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# Weathering Effect on Surface Characteristics of Superhydrophobic/ Hydrophobic Nanocomposites Coating

***Abstract**- Superhydrophobic and hydrophobic nanocomposites coating synthesized by electrospinning, polymer solution of (PS/DMF, PMMA/THF and Si/Th) were prepared in different wt% of composition for each solutions and also prepared with addition of $TiO_2$ nanoparticles. Coated specimens were exposed to accelerated weathering test for 6 months. The aim of this research is to study weathering changes and physical properties of these superhydrophobic and hydrophobic nanocomposites coating to demonstrate these coatings in which can keeps their hydrophobicity properties for long period of time. Viscosity, surface tension, contact angle, roughness surface and hardness tests were calculated for all specimens before and after submitted to accelerate weathering test. Also SEM shows morphology of surfaces in which that (PS/DMF) coated specimen have higher amount of bulge or beads, (PMMA/THF) coated specimen having little amount of bulge or beads and defect as compared to specimen before coating, (Si/Th) owns less bulge or beads and defect but having little percent of contaminations at the surface as compared to other coated specimen.*

***Keywords**- (PS) Polystyrene, (PMMA) Polymethylmethacrylate, (Si) Silicone Rubber R.T.V., (DMF) N,N-Dimethylformamide, (THF) Tetrahydrofuran , (Th) Thinner.*

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## 1. Introduction

Hydrophobic surfaces have attracted a lot of attention because of their unique properties such as self-cleaning, antisticking, and anticontamination. Although research on water-repellent surfaces began many decades ago, it was only recently a lot of papers on superhydrophobicity appeared in the literature especially after the micro-nano-binary microstructure of lotus leaf was studied [1]. Some of the recent reviews describe the rapid progress in the preparation of hydrophobic surfaces and their functional applications and also on the theory relating roughness and wettability [1–2]. The hydrophobicity of solid surfaces is influenced both by the presence of binary geometric structures at micronanometer scales and the chemical composition [2]. Hydrophobic coating is the result of water drop on coated surface in which determined by contact angle test to calculate the value of wettability for coated surface, contact angle between ((=>90$^o$) – (=<150$^o$)) owns hydrophobic appellation and contact angle that owns an angle higher than 150$^o$ known as Superhydrophobic[1]. Electrospinning technique known as most efficient method to produce nanofibers and nanocomposite coating that owns hydrophobicity characteristics that become popular in public to nanotechnology due to the production of nanofibers with diameter in range of (2nm-5μm), this sort of process basically contains syringe pump, high voltage provenance and collector, polymer solution that prepared set in syringe pump and push in stable flow and the needle with metal type and very small diameter is linked to provenance of high voltage in range of (3KV-30KV) [2]. Viscosity for solution of polymer owns series factor on coating produced by electrospinning process, which reliably on polymer concentration and the molecular weight of polymer, viscosity considered an important factor that effect on electrospinning technique, the most important factors affecting on viscosity is molecular weight and the concentration of the polymer. Other ingredient effect on electrospinning for the composition of polymer solution is Surface tension which effect on reduce fluid surface area [3]. Surface roughness define the changes alteration on coated substrate and how react to the ambient environment, higher roughness value is undesirable, hard and expensively to control the product. Also granted unwanted properties for the fabrication of hydrophobic coating which generally known that owns very smooth surface properties [4]. Hardness is the resist of surface deformation produced by indentation and shows how surface can interact to the environmental situation and defect that can stick and arise with its properties.

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Shore hardness describe hardness of soft materials like polymers by sharp and small indenter inside material in which penetration the coated surface and measure its hardness under specified situation.

## 2. Experimental Part

*1. Materials Used*

1. Polystyrene manufactured in panreac Co. for didactic (Espan).
2. Silicon Rubber R.T.V. resin manufactured in Ahmed Munaf Co. (Iraq).
3. Polymethylmethacrylate manufactured in MME.Co. (UAE).
4. N,N-Dimethylformamide manufactured sigma-aldrich (SCR).
5. Thinner manufactured by al-murjan Co (Iraq).
6. Tetrahydrofuran was supplied from (CDH) Ltd. (India).
7. Epoxy resin manufactured by Sikadur® LP Co. (USA).
8. Ethanol (ethyl alcohol) manufactured in pubchem national Lab. Co (UK).

