

Research Article

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Evaluation of the wettability of prepared anti-wetting nanocoating on different construction surfaces

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Abstract: Generally, the major problems of moisture damage are caused by wetting, and particularly in construction, which has led to extensive research for the production of hydrophobic (anti-wetting) coatings. The aim of this research is to prepare an anti-wetting (hydrophobic) nanocomposite coating for different construction surfaces (ceramic, brick and gypsum). Hydrophobic nanocomposite coating was synthesized using electrospinning technique. Polymethyl methacrylate and polystyrene (PS) solutions were prepared in different ratios and then separately reinforced with ZrO_2 and ZnO nanoparticles. Contact angle, surface roughness, surface free energy and weathering effects were calculated for all specimens after being coated. All previously selected materials surfaces showed superhydrophobic and hydrophobic properties. The best results were obtained on ceramic surfaces after coating with PS/ ZrO_2 . The water contact angle was 153° while the surface roughness was $0.491 \mu\text{m}$ and also showed the lowest surface free energy which was 5.5 mJ/m^2 . Weathering conditions tend to decrease the values of contact angle and this is due to the environmental effect of the weathering but they still have their hydrophobic properties. SEM test was used to determine the surface morphology and nanoparticle size for ceramic surfaces coated with PS and nano- ZrO_2 .

Keywords: anti-wetting, contact angle, nano-zirconia, nano-zinc oxide, surface coating

1 Introduction

Most developing countries are more interested in and focused on nanotechnology because of the benefits that provide in terms of environmental protection, military, industrial, and research. The materials surfaces' coating provides many advantages in different applications including biocompatibility, wear protection, thermal and mechanical stability and the reduction of friction and corrosion [1]. The hydrophobic coatings become a very important technique to avoid wetting problems in surfaces due to the capability of the coated surface to hydrophobize water and does not absorb it. Surfaces with a droplet water angle above 90° are defined as hydrophobic, while surfaces with an angle above 150° are defined as superhydrophobic. Hydrophobicity provides self-cleaning, anti-corrosion, anti-wetting, antibacterial, etc. [2].

The surface wettability of a solid material is determined by its surface energy. The contact angle given by Young's equation is used to determine the wettability of a solid surface. There are three separate phases when examining a drop of liquid on a substrate. As a result, three surface tensions must be considered: solid–liquid, liquid–vapor, and solid–vapor (SV). Young's equation describes the relationship between the cosine of the drop's contact angle with the surface and the three surface tensions:

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

Inorganic ceramic surfaces, such as metal oxides, are considered to have higher surface energy than an organic material surface since the hydroxyl groups and molecular water are adsorbed on the surface at ambient air atmosphere. Surface organic contamination can alter wettability under normal circumstances [3].

The surface roughness is tested in this research on all coated specimens to define the changes over the concerned substrate and how to interact within different

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environments, high amount of roughness is unfavorable and would be difficult to control the preparation process, also giving undesirable properties for the hydrophobic coating which known generally having very smooth surface characteristics [4].

Young's equation is applied to the surface energy. This equation, however, does not apply to rough surfaces because water cannot form a droplet on a porous surface since it gets absorbed into pores by the capillary effect. However, even on a dense surface, roughness affects the contact angle. The roughness factor r increases both hydrophilicity and hydrophobicity, according to Wenzel's modification of Young's equation.

$$\cos \theta' = r(\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} = r \cos \theta. \quad (2)$$

According to this equation, the hydrophobicity is increased when the water contact angle is greater than 90° . On the other hand, when the water contact angle is less than 90° , the surface's hydrophilicity is increased. Figure S1 depicts the change in water contact angle for different metal oxides under ultraviolet (UV) illumination; it is obvious that the UV has a massive effect.

The electrospinning technique (E-spin) is considered one of the best processes for the fabrication of nanocoating and nanofibers. Last few years, the interest of researchers has risen in nanotechnology due to the possibility of nanofibers production with a diameter in nanosize [5]. The selected surfaces' materials were chosen due to their industrial needs in common and daily people's life in particular for construction and building [6].

