد**

2023م. 1444هـ.

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

﴿ يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ ۚ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ﴾

[اية 11 :المجادلة ]

# الاهداء

# الخلاصة

هذه دراسة في محاولة تحسين الخواص الميكانيكية لسطوح الطابوق باستخدام الطلاء المركب بطريقة (spraying) الحاوي على ثنائي أوكسيد التيتانيوم الذي يمنع تحفيزه الضوئي تراكم المواد العضوية / غير العضوية التي تتلامس مع السطح، بينما تساعد قابليته المحبة للماء في عملية التنظيف وذلك لأنه يجعل السطح يجف بشكل أسرع. مع إضافات سيراميكية مثل الكالسايت( $CaCO_3$). تم استخدام البوليستايرين (PS) polystyrene ) المذاب بمادة ثنائي مثيل فورماميد (DMF) N,N-Dimethylmethanamide كمادة أساس . تم الطلاء لفترات مختلفة للعينات (s 15, 30, 5 ,10) . أظهرت كل فترة زمنية مدى مختلف من الخواص الكارهة للماء و الصلادة للسطح .حيث أظهرت فترات ( s 30 , 5) افضل زوايا تماس للعينات والفترة (s 15) اعلى قيمة صلادة . تم استخدام فحوصات لتوصيف المضافات ولتقييم البنية والسطوح والخواص الفيزيائية والميكانيكية للطلاءات مثل فحص حجم الدقائق , حيود الاشعة السينية , الفحوصات المجهرية باستخدام المجهر الإلكتروني , فحوصات الصلادة ,زاوية التماس , وفحوصات الطبوغرافية باستخدام المجهر AFM .

# Abstract

This is a study in an attempt to improve the mechanical properties of brick surfaces by using a composite coating with (spraying) method containing titanium dioxide, whose photocatalysis prevents the accumulation of organic / inorganic materials that come into contact with the surface, while its hydrophilic ability helps in the cleaning process because it makes the surface dry faster . With ceramic additions such as calcite ($CaCO_3$). Polystyrene (PS) dissolved in N,N-Dimethylmethanamide (DMF) was used as a base material. The samples were painted for different periods (10, 5, 30, 15 s). Each showed A time period has a different range of hydrophobic properties and surface hardness.The periods (5, 30 s) showed the best contact angles for the samples and the period (15 s ) the highest hardness value.Tests were used to characterize the additives and to evaluate the structure, surfaces, and physical and mechanical properties of the coatings, such as examining the particle size, X-ray diffraction, microscopic examinations using electron microscopy, hardness tests, contact angle, and topographic examinations using microscopy AFM.

# CHAPTER one

## 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.

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.

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.

Some disasters and tragedies have occurred in buildings, factories, cars, skyscrapers, and other items as a result of faults related to wetness, corrosion, 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

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 brick is the one of the most often used building materials in Iraq. The latest developments in the research that have been conducted on building materials. **[1,2]**.

# CHAPTER Two

## Theoretical Part

## 2.1. Surface engineering

Definition: Modification of near-surface structure, chemistry or property of a substrate in order to achieve superior performance and/or durability. It is an enabling technology and can impact a wide range of industrial sectors.

- Combining chemistry, physics, and mechanical engineering with metallurgy and materials science, it contributes to virtually all engineering disciplines.

- It can be done on a given surface by metallurgical, mechanical, physical, and chemical means, or by producing a thick layer or a thin coating.

- Both metallic and non-metallic surfaces can be engineered to provide improved property or performance .Figure 2.1 shows the surfaces engineering method .

The surface engineering is a generic approach toward the enhancement of the:

performance of engineering component with respect to the following:

• Increase the resistance to corrosion, wear, oxidation, and sulfidation.

• Enhance the mechanical properties, electrical and electronic properties, thermal

conductivity, and insulation.

• Reduce the friction coefficient and improve lubrication characteristics.

• Improve aesthetics characteristics. [3]

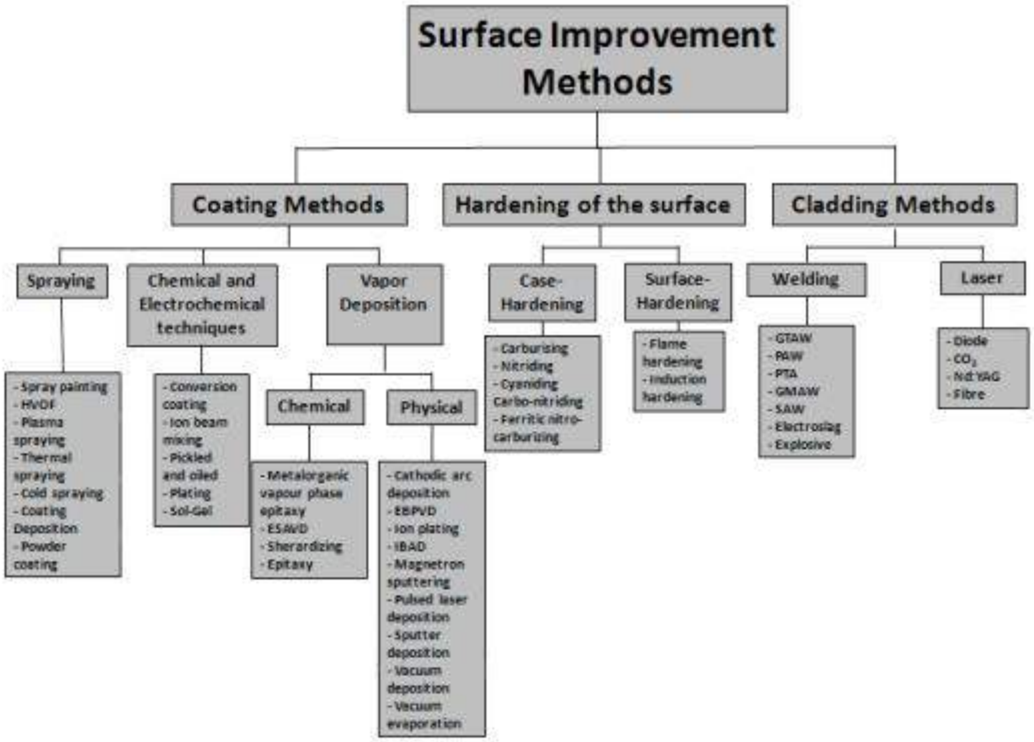



**Figure 2.1: Diagram showing surface improvement methods**

## 2.2. Hydrophillic and Hydrophopic

Sometimes water spreads evenly when it hits a surface; sometimes it beads into tiny droplets. While people have noticed these differences since ancient times, a better understanding of these properties, and new ways of controlling them, may bring important new applications.

Materials with a special affinity for water those it spreads across, maximizing contact are known as hydrophilic. Those that naturally repel water, causing droplets to form, are known as hydrophobic. Hydrophilic and hydrophobic materials are defined by the geometry of water on a flat surface specifically, the angle between a droplet’s edge and the surface underneath it (Fig 2.2) . This is called the contact angle. If the droplet spreads, wetting a large area of the surface, then the contact angle is less than 90 degrees and that surface is considered hydrophilic, or water-loving (from the Greek words for water, hydro, and love, philos). But if the droplet forms a sphere that barely touches the surface like drops of water on a hot griddle the contact angle is more than 90 degrees, and the surface is hydrophobic, or water-fearing. But the terminology doesn't stop there: Most current research on hydrophobic and hydrophilic materials is focused on extreme cases namely, superhydrophobic and superhydrophilic materials. [4].

Because the natural world is full of hydrophobic and hydrophilic surfaces, the basics of the phenomenon have been known by scientists for at least two centuries. Figure 2.3 show the hydrophilic and hydrophopic surfaces.

For example, the lotus leaf is a well-known example of hydropjobic material , protecting the water dwelling plant from becoming waterlogged.

Figure 2.2: showing that the drop is not expelled for lotus flower.

New technologies have also contributed to the field: The ability to create nanopatterned surfaces, with bumps or ridges just a few billionths of a meter across, has enabled a new generation of water-grabbing and water-shedding materials; new high-resolution imaging of surfaces in motion has enabled better understanding of the processes involved. [5].