*II. Methods*

1. Electrospinning Instrument

Electrospinning device were used to fabricate nanocomposite coating, consist of a syringe pump, high voltage source (5KV - 30KV) and collector. The polymer solution after prepared put into syringe pump with 3ml size and then placed on electrospinning device.

2. Contact angle Instrument

The contact angle were measured according to the sessile drop technique by goniometer. A drop of distilled water with a tight syringe was placed on the surface. Contact angles associated with the surface were measured at both left and right sides of the drop. The contact angles of surfaces were calculated from the average of the measured values by applying following eq. (1).

$$CA_{av} = \frac{(CA_L - CA_R)}{2} \quad \ldots\ldots\ldots\ldots (1)$$

Where

$CA_{av}$ is average contact angle, $CA_L$ is left side angle of a drop and $CA_R$ is right side angle of a drop.

3. Viscometer Instrument

Digital LCD rotary viscometer tester NDJ-8S type were used consisting of rotary rod, the speed of rotary were determined by its screen. Prepared polymer solution were placed with the rotary rod then digital screen gives the results.

4. Surface Tension Instrument

Torsion balance surface and interface tension (O) ring model type were used. The polymer solution was placed in a petri dish. A ring is dipped in the solution. The handle was moved up very slowly until arc bubble of solution is obtained and results are taken on the gauge. Surface tension was calculated according to eq. (2).

$$\gamma = \frac{F}{4\pi R} C \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where:

$\gamma$: Surface Tension.

F: Force acting on the ring.

R: Center diameter of the ring.

Correction Factor (Harkins No.).

5. Roughness Instrument:

Roughness results were recorded on roughness screen tester. The Hand-held roughness TR200 roughness gauge were used with random signal-μm method it consists of a spring loaded with a stitch needle that penetrates the surface of the specimen and then registers the number shown on the screen of the device.

6. Scanning Electron Microscope Instrument

SEM Instrument ZEISS Type were used to show the morphology of coated specimens.

7. Accelerated weathering Instrument

Accelerated weathering test is future possibilities of material and their durability at certain environmental conditions. This simulation will speed up process of weathering and estimate their effect on the materials. This test process is used to calculate future degradation or materials corrosion. Accelerated weathering test were made to coated specimen after being subjected to the following cycle:

**1.** Ultraviolet lights UV.
**2.** High temperature up to $50^o$.
**3.** Humidity.
**4.** Rains and Moistures.

## 3. Preparation Technique

Polymer solution of PS/DMF, PMMA/THF and Si/Th were prepared in different compositions by wt%. The PS prepared from 5% to 20% using DMF solvent. PMMA was prepared from 3% to 5% using THF solvent, and Si was prepared from 10% to 20% using Th solvent, same polymer solutions prepared with addition of $TiO_2$ nanoparticles in 0.1% amount severally. After all polymer solution prepared, they were placed on a magnetic stirrer for 6-12 hours to make a homogenous polymer solution and each solution was put into syringe pump of 3ml size needle with a small nozzle diameter, and put into the electrospinning device.

For (20%PS/DMF) solutions, this type of coating can't stick with glass substrate in direct and to avoid this kind of case is uses of (EP) as matrix for (PS/DMF) solution to force the coating of (PS/DMF) well enough to adhesion with surface, also surfaces coated with (PMMA/THF) and (Si/Th) don't need EP as matrix to stick on surface. EP resin was made by ratio (9:1) of (EP:Hardener) and diluted with ethanol in 25%wt, the reason of diluted EP in that value is to owns medium viscosity of polymer solution to be good to passing through tip of the needle easily, only EP resin owns high viscosity and can't pass the tip of needle [5].

Preparation technique done by mixing each of polymer used with its solute in known wt% and put into beaker with stirrer and leave about 8 hours to achieve in homogenous polymer solution then each of polymer solution prepared set or put into syringe pump with 3ml size , and the syringe pump set on electrospinning device to coat the concerned substrate.