Zirconia's high mechanical properties, chemical inertness, toughness, high fatigue and wear resistance, low thermal conductivity and high heat resistance, and corrosion resistance [7]. As well as zinc oxide is used for coating surfaces due to its chemical and physical properties, as it is characterized by its high electrochemical correlation coefficient, and high optical and chemical stability as well. It also has the ability to absorb moisture and is resistant to sunlight and high quality has put these ceramic oxides on the radar in many industries and application areas ranging from refractory to medical products, pigments, electronics, and coatings [8].

Many researchers have investigated the hydrophobic properties of different materials. In (2020), Małgorzata and Danuta evaluated the protection of porous lightweight concrete using two organosilicons hydrophobic coatings. The water contact angle of the prepared concrete was used to determine the wettability of the surface. The results showed that the lowest contact angle of 40.2° was obtained before hydrophobization, while 102.3° and 112.2° after hydrophobization with a water-based

methyilsilicone resin and organic solvent-based methylsilicone resin, respectively [9]. In 2021, Soulios *et al.* evaluated the effect of artificial aging cycles (635 cycles of alternating UV light (102 min) and water spray (18 min)) on the durability of the hydrophobic treatment on bricks and mortars. The samples were treated with two different water-repellent coatings, cream silane with 40% water (FC), and cream silane with 80% water (BS). The results showed that the contact angle for brick before aging was 130 and 128° and after aging was 104 and 111° for FC and BS, respectively. For mortar, the contact angle before aging was 130 and 125° for FC and BS, respectively, while after aging the contact angle of mortar with FC coating was significantly reduced and unmeasurable but for BS coating it was 111° [10]. While in 2022, Zhang *et al.* fabricated self-cleaning superhydrophobic coatings using fluorine resin reinforced with carbon nanotubes nanoparticles (CNTs) and SiO_2 . The mixing ratio of CNTs to SiO_2 is 2–3. The results showed that the prepared coating possesses a contact angle of 156.8° and demonstrates good chemical resistance, thermal stability, and mechanical stability [11].

The purpose of this article was to study the hydrophobic characteristic by preparing an anti-wetting coating composite for different hydrophilic surfaces (ceramic, brick and gypsum) and evaluate it using the contact angle and surface roughness tests to find out if the coated surfaces became hydrophobic or remained hydrophilic.

2 Experimental part

Polymethyl methacrylate (PMMA) and polystyrene (PS) granules were used to prepare hydrophobic coatings. PMMA was mixed with its solvent tetrahydrofuran (THF) in different ratios (1–5%) while PS was mixed with its solvent dimethylformamide DMF from 5 to 20% to achieve the best contact angle (best hydrophobic surface), after that ZrO_2 and ZnO nanoparticles were separately added to the mixture to enhance the properties of the prepared anti-wetting nanocomposite coating. Different surfaces with a hydrophilic nature such as (ceramic, brick and gypsum) were used as a substrate to evaluate the wetting problems. The specimens were prepared by crashing the ceramic tile, building brick and gypsum into smaller parts with $100 \text{ mm} \times 40 \text{ mm} \times 10 \text{ mm}$ in dimension. The selected surfaces were cleaned with ethanol and then dried at (35°) to obtain a surface with the smooth and soft surface with no scratches [12]. After that, a magnetic stirrer was used for a few hours to obtain complete homogeneity. At first, a piece of glass was coated with the prepared solution by

the E-spin process to specify the PMMA and PS ratios that give the optimum contact angle; 4% of PMMA and 20% of PS were the best ratios which achieved contact angles of (133°) and (141°), respectively; then, ZrO_2 and ZnO nanoparticles were added to enhance the contact angle of the prepared solutions [13].

The electrospinning process contains three major important tools (syringe, voltage and collector); also, it owns positive and negative electrodes, one of them is connected to a tip of the needle and the other with a plate collector. The prepared solution was set up in a 3 mL syringe with a very small output micro-nano-size needle, while the used voltage was (6.5 kV) [14]. After turning on the voltage up to 6.5 kV, an electric current passes through the needle and generates an electrostatic force which in turn regulates the droplet of the solution (surface tension of solution). By rising the voltage higher than 6.5 kV, it will generate an electrospray that gives larger micro size. Therefore, the voltage must not exceed 6.5 kV. When the current stabilized, it will evaporate the solute and only the polymer remains on the coated surface [15]. Figure 1 shows the process of electrospinning.