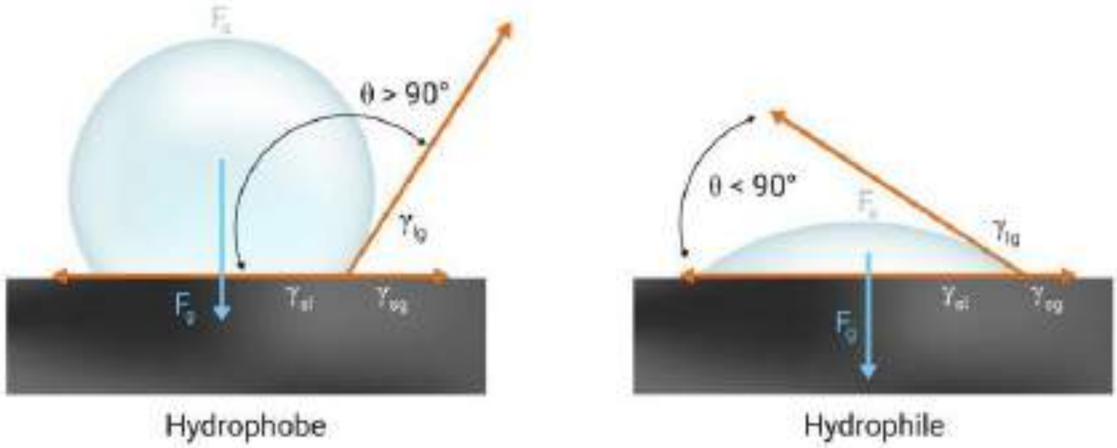


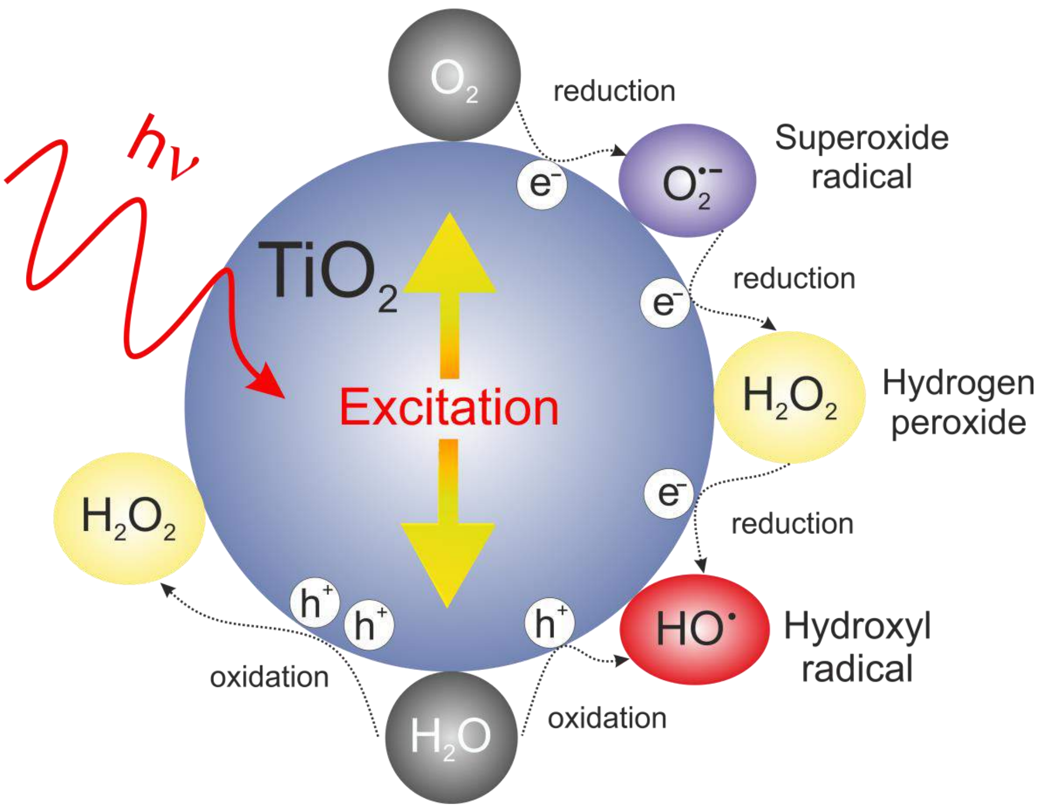

Figure 2.3: show the hydrophilic and hydrophopic surfaces.

## 2.3 Self-cleaning surfaces

The bio-inspired nanotechnology of self-cleaning surfaces and coatings are nowadays being much attracted in the field of energy and environment because of the ever-increasing demand of uncontaminated, self-disinfected and hygienic surfaces. Such surfaces/coatings can be adopted on glass windows, automobile windshields, building construction materials, paints; on optoelectronic devices like solar panels, etc. The mechanism of photocatalytic self-cleaning and superhydrophilicity of nano $TiO_2$ based systems is carefully investigated. The photogenerated reactive oxygen species generated during photoexcitation of electrons from the valence band to the conduction band of $TiO_2$ is responsible for its photocatalytic behaviour, anti-bacterial property and superhydrophilicity. [6]

$TiO_2$-semiconductor heterojunctions, hybrids of $TiO_2$ with graphene and graphitic monolayers, tailoring the exposed crystal facets in $TiO_2$, metal and non-metal doping and dye sensitization, attributing to visible light photocatalytic self-cleaning activity are focused in detail. Figure 2. 4 shows Mechanism of photocatalysis.

Nature is always an inspiration for scientists and engineers - learning from her at all times make an expeditious development in science and technology. Self-cleaning surfaces and coatings are one such attempts to mimic the variegated forms of Mother Nature. With the aid of water, self-cleaning surfaces keep itself always clean. These smart surfaces are mainly classified into- (a) superhydrophobic surfaces with a strong revulsion to water so that over the surface the water rolls and take the dirt particles away in tow; (b) superhydrophilic surfaces with an extreme love for water and on which the water sheets. [7]




**Figure(2.4) : Mechanism of photocatalysis**

The research on super-wettability surfaces and their practical applications began in the 21st century  at a rapid growth with the advent and development of nanotechnology. Lotus-effect is widely considered as a famous example for self-cleaning surfaces that has superhydrophobicity-induced mechanism of removing mud and dirt by water or rain.

As the research progressed, scientists fabricated superhydrophilic surfaces by both physical and chemical methods. Laser treatment, physical vapour deposition and spray-coating were some of the physical fabrication methods used in the preliminary stages of superhydrophilic research.[8]

Titanium dioxide ($TiO_2$) is considered promising as a 'photoresponsive' wetting material after the discovery of its photoinduced superhydrophilic behaviour . Being a semiconductor, on excitation of $TiO_2$ with suitable light energy, organic dirt molecules adsorbed onto the surface are decomposed initially by the process called photocatalysis, followed by washing with water flow finally leaves the surface clean and sterilized. Compared to other semiconductors, the superior optoelectronic properties, photostability, low-cost production, non-toxicity and environmental friendliness make $TiO_2$ a widely acceptable candidate for superhydrophilic self-cleaning surfaces and coatings. The structural organizations, surface properties and intrinsic electronic characteristics account for its distinct photocatalytic efficiency and photoinduced wettability. Recent years have shown with the development of self-cleaning coatings and surfaces with anti-reflective, anti-fouling and anti-fogging properties. The sectors where such coatings have potential applications widely include automobile industry (car bodies, glasses and rear windows), textile industry, medical industry (especially medical aids.[9,10]

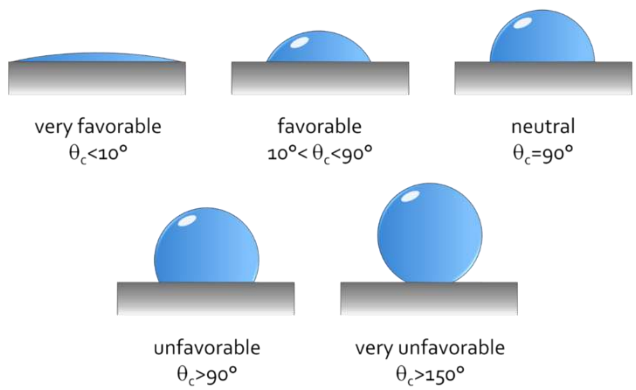
**Table 1.** An overview of such self-cleaning surfaces.

| Artificial Bioinspired Surface Architecture | Surface Properties | Surface Texture and Chemistry |
|---|---|---|
| Lotus leaf | Superhydrophobic, low adhesion | Hydrophobic epicuticular wax and papillae giving dual (micro/nano) scale roughness responsible for superhydrophobic self-cleaning effect. PDMS used for fabrication of lotus leaf replica. WCA~160° while WCA of flat PDMS surface~110°. |
| Gecko feet | Superhydrophobic, high adhesion | Nanopillar array with nanoscale ends (spatula) creating high adhesive forces due to van der Waals interactions. PDMS on nanopillar arrays fabricated by using electron-beam lithography covered with poly(dopamine methacrylamide-co-methoxyethyl acrylate). |
| Rose petals | Superhydrophobic, high adhesion | Hierarchical micro papillae and nanofolds giving sufficient surface roughness for superhydrophobic properties and high adhesive forces due to Cassie impregnating wetting state. Poly vinyl alcohol for fabrication of rose petals template. WCA~154.6°. |
| Fish scale | Superoleophilic in air, superoleophobic in water | The scales have oriented pappilae, 100–300 µm long and 30–40 µm in diameter, arranged in a radial direction, which provide excellent self-cleaning properties. Polyacrylamide for replication of the fish scale structrure. WCA~160° OCA < 5° in air and >~160° in water. |
| Shark skin | Hydrophilic, oleophilic | Small tooth-like scales. Replica of the surface by using polyvinylsiloxane WCA0° in air and 109° in water. |
| Rice leaf | Superhydrophobic, low adhesion, anisotropic | Dual scale (micro&nano) surface roughness arranged parallelly to surface giving anisotropic wettability. PDMS surface chemically modified with alkanethiol to enhance hydrophobicity. WCA~136°. |
| Snail shell | Hydrophobic, oleophilic | Surface roughness of a composite of aragonite and protein. Possibility of many applications, incl. ceramic tiles, sanitary fittings used in toilets and bathrooms and kitchens. WCA 80° OCA 10°. |
| Butterfly wings | Superhydrophobic, low adhesion | Micro-nano hierarchical and periodic structure. Hydrophobic fumed silica (HDK H2000) in segmented thermoplastic polydimethylsiloxane-urea copolymer. WCA~150°. |

PDMS—Polydimethylsiloxane; WCA—water contact angle; OCA—oil contact angle.