In the end of needle a high voltage source is connected within, the voltage used was (8.5KV for PS/DMF and PS/DMF/$TiO_2$), (9.5KV for PMMA/THF and PMMA/THF/$TiO_2$) and (6.5KV for Si/Th and Si/Th/$TiO_2$). These amount of voltage depended due to the Tylor Cone principle, so each solution put in electrospinning rise the voltage until we achieve helical and spherical shape of needle drop Tylor Cone. Figure 1 shows preparation technique [6].

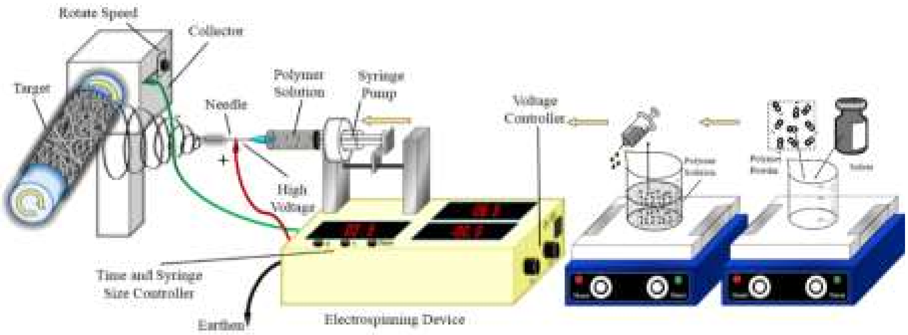


**Figure 1: Preparation Technique and Electrospinning Installation**

Viscosity and surface tension of the surface has measured to all polymer solutions that prepared with and without addition of $TiO_2$ nanoparticles. The choice of $TiO_2$ nanoparticles was made because it shows excellent result when used with polystyrene polymers for thin film and coating to enhance hydrophobicity of the surface, as proved by Azimiradi R. and S. Safa in (2016) [6].

Each of sample prepared has tested to contact angle to see the hydrophobicity of surface also submitted and exposed to accelerated weathering test for 6 months for cycle (UV, temperature at $50^o$ and Rains) to see changes happened to these fabricated coating surfaces.

Hardness and surface roughness has tested to all coated specimens before and after exposed to accelerated weathering test to see alteration properties for both before and after weathering effect on surfaces. SEM test shows the morphology of the surface for (PS/DMF), (PMMA/THF) and (Si/Th) in respectively.

## 5. Results and Discussions

Viscosity and surface tension of the surface were calculated to all polymer solutions before and after add of $TiO_2$ nanoparticles, viscosity test shows that specimen with (20%PS) has that higher value and the reason is amount of polystyrene that add to (DMF) N,N-Dimethylformamide and higher viscosity shows coated surface with high amount of bead while less viscosity gives coated surface with less bead that form on the surface. For surface tension shows that higher value also located to (20%PS) specimen which about (32.53 $N.m^{-2}$) this happened by two cases, primary one is existence of free solvent molecules in high ratio in which molecules mixed together and form beads, second case is molecular weight and polymer concentration used that affect on the results for both viscosity and surface tension test [7]. The relation between viscosity and surface tension is in direct, Table 1 shows results of viscosity and surface tension test.

**Table 1: Results of viscosity and surface tension test**

| **Polymer Solution** | | |
|---|---|---|
| 90%EP/Ethanol | 16 | 32.2 |
| 20%PS | 23.72 | 32.53 |
| PS/$TiO_2$ | 23.6 | 21.03 |
| 4%PMMA | 15 | 20.59 |
| PMMA/$TiO_2$ | 10.04 | 13.84 |
| 15%Si | 13.68 | 17.38 |
| Si/$TiO_2$ | 15.19 | 14.48 |

Contact angle were calculated for all coated specimens before and after exposed to accelerated weathering test for 6 months. Before exposed to weathering, contact angle was tested to (PS/DMF), (PMMA/THF), (Si/Th), (PS/DMF/$TiO_2$), (PMMA/THF/$TiO_2$) and (Si/Th/$TiO_2$) which shows that higher contact angle was for (PS/DMF) about (160.739°) and gives superhydrophobic properties because the production of nanofibers that owns very high surface area in which work on repelling water in high ratio also same reason for (PMMA/THF) coated specimens that shows superhydrophobic properties, while for (Si/Th) shows hydrophobic characteristics because of high molecular weight of silicone rubber R.T.V which the method of fabrication transformed from electrospinning to electrospray and gives nanocomposite coating without fibers and beads , (Si/Th/$TiO_2$) contact angle improved due to the existence of $TiO_2$ nanoparticles. Figure 2 show contact angle results before exposed to accelerated weathering test [8].