The contact angle of the coated surfaces was measured using the image of a sessile drop method which is illustrated in [17]. Figure S2 shows the contact angle variation from hydrophilic to hydrophobic. The TR200 roughness gauge with the random signal- μm method was used to determine the surface roughness and also the effect of the nano-additives on the prepared coating. The surface free energy was determined using the Neumann

model which is illustrated in [18,19], while the morphology of the coated surfaces was tested by scanning electron microscope (SEM). Finally, the coated specimens were exposed to weathering effects that included cycles of UV light, temperature at 50° and Rains using the accelerated weathering test device system. The coated specimens were placed inside the apparatus and weatherized for 180 h, knowing that each 1 h represents one day inside the system. Averages of six specimens were evaluated for each test.

3 Results and discussion

3.1 Contact angle test

Contact angle was calculated for all selected surfaces. At first, all surfaces (ceramic, brick and gypsum) were tested before coating, and all of them showed contact angles below 90° , because of the porosity and the roughness which absorb the droplet water faster and also keep these droplets inside the material and lead to wetting problems. After coating with the prepared solution, all surfaces were tested using the CA test. The CA results of the coated surfaces (ceramic, brick and gypsum) revealed high improvement, where the ceramic specimens coated with PS/ZrO_2 showed superhydrophobic properties. Whereas specimens coated with (PMMA), (PMMA/ ZrO_2), (PMMA/ ZnO), (PS) and (PS/ ZnO) showed hydrophobic properties. The PS

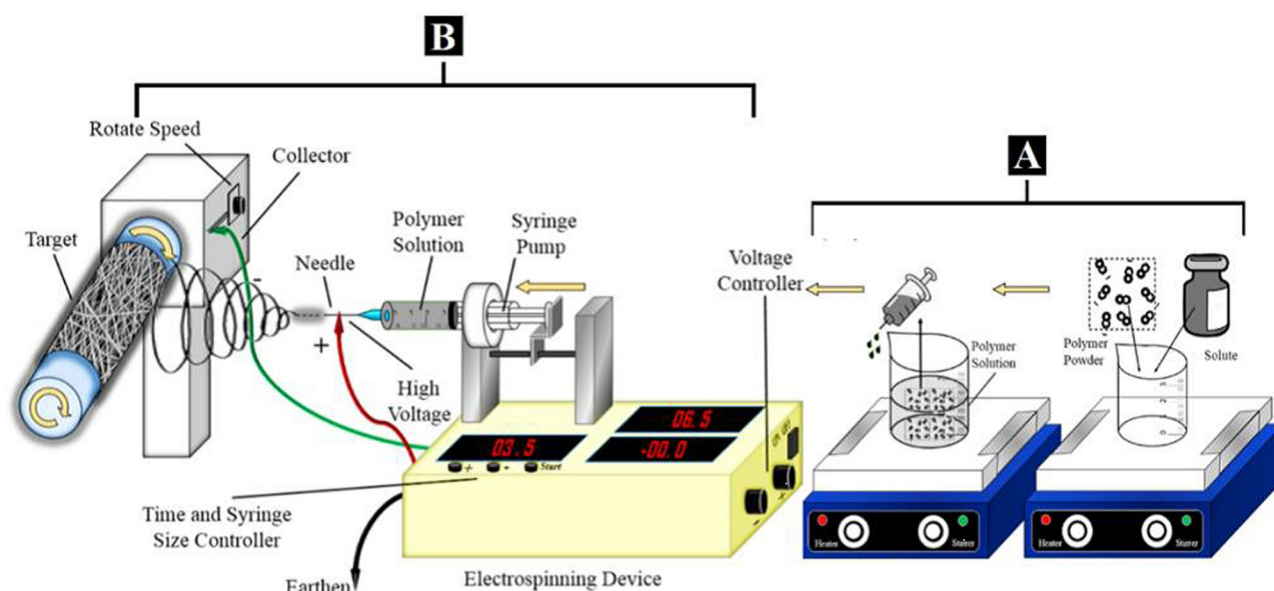


Figure 1: Electrospinning process: (A) homogeneity process using magnetic stirrer, (B) Electrospinning set up [16].

coating shows higher CA results in comparison with PMMA. The specimens which coated with ZrO_2 show the highest contact angles, which means the nano- ZrO_2 causes a high decrement in the roughness of the surface, also due to the great bonding between the polymers chains, also because ZrO_2 nanoparticles provide a high surface area which makes the surface more uniform to repel water. Additionally, the presence of nanoparticles improves bonding and adhesion with the surface and prevents humidity and moisture to accumulate inside the pores of the substrate [20]. After coating the tested surfaces showed CA values ranging from (95.213–129.312°) with PMMA and (107.865–153.879) with PS coatings. Figure 2 shows the CA results after coating with PMMA and PS for (ceramic, brick and gypsum) surfaces, respectively.