## 2-4 Surface wattability

When a solid surface comes in contact with a liquid, the complex effects of the surface morphology (roughness), its chemical composition and the short- and long-ranged intermolecular forces developing with the liquid (van der Waals' forces, hydrogen polar bonding, electrostatic attractions with lone electrons pairs, etc…) determine an equilibrium condition in which the surface may or may not be wetted by the liquid, depending on how much favorable the interactions between the two are. As is known, the self-cleaning properties of the surface are primarily related to the contact angle formed by the drop of liquid placed on the substrate after reaching equilibrium. The surface of the coating material is perfectly wetted when $\theta = 0$, while it is hydrophobic when $\theta \geq 90°$ figure(1.5) show Different kinds of interactions between the two interfaces determine the shape of the liquid droplet and the resulting contact angle. Generally, during measurements the contact angle hysteresis is determined by the difference of increasing and decreasing contact angle. The ideal state could only occur if the solid surface was completely smooth, chemically homogeneous, and the measurement was carried out slowly enough so that the state of all surfaces was as close to equilibrium as possible. In fact, roughness has a significant effect on surface wettability. [11]




Figure(2.5) show Different kinds of interactions between the two interfaces determine the shape of the liquid droplet and the resulting contact angle.

## 2-5 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.

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.

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 qualities.This type of treatment aids in corrosion resistance, anti-wetting, and self-cleaning.[ 12]

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.. The latest developments in the research that have been conducted on building materials, most of them do not focus on treating the surface of the material, but rather work on strengthening the base material, and a few of them work on solving brick problems..[13]

## 2-6 Materials of the spray gun method:

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

## 2.6.1 polystyrene (PS)

Polystyrene (PS) plastic is a naturally transparent thermoplastic that is available as both a typical solid plastic as well in the form of a rigid foam material. PS plastic is commonly used in a variety of consumer product applications and is also particularly useful for commercial packaging. The solid plastic form of polystyrene is commonly used .[14]

Now that we know what it is used for, let's examine some of the key properties of Polystyrene. Polystyrene is typically (but not always) a homopolymer meaning that it is composed only of the monomer styrene in combination with itself. Depending on the type of PS it could be classified as a "thermoplastic" or a "thermoset" material. The name has to do with the way the plastic responds to heat. Thermoplastic materials become fully liquid at their melting point (210-249 degrees Celsius in the case of Polystyrene), but they begin to flow at their glass transition point (100 degress Celsius for PS). A major useful attribute about thermoplastics is that they can be heated to their melting point, cooled, and reheated again without significant degradation. Instead of burning, thermoplastics liquefy, which allows them to be easily injection molded and then subsequently recycled. Thermoset plastics, by contrast, will not reliquify once they are "set" in solid form.

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).[15]

## 2.6.2 Additives :

2-6-2-1 $TiO_2$:

Titanium dioxide ($TiO_2$) is a bright white substance used primarily as a vivid colourant in a wide array of common products. It also has a number of lesser-known qualities that make it an extremely useful and important ingredient in our battle to fight climate change and prevent skin cancer.

Titanium dioxide is a white inorganic compound, which has been used for around 100 years in a vast number of diverse products. It is depended on for its non-toxic, non-reactive and luminous properties, which safely heighten the whiteness and brightness of many materials.[16]

It is the whitest and brightest of the known pigments, with reflective qualities; it can also both scatter and absorb UV rays

Due to its various properties, titanium dioxide has been found to be useful for many different environmentally friendly applications.

When used in a paint coating on the outside of buildings in warm and tropical climates, the white, light-reflecting qualities of $TiO_2$ can lead to considerable energy savings, as it reduces the need for air-conditioning.

Also, its opaqueness means it doesn't need to be applied in thick or double coats, improving resource efficiency and avoiding waste.

As a photocatalyst, $TiO_2$ can be added to paints, cements, windows and tiles in order to decompose environmental pollutants. As a nanomaterial , it can also be used as a crucial DeNOx catalyst in exhaust gas systems for cars, trucks and power plants, thus minimising their environmental impact.[17]

Researchers are discovering new potential uses for titanium dioxide in this form. This includes clean energy production. Figure (1.6) : shows (a) Photocatalytic and (b) self-cleaning mechanisms of $TiO_2$ nanocomposites.

Titanium dioxide has a number of unique characteristics that make it ideally suited to many different applications.[18]

It has an extremely high melting point of 1 843ºC and boiling point of 2 972ºC, so occurs naturally as a solid, and, even in its particle form, it is insoluble in water. $TiO_2$ is also an insulator.

$TiO_2$ absorbs UV light. This property makes it appear bright white under light, unlike other white materials that can look slightly yellow.

Importantly, $TiO_2$ also has a very high refractive index (its ability to scatter light), even higher than diamond. This makes it an incredibly bright substance and an ideal material for aesthetic design use.

Another crucial property of $TiO_2$ is that it can show photocatalytic activity under UV light. This makes it effective for environmental purification, for different kinds of protective coatings, sterilisation and anti-fogging surfaces, and even in cancer therapy.

- **Brilliant**
  Brilliance, colour strength, opacity and pearlescence unlike any other substance.
- **Resistant**
  Resistance to heat, light and weathering prevents degradation of paint and in films and embrittlement of plastics.
- **Protective**
  Ability to scatter and absorb UV radiation makes $TiO_2$ a crucial ingredient for sunscreen, protecting the skin from harmful, cancer-causing UV rays.
- **Powerful**
  Is used as a photocatalyst in solar panels and can also reduce pollutants in the air.

Titanium is one of the most common metals on earth, but it does not occur naturally in this elemental form. $TiO_2$, also known as titanium (IV) oxide or titania, is the naturally occurring compound created when titanium reacts with the oxygen in the air. As an oxide, titanium is found in minerals in the earth's crust. It is also found with other elements, including calcium and iron.

Its chemical formula is $TiO_2$, which means it consists of one titanium atom and two oxygen atoms (hence dioxide). It has a CAS (Chemical Abstracts Service) registration number of 13463-67-7.

$TiO_2$ is typically thought of as being chemically inert, meaning it does not react with other chemicals and is, therefore, a stable substance that can be used in many different industries and for various applications.[19]

- Titanium dioxide nanoparticles in the form of anatase have received considerable attention in the construction industry in recent years due to their potential to add new functionalities to infrastructures, i.e., self-cleaning properties and the ability to remove air pollutants through photocatalysis.

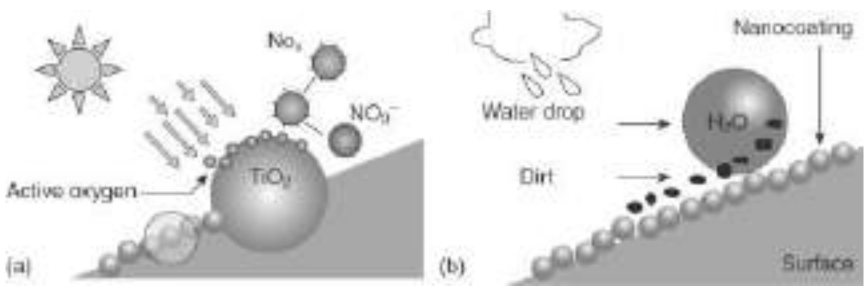



Figure (2.6) (a) Photocatalytic and (b) self-cleaning mechanisms of $TiO_2$ nanocomposites.

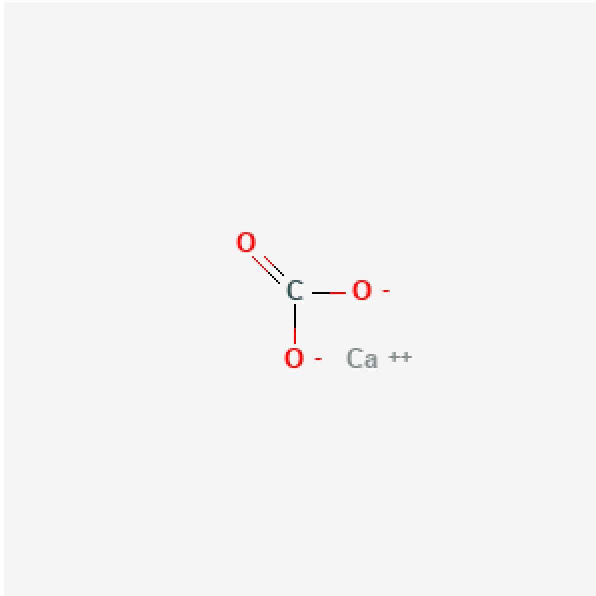
## 2-6-3Modification additives :

2-6-3-1. $CaCO_3$ :

Calcium carbonate appears as white, odorless powder or colorless crystals. Practically insoluble in water. Occurs extensive in rocks world-wide. Ground calcium carbonate results directly from the mining of limestone. The extraction process keeps the carbonate very close to its original state of purity and delivers a finely ground product either in dry or slurry form. Precipitated calcium carbonate is produced industrially by the decomposition of limestone to calcium oxide followed by subsequent recarbonization or as a by-product of the Solvay process (which is used to make sodium carbonate). Precipitated calcium carbonate is purer than ground calcium carbonate and has different (and tailorable) handling properties.[20]