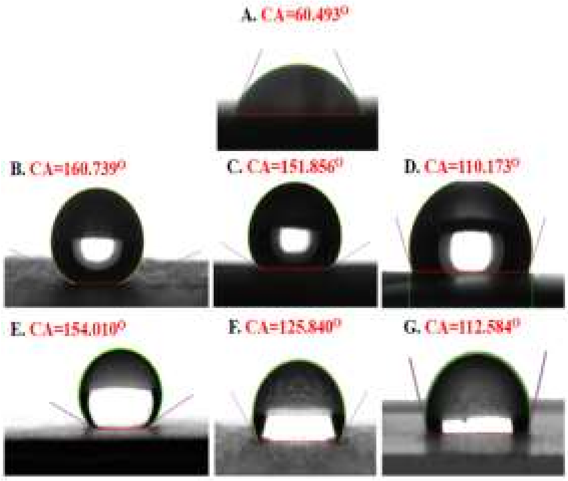


**Figure 2: Contact Angle Test before Weathering Test A. None (before coating) - B. (PS/DMF) - C. (PMMA/THF) - D. (Si/Th) - E. (PS/DMF/$TiO_2$) - F. (PMMA/THF/$TiO_2$) - G. (Si/Th/$TiO_2$).**

After exposed to accelerated weathering test, contact angle also tested to (PS/DMF), (PMMA/THF), (Si/Th), (PS/DMF/$TiO_2$), (PMMA/THF/$TiO_2$) and (Si/Th/$TiO_2$) shows decreases in contact angle results in which weathering effect on some properties of product coat in way that changes there form and shape of coat but with almost steady result and not big different with contact angle which keeps its characteristics of superhydrophobicity even after exposed to accelerated weathering test for 6 months. Figure 3 show contact angle results after exposed to accelerated weathering test [8].

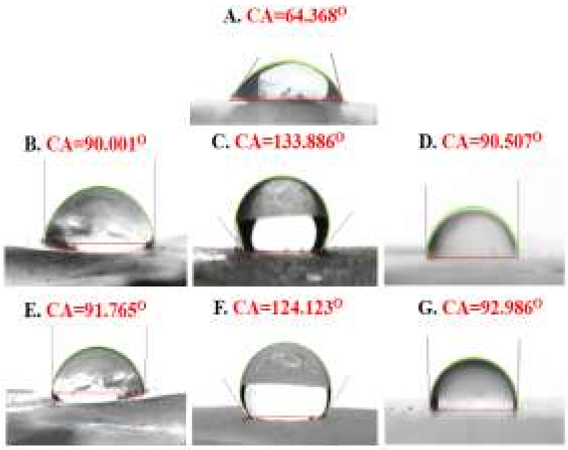


**Figure 3: Contact Angle Test after Weathering Test A. None (before coating) - B. (PS/DMF) - C. (PMMA/THF) - D. (Si/Th) - E. (PS/DMF/$TiO_2$) - F. (PMMA/THF/$TiO_2$) - G. (Si/Th/$TiO_2$).**

Surface roughness is an important parameter used to determine the suitability of a surface for a particular purpose. The irregularities on a machined surface impact the quality and performance of that surface and the performance of the end product.

Rougher surfaces typically wear more quickly than smoother surfaces and are more vulnerable to corrosion and cracks, but they can also promote adhesion. A roughness tester, also referred to as roughness gauge or roughness meter, is a portable device that is used to quickly and easily measure the surface roughness (surface finish) of an object. Surface roughness tested for all coated specimen and show good enhancement after been coated. Substrate before coating has about (1.115µm) amount of roughness and appear excellent improvement after coating with (4%PMMA/THF) which about (0.534µm) and (20%PS/DMF) about (0.614µm), the changes in surface roughness is due to the formation of beads at the surface also environment of coating procedure effect on product and case some irregular to coated surface[9,4]. Weathering effect on roughness of coated surface in which increase after 6 months but almost stability due to the great bonding at the surface. Figure 4 show roughness result before and after exposed to weathering test.