3.2 Surface roughness test

Roughness of the surface was examined for all nanocoating types. The results revealed that there was a good enhancement in surface roughness after the coating process. Figure 3 shows the surface roughness results for the coated surfaces (ceramic, brick and gypsum) with PMMA and PS, respectively. Before coating the highest roughness value was (6.753 μm) on the brick surface, while the PS/ ZrO_2 coating provided the best roughness values which showed 0.491 μm in ceramic. For all specimens, the PS coating shows higher results in comparison with PMMA. After coating the tested surfaces showed surface roughness values ranging 3.129–0.653 μm with PMMA and 2.944–0.491 μm with PS coatings. This behavior occurred due to the decreasing of porosity in the surface after coating which completely close the pores at the surface, also these nanoparticles filled the pores and flaws in the surface by creating a thin hydrophobic

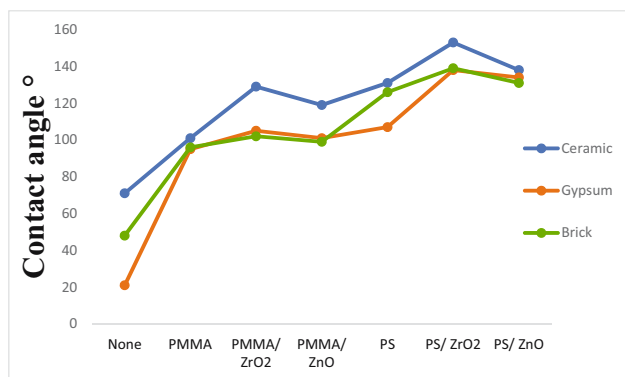


Figure 2: CA results for different coated surfaces.

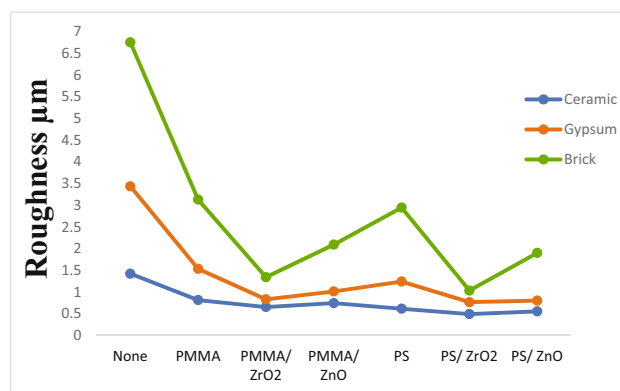


Figure 3: Roughness surface results for different coated surfaces.

layer, while in the higher roughness values, the nanoparticles may be partially filled the pores of the rougher surfaces.

3.3 Surface free energy test (SFE)

The results showed that the SFE values decrease with increasing contact angles. As a result of that, the PS coatings give lower SFE values in comparison with PMMA which means less spreading of the droplet on the surface. The lowest value in PS coating was 5.5 mJ/m^2 while in PMMA coating was 9.4 mJ/m^2 with nano- ZrO_2 . The other coating ratios showed higher SFE ranging (11.2–30.9 mJ/m^2) and (6.9–17.9 mJ/m^2) for PMMA and PS, respectively. This occurred due to two reasons. The first reason is the high ratio of the molecules of free solvent, where the molecules will mix with each other and form the beads on the surface and the second is the molecular weight and the concentration of the polymer that used in the solution also has an effect on the SFE [9]. Figure 4 shows the SFE results for the coated surfaces (ceramic, brick and gypsum) with PMMA and PS, respectively.