**Physical properties**

- High brightness
- Blocky particle shape
- Odorless
- Thermal conductivity
- Insoluble in water
- Relatively soft (3 on Mohs scale)




Chemical Structure Depiction

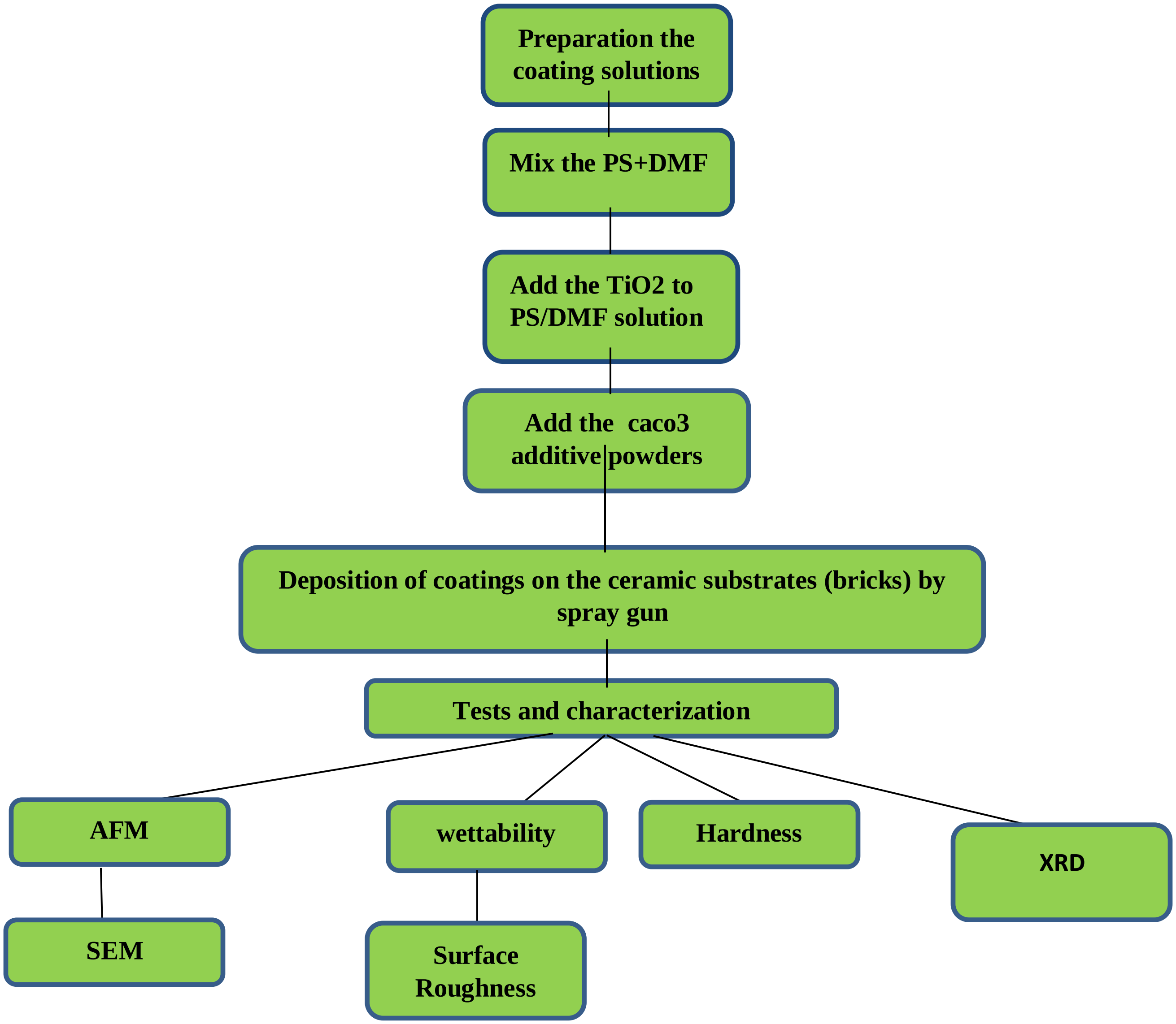
**Sources/Uses**

Calcium carbonate ($CaCO_3$) occurs in nature as limestone, chalk, marble, dolomite, aragonite, calcite and oyster shells. Natural calcium carbonate can be found in the minerals calcite and aragonite (limestone, chalk, and marble). Calcium carbonate is used in the manufacture of quicklime, Portland cement, and paints. Pharmaceutical grades are used in cosmetics, foods, and drugs. Used in paints, rubber, plastics, ceramics, polishes, inks, pharmaceuticals, adhesives.[21]

# CHAPTER THREE

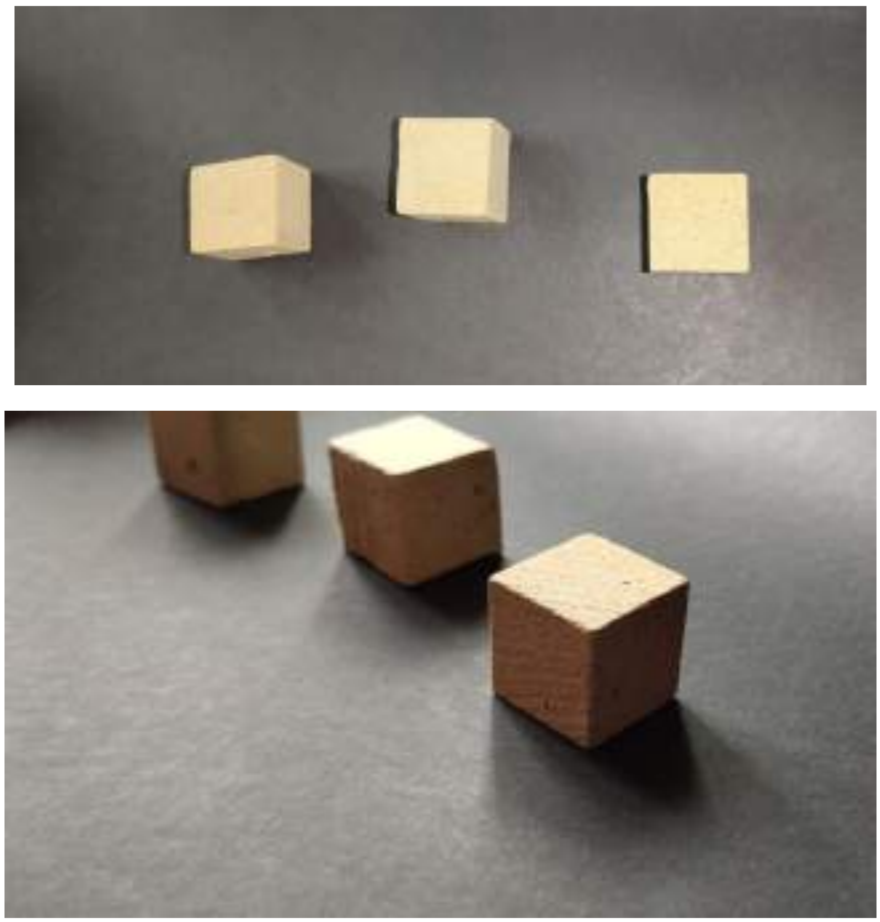
## Exipremental work

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



## 3-1:Preparation of substrates

The bricks were examined by efflorescence and absorption tests in the laboratory, to ensure that the quality according to the Iraqi standard. Then the bricks were cut into dimensions(2*2*3 $cm^3$) by using of a manual saw fig (3-2) showing the substrate befor coating , washed and cleaned with alcohol and water, and dried using a kiln at a temperature (100 ºC) to achieve a smooth surface free of scratches and cracks.



**Figure(3-2) substrate befor coating.**

## 3-2: Efflorescence and absorption test

These tests was done in the laboratories of the of Ceramic Engineering Department according to Iraqi Standard No.25 of the year 1988.The results as shown in the chapter four .

## 3-3: Preparation of nanocomposite coatings solutions

Table (3-1) shows the chemicals materials used for preparation of coatings solutions .

Table (3-1) list of chemicals

| 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 | CaCO3 | 99 | White fine micro particle | Sinopharm chemical reagent Co.,Ltd |

The preparation of coatings solutions was done as shown into this flowing steps :

1.At room temperature the polystyerene is a thermoplastic polymer that is solid (glassy). To prepare the solution PS dissolve in N,N-Dimethyl formamide .

2.The polystyrene and N,N-Dimethyl formamid(DMF) solvent were chosen to be the main component .firstly , 44g of polystyrene were dissolve in 47g of N,N-Dimethyl formamid (DMF) solvent in the lab by magnetic sterrir for 4 hours .

3.Was added the 0.3 g tio2 and 4g caco3 to the polymer solution by magnetic sterrir for 30 minutes and coated the samples directely .

## 3-4: Spray gun coating process

The Spray gun fig (3-3) show spray gun used in this work is an equipment that can spray paint or varnish using air pressure to apply it or spread it on a surface.

This gun can be used to coated on any type of surface or substrate, be it metal, wood, stone, clay (ceramics), and porcelain, plastic, glass, and textile. For this reason, spray gun is fundamental tools for any type of manufacturing industry and repainting services, since it allow industrial finishing of any of its products economically and efficiently.

figure(3-3) spray gun .