**Figure 4: Surface Roughness Result Before and After Weathering Test.**

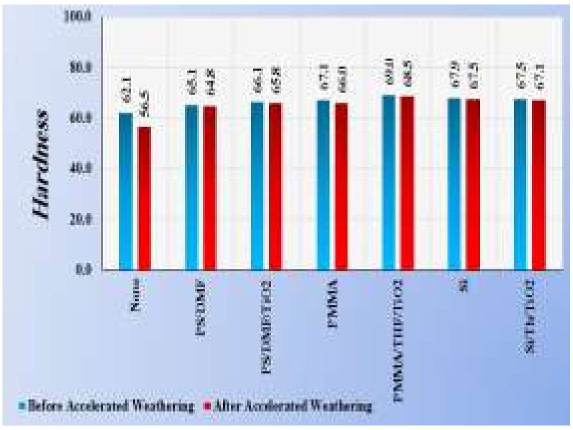


**Figure 5: Hardness Result Before and After Weathering Test.**

Hardness of shore D type was tested for all coated specimen and show good enhancement after been coated. Substrate before coating has about (62.1 No. of shore D hardness) value of hardness and appear excellent improvement after nanocomposite coating. Weather effect on decrease hardness of surface but after coating show good improved to result in which show steady hardness before and after submitted to accelerated weathering test, in which coating help to keeps its properties for longer time in addition of hydrophobicity feature Figure 5 show roughness result before and after exposed to weathering test.

The results shows almost nearby no. of hardness before and after exposed to weathering test due to the coating strength that bore the circumstances surrounding it like uv, temperatures and rain, meanwhile, this environmental were accord with weathering test. Another reason of having this equality values of hardness is the thickness of coating which indicate about 3-5mm, and results shows that after coating the hardness no. increase due to the great boning of the product coat.

Scanning electron microscope shows the morphology of the optimum specimen has contact angle and it was (PS/DMF), (PMMA/THF), and ($Si/Th/TiO_2$). These coated specimen was tested to SEM image and shows that (PS/DMF) coated specimen have higher amount of beads, (PMMA/THF) coated specimen having little amount of beads and defect as compared to specimen before coating, ($Si/Th/TiO_2$) owns less beads and defect due to existence of nanoparticles but having little percent of contaminations at the surface as compared to other coated specimen.

We achieve micro to nano scale from (PS/DMF) and (PMMA/THF) as shown in next figures with 1μm of magnification, meanwhile, for ($Si/Th/TiO_2$) we obtain only micro scale at most margination of 50 μm due to high molecular weight of silicon which tend to give micro particles instead of nanofibers as with (PS/DMF) and (PMMA/THF) polymer solutions. Figure 6 SEM images for (PS/DMF), Figure 7 SEM images for (PMMA/THF) and Figure 8 SEM images for ($Si/Th/TiO_2$) [10].