3.4 Weathering effects

The coated specimens were exposed to weathering effects that involve cycles of UV light, temperature at 50° and Rains using the accelerated weathering test device system. The contact angle values were relatively comfortably maintained for long periods of time with little decrease in these values. Physical changes generated by the environmental exposure are initiated by breaking the chemical bond due to the absorption of UV light; also, the ceramic surface showed

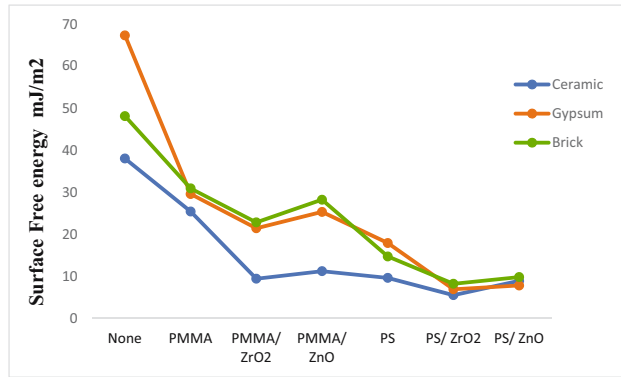


Figure 4: Surface free energy results for different coated surfaces.

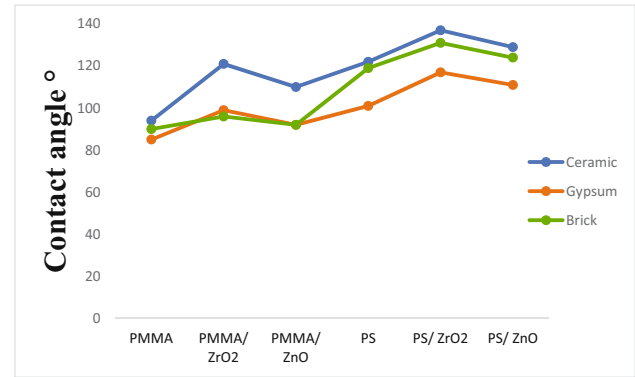


Figure 5: CA results for different coated surfaces after exposure to weathering effects.

a low amount of moisture which proves the hydrophobic properties of the coating. The contact angle results for gypsum surface coated with PMMA showed a chemical breakdown when exposed to the UV light. Meanwhile, gypsum specimens that were coated with PS/ZrO₂ and PS/ZnO maintained their properties after exposure to the same weathering conditions due to the great bonding between the polymer chains within the prepared coating and the presence of nanoparticles of ZrO₂ and ZnO that serve as bridges between resultant nanofibers coating. It was also noticed that by comparing these results with the results of PMMA, it concluded that the rate of influence by weathering conditions was higher for both PS/ZrO₂

and PS/ZnO, this behavior occurred because PMMA possesses higher resistance to UV and temperature effects. Figure 5 shows the CA results after coating with PMMA and PS for (ceramic, brick and gypsum) surfaces, respectively, after exposure to weathering effects.

3.5 Microscope tests

The best coating results which obtained with PS reinforced with ZrO₂ for ceramic surface were scanned by