## 3-4-1:Parts of a spray gun

The spray gun was divided into these basic parts:

- Airhead
- Flow regulator
- Nozzle or peak
- Tank (depending on its type the gun can have a deposit or be connected to a tank)

## 3-4-2: work sequences of spray gun

In just a few words, the spray of coating happens when the coating is applied to an object (the surface to be coated) through the compressed air gun.

When the trigger is pressed, the coating mixes (although in some systems it does not mix) with the compressed air stream and is released in a fine spray.

The consistency and pattern of paint can be defined and regulated by the correct use of the cup or tank where the paint is placed, and the nozzle that is chosen.

Regardless of the type of technology used to coating , it is extremely important to frequently disassemble the nozzle of the spray gun to clean it and prevent it from becoming clogged with traces of dry paint.

## Advantages of spray gun are :

- Allow the coating to be applied uniformly on the surface.
- Allows different types of surface (even irregular or rough) to be coated efficiently.
- Save time and production costs.
- Can be configured for automated use.
- There is good diversification for specific applications.
- There are different ways to configure each gun according to the need for finishing.

## 3-4-3: coating process

In this step the coating solution was diluted in addition to the purpose of dyeing the samples easily with a spray gun.

***Here a figure show conglomerate the solution and the solution after diluted***.

The specimens were placed on a movable stand at 120cm distance from the nozzle of the gun fig (3-5) show the setting of the specimens into coating process .Spraying was done for different periods, for each coatings as shown in table (3-2) the tank was shaken and the coating was heated to prevent it from freezing and to maintain temperature stability**.**

Fig (3-5) setting of specimen in the coating process.

Table (3-2) coatings parameters

| Specimen No. | Coating time (sec) |
|---|---|
| 1 | 15 |
| 2 | 30 |
| 3 | 5 |
| 4 | 10 |

## 3-5: characterization and tests

The powders used in the preparation of coating solutions and the deposited coatings were characterized using the following characterization methods and tests .

## 3-5-1: 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 ($\lambda$ = 1.5405 Å) was used , and the scanning speed was about 5º/min from (10◦ to 50◦) of 2Ө (Bragg angle) and the power that applied is ( 40 kv/30 mA).

## 3-5-2 : Laser Particle Size Analysis (PSA)

Type of Laser Particle Size Analyzer that used in this study was (Better Size 2000) at Babylon University's /College of Materials Engineering at Ceramic and Building Materials Department . The device provides information regarding particle size and distribution, and the theory that it is based on named (Mie theory).The light travels between space filtering and sawing ray eyepiece to filter the illuminator and shape parallel monochromic illuminator ray with larger surface area, the illuminator ray irradiates the molecules in the measuring region, and the illuminator diffractive phenomena happens.

## 3-5-3 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.

## 3-5-4: 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 $TiO_2$ 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.

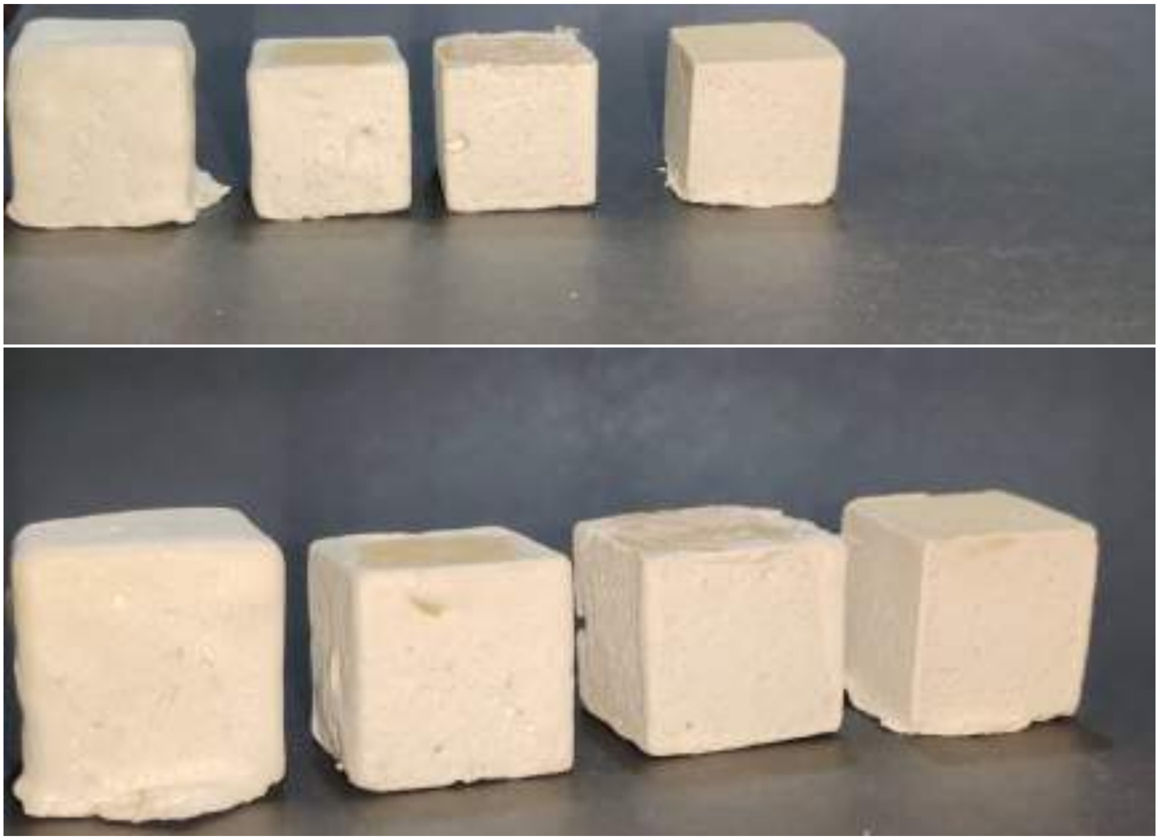
## 3-5-4 : Micro-hardness test

At the University of Babylon, the hardness of coated specimens was examined using an HVS-1000, Laryee, Digital Micro-hardness tester fig (3-6) . with a force of 0.50N and a holding duration of 10 seconds.

**Figure (3-6) : hardness instrument**

*

* Another important tests (AFM) should be taken which  is a tool for evaluating the surface topography and morphology but we didn’t test due to the lack of appropriate tools for examination within the university.



# CHAPTER four

## Results and discussion

# 4-1 Efflorescе and absorption :

**Table (4-1) shows the result of efflorescе and absorption test**

| عدد النماذج | نوع الطابوق | صنف الطابوق المطلوب | التاريخ |
|---|---|---|---|
| | مثقب | A | 2022/11/14 |

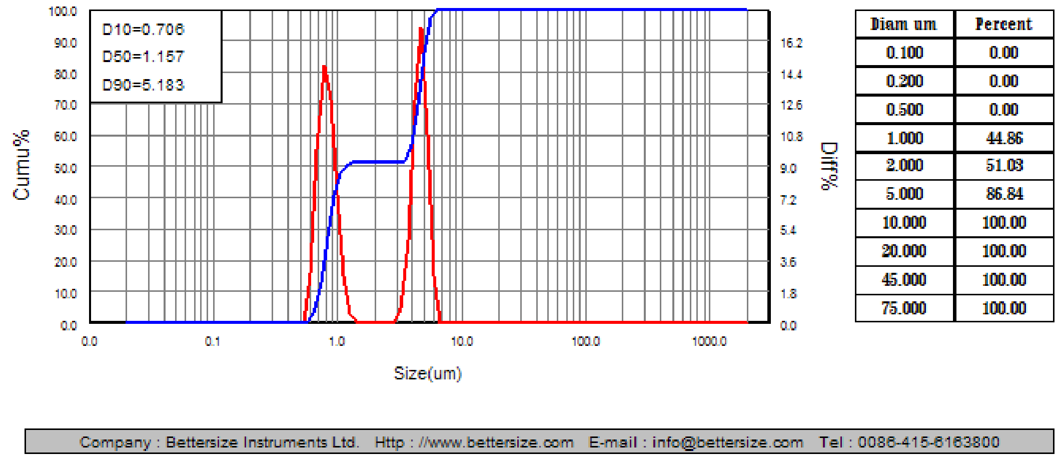
| | | | | | | |
|---|---|---|---|---|---|---|
| متجانس | تجانس الحرق | قليلة | التشققات | متعامدة | تعامد السطوح | المظهر العام |
| 97% | نسبة الطابوق السليم | اصفر | لون الطابوق | مستقيمة | استقامة الجوانب | |
| | | | | 1.2% | نسبة التثلم | |
| 3 mm | | 5mmاقصى حد لاستوائية السطح المسموح بها | | | | |
| 16.69% | | 25%نسبة حجم الثقوب المسموح بها من حجم الطابوق | | | | |
| للطول ∓3نسبة التفاوت المسموح بيها حسب المواصفة للسمك الابعاد القياسية للطابوقة ∓4والعرض و 240*115*75 mm³) | | 78 :معدل السمك | معدل العرض : * 115 | | معدل الطول 240: | الابعادmm |

| التفاوت المسموح به حسب المواصفة العراقية رقم 25 لسنة 1988 وحسب الصنف A | | المعدل | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | رقم العينة |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| حدود المواصفة حسب الصنفA | | | | | | | | | | | | | المقاومة الإنضغاط N/mm² |
| الحد الادنى لتحمل الضغط N/mm² | | | | | | | | | | | | | |
| تحمل الضغط لطابوقة واحدة | معدل تحمل الضغط لعشرة طابوقات | | | | | | | | | | | 25.05 | |
| 16N/mm² | 18 N/mm² | | | | | | | | | | | | |
| الحد الاعلى للنسبة المئوية الوزنية لامتصاصية الماء | | | | | | | | | | | | | الإمتصاصية % |
| امتصاص طابوقة واحدة | معدل امتصاص عشرة طابوقات | | | | | | | | | | | 15.41 | |
| 22% | 20% | | | | | | | | | | | | |
| التزهرالمطلوب في الصنفA وهو خفيف يعني ان لا تزيد نسبة التزهر عن 10% من مساحة الطابوقة | | | | | | | | | | | | *خفيف | التزهر |

The values were acceptable according to Iraqi Standard No. 25 of 1988, where the absorbance value was 15.41% Where the minimum absorption is 22 % and the efflorescе was less than 10% so the class of brick is A .