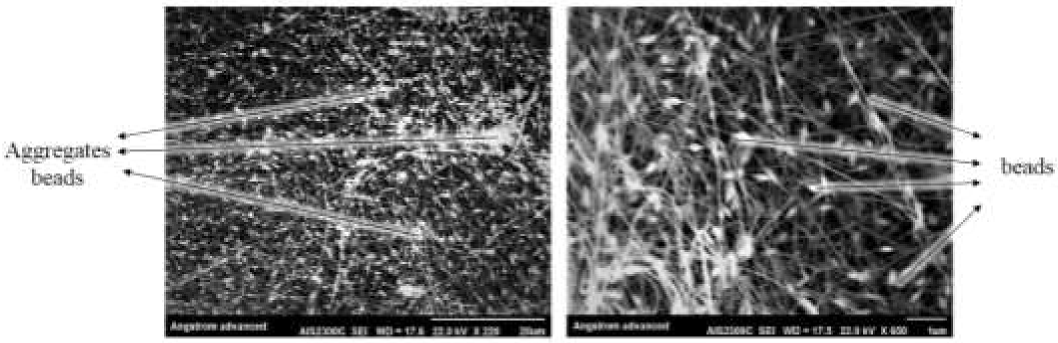


**Figure 6: Show SEM Images for Specimen Coated with (20%PS/DMF)**

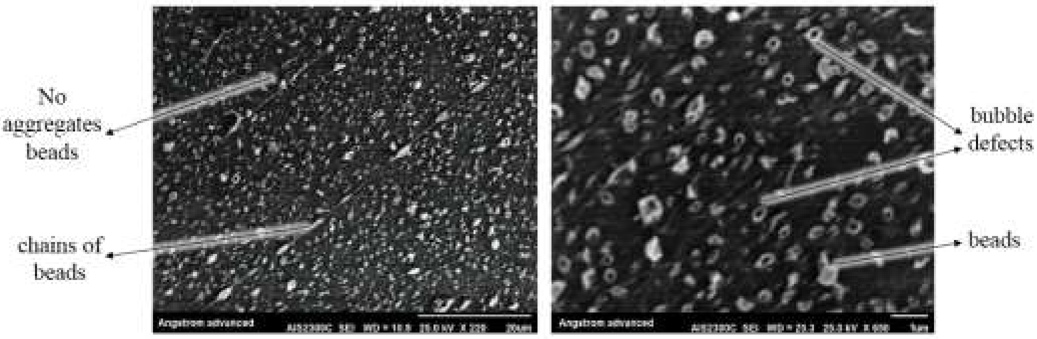


**Figure 7: Show SEM Images for Specimen Coated with (4%PMMA/THF)**

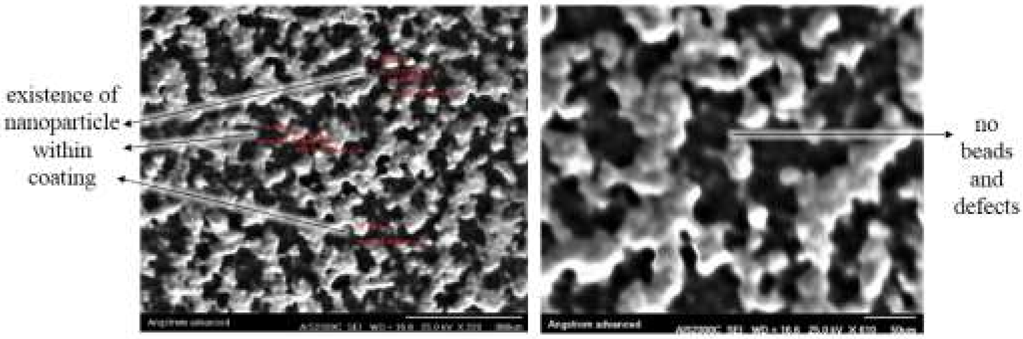


**Figure 8: SEM images for (20%Si/Th/$TiO_2$) - Metal substrate**

## 6. Conclusions

1. Higher value of viscosity was for (PS/DMF) about (23.72 $m^2.sec^{-1}$) and the lowest value was for (PMMA/$TiO_2$) about (5.93 $m^2.sec^{-1}$).
2. Higher value of surface tension was for (PS/DMF) about (32.53 $N.m^{-2}$) and the lowest value of surface tension was for (PMMA/$TiO_2$) about (13.84 $N.m^{-2}$)
3. Higher contact angle to calculate the wettability of the surface was for (PS/DMF) coated specimen about (160.739$^o$).
4. All coated specimen shows changes in their properties from hydrophilic to superhydrophobic and hydrophobic properties which consider as excellent enhancement to wettability also good improvement to the properties of surface roughness and hardness test which keeps there properties even after exposed to weathering test but for contact angle weathering effect on its results due to the cycle of (UV, temp. at 50$^o$ and rain) but almost steady in result as compared before weathering test.
5.(PS/DMF) coated specimen appearing have higher amount of beads, (PMMA/THF) coated specimen having little amount of beads and defect as compared to specimen before coating, (Si/Th/$TiO_2$) coated specimen with less beads and defect but having little percent of contaminations at the surface as compared to other coated specimen.

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