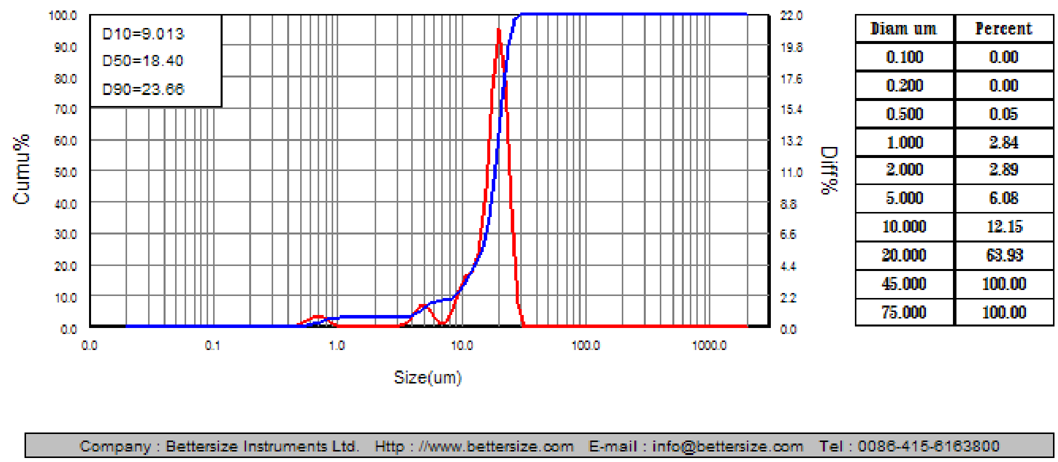
## 4-2 The particle size analysis:

show Figures(4-1 ) to (4-2) the results from the PSA for all powders that , $CaCO_3$) respectively. The size of $TiO_2$ powder used in this study(nano distributed in the field (0.5 -7µm) with the average value (1.157 µm). Likewise, the particle size for $CaCO_3$ powder distributed in the field (0.5-30µm) with the average value of (18.40µm).




| Diam um | Percent |
|---|---|
| 0.100 | 0.00 |
| 0.200 | 0.00 |
| 0.500 | 0.00 |
| 1.000 | 44.86 |
| 2.000 | 51.03 |
| 5.000 | 86.84 |
| 10.000 | 100.00 |
| 20.000 | 100.00 |
| 45.000 | 100.00 |
| 75.000 | 100.00 |

Figure (4-1) results of PSA of $TiO_2$ powder .




| Diam um | Percent |
|---|---|
| 0.100 | 0.00 |
| 0.200 | 0.00 |
| 0.500 | 0.05 |
| 1.000 | 2.84 |
| 2.000 | 2.89 |
| 5.000 | 6.08 |
| 10.000 | 12.15 |
| 20.000 | 63.93 |
| 45.000 | 100.00 |
| 75.000 | 100.00 |

Figure (4-2) Results from PSA of $CaCO_3$ powder.

## 4-3 X-ray Diffraction Results :

Figures (4.3) to (4.4) shows the XRD patterns of (nano $TiO_2$, $CaCO_3$) powders respectively ,which scanned in diffraction angle (2θ) from 10°,20° to 60°. 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).

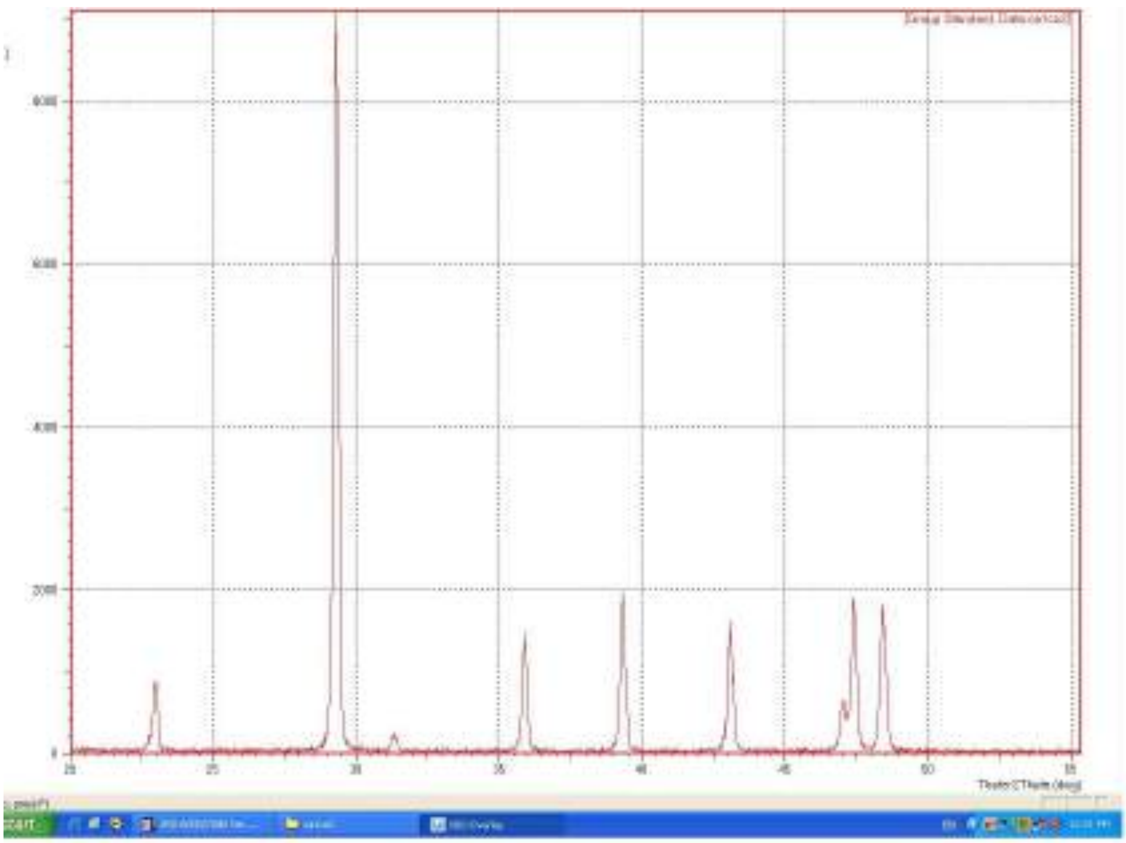


Figure (4-3) XRD patterns of $TiO_2$ powder .

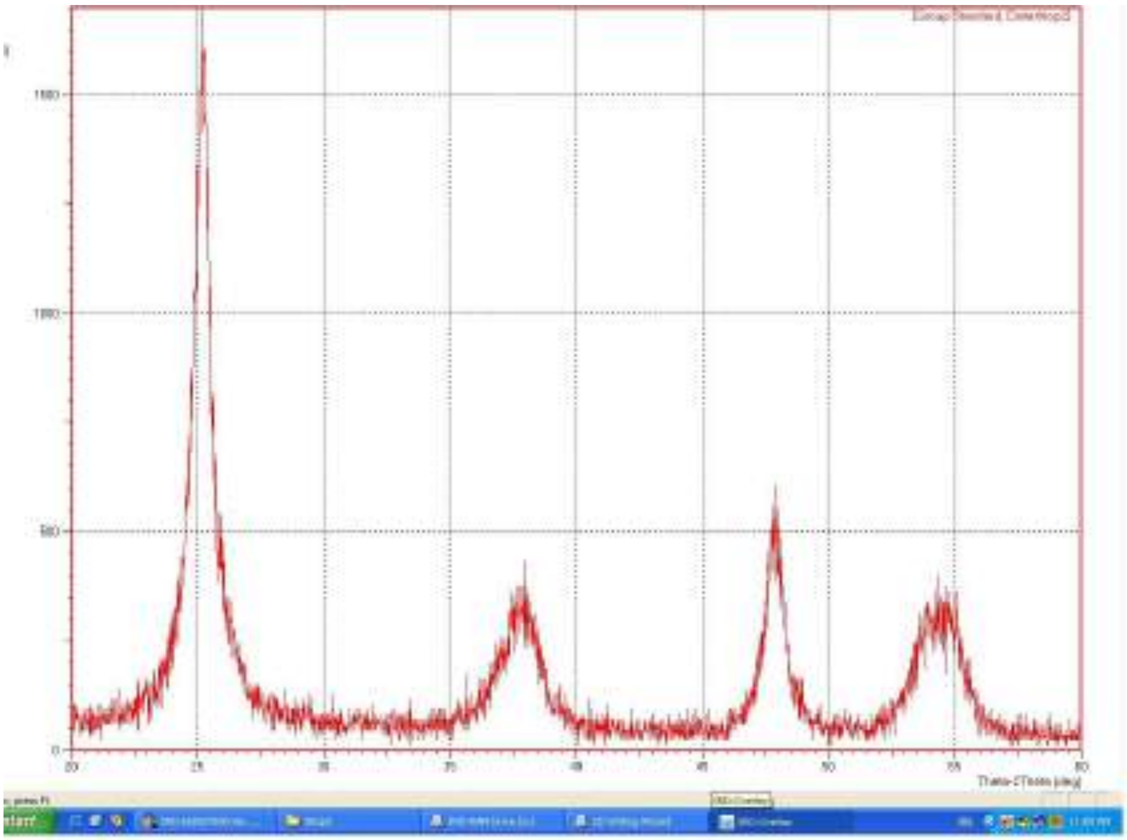
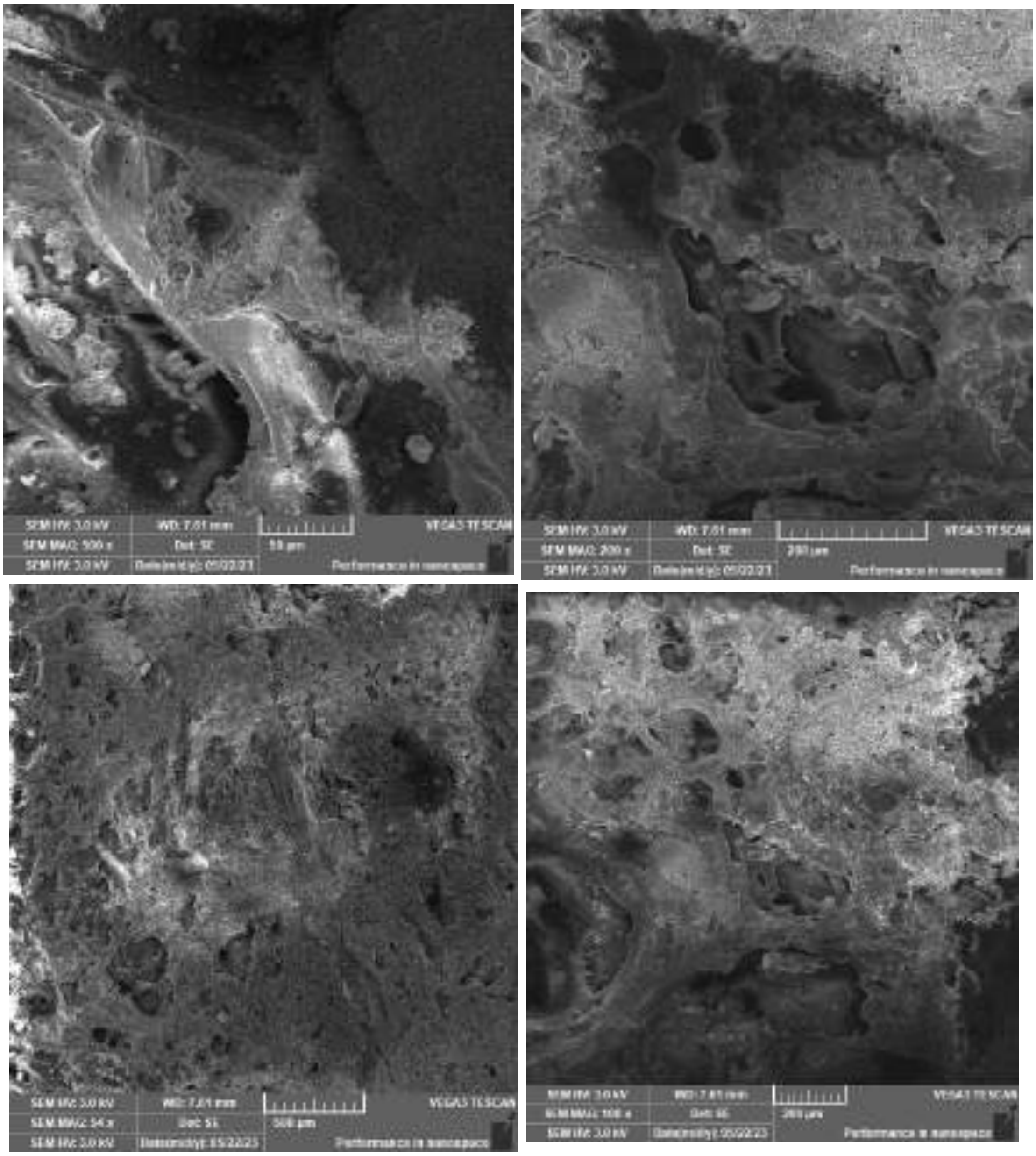


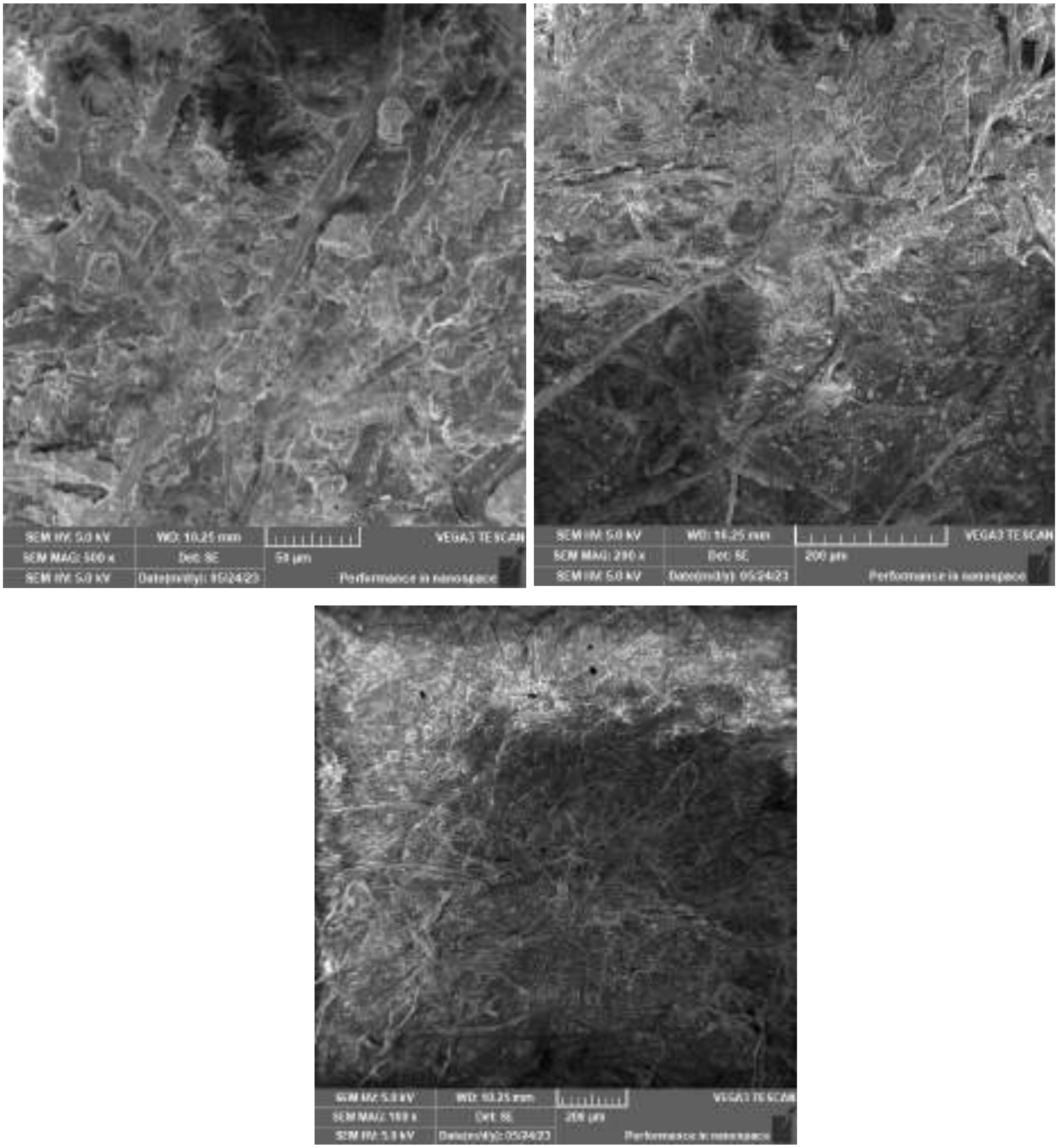
figure (4-4) XRD patterns of $CaCO_3$ powder.

## 4-4 Scanning Electron Microscope (SEM) Images

Figure(4-5)(4-6) show the SEM images .These results show the porous structure of coating layer and paricle disturbution of additive through the coating layer . Notice that 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 (4-5) for samples with nano $TiO_2$ added, we note the nanoparticles of $TiO_2$ and the porous structure of the coating layer as well, and we note that the cracks have decreased. As for the figurs (4-5) (4-6) for the samples with $CaCO_3$ added, we note 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 .



Figure(4-5) SEM images for specimen 1 at different magnifications .




Figure(4-6) SEM images for specimen 4 at different magnification .

## 4-5 Contact Angles(CA) Result

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 (4-2) and figure from (4-7) to (4-10) show the CA results . because of the addition of tio2 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. due to the high porosity of brick, 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 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.

Figure (4-7): images for CA of specimen 1.

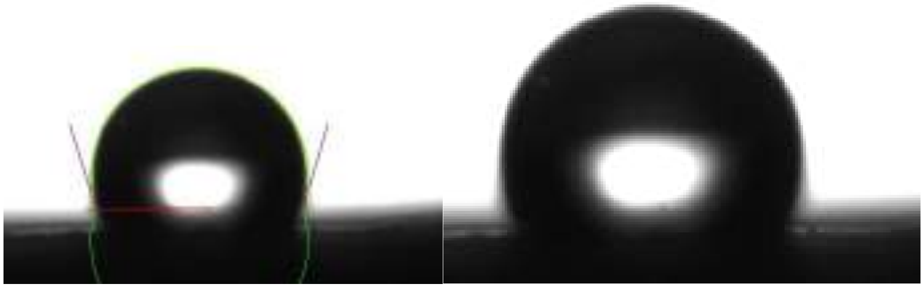


Figure (4-8): images for CA pf specimen 2.

**Table (4-2): CA results**

| Specimen No. | CA |
|---|---|
| 1 | $88.6108^{O}$ |
| 2 | $107.2175^{O}$ |
| 3 | $110.403^{O}$ |
| 4 | $106.738^{O}$ |

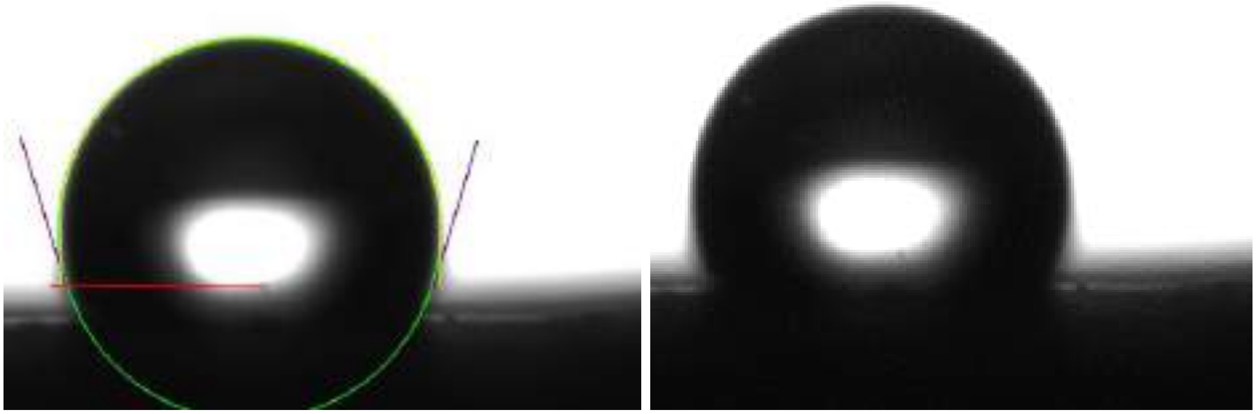


Figure (4-9): Images for CA of specimen 3 .

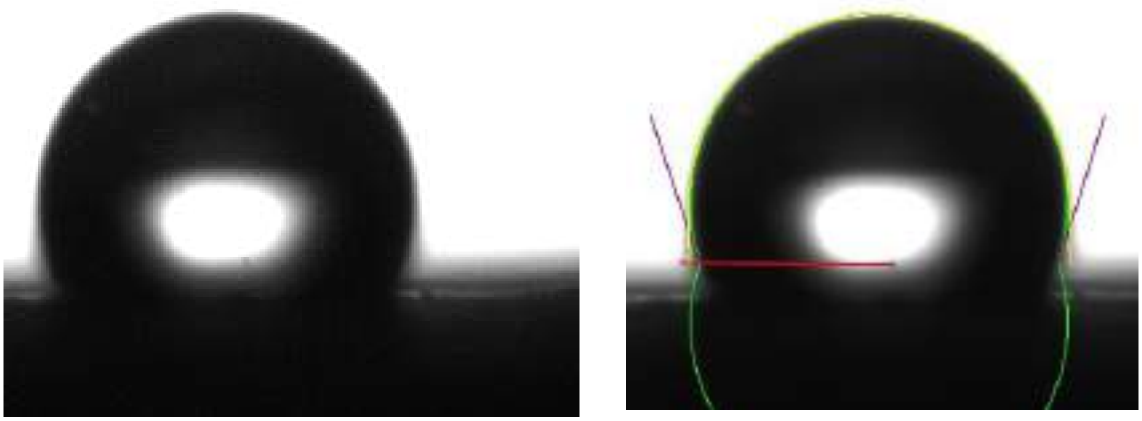


Figure (4-10) : Images for CA of specimen 4.

# 4-6 Micro-Hardness result:

The hardness of coated specimens was examined using an HVS-1000, In Laryee,.Digital Micro-hardness tester with a force of 0.50N ( at 0.25N there was no effect ) and a holding duration of 10 seconds. Tresults 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 $TiO_2$ , $CaCO_3$ in the composite coating could improve the hardness of the substrates from 6.82 Hv to about (31.51 Hv) due to the nature of those hard ceramic particles in providing the matrix material with improved mechanical properties

Table (4-3) Hardness results.

| Specimen No. | Hardness Hv |
|---|---|
| 1 | 31.51 |
| 2 | 6.82 |
| 3 | 3.77 |
| 4 | 6.44 |

## 4-7 surface Roughness Result

Surface roughness test was examined for the coated specimens. The surface roughness results depend on the use of surface in nature. Figure (4-11) show surface roughness results for substrates after coating. The surface of much coting 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, we note that the roughness of all samples has decreased and improved after coating with nanocomposite coating solutions, and that the best improvement in roughness has been recorded the values (1.995) in the surfaces and (1.446) this corresponds to the surface behavior in the lotus effect. The lotus effect was attributed to the self-cleaning capabilities of the leaves of Nelumbo, the lotus flower, which are a result of ultrahydrophobicity.Water droplets pick up dirt particles due to the surface's micro- and nanoscopic architecture, which reduces the droplet's adherence to that surface.

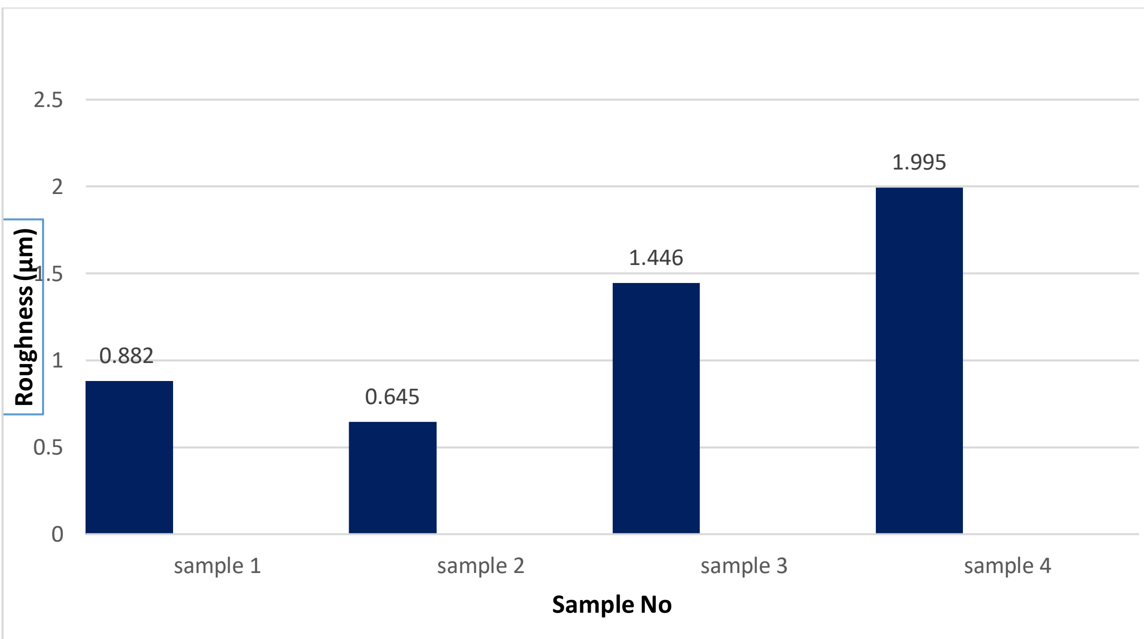



**Figure (4-11): Surface roughness results for brick**

# CHAPTER five

## Conclusions

## 5-1 : Conclusions :

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

**2-** The results showes that porous and uniform self-cleaning composite coatings , hydrophobic and self-cleaning in terms of contact angle (110.403-106.738), Micro hardness (3.77-31.51Hv), roughness (0.882-1.995Ra).

**3-** The results showed that the research was successful in protecting the surfaces of bricks 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.

# CHAPTER six

# Recommendation

# CHAPTER seven

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