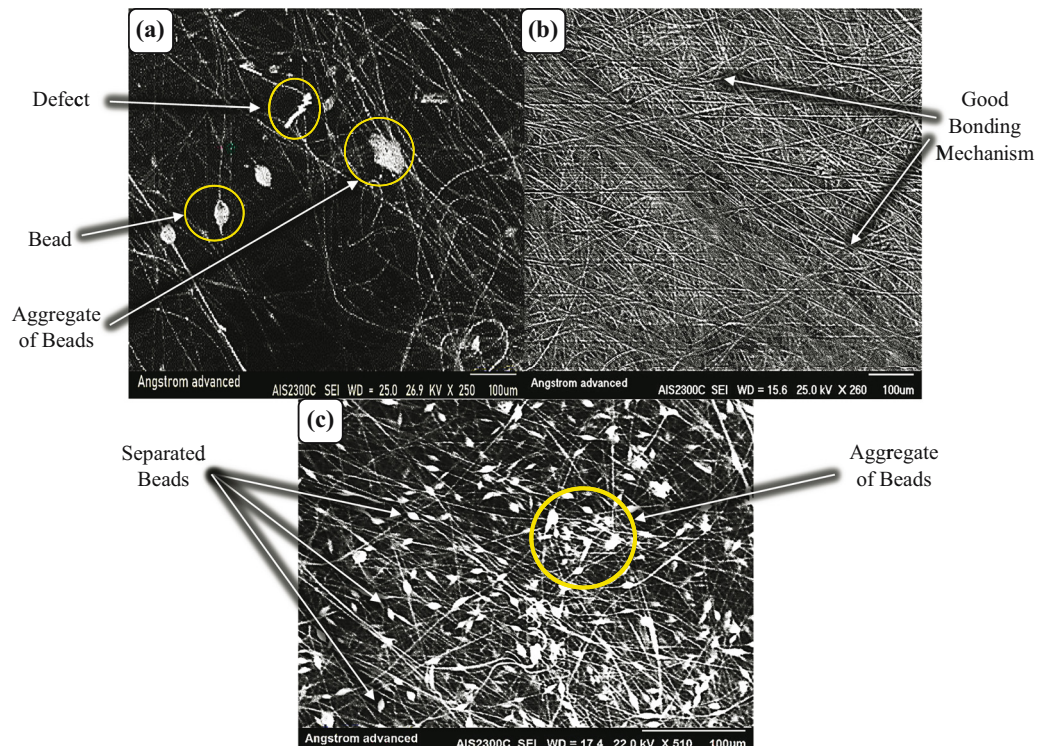


Figure 6: SEM image of the prepared specimens: (a) PS, (b) PS/ZrO₂, and (c) PS/ZnO.

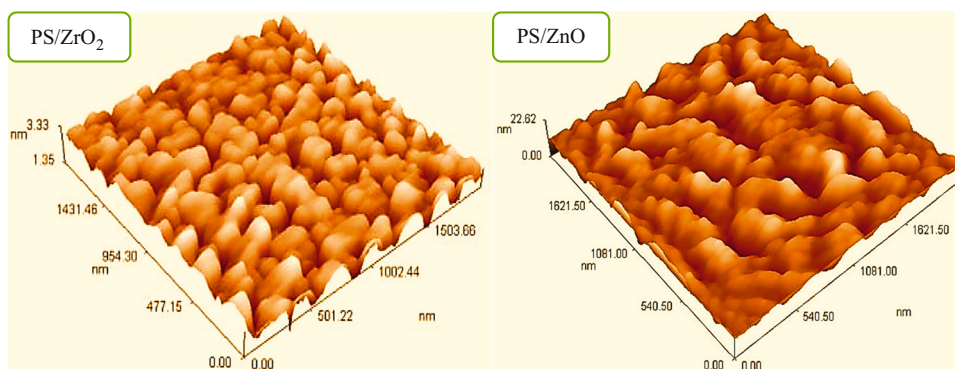


Figure 7: AFM images for PS/ZrO₂ and PS/ZnO.

SEM to investigate the morphology of the surface. Figure 6a shows the SEM of PS coating which reveals some aggregate of beads and various defect which is composed due to the polymer solution that possesses lower viscosity which directly adhere to the surface [21]. Figure 6b shows the SEM of PS/ZrO₂ which reveals a good bond mechanism due to the presence of nano-ZrO₂ which make it strongly stick and adhere to the surface while Figure 6c shows the SEM of PS/ZnO coating which reveals more beads with medium viscosity resulting in a blend of beads and many aggregates [20]. The particle size of PS/ZrO₂ and PS/ZnO was measured using the atomic force microscopy (AFM) test. The resulting images showed that a different distribution at the surface was observed, ranging from micro- to nano-altitude, and the nano-altitude takes more area which shows a perfect pyramid rough structure form which is about (3.33 nm) for PS/ZrO₂ and (22.62 nm) for PS/ZnO as illustrated in Figure 7.

4 Conclusions

This work attends to treatment of the wetting problem that occurs in buildings. Based on this issue the surfaces of (ceramic, brick and gypsum) were chosen due to their high porosity to prepare nanocoating from nanocomposite materials that possess hydrophobicity properties. Hydrophobic and superhydrophobic nanocomposites coating were successfully fabricated by electrospinning technique using PS and PMMA polymer solution with the addition of nano-ZrO₂ and ZnO nanoparticles. The results showed excellent enhancement of surface for all selected surfaces after coating with the prepared nanocoating, which turns their characteristics from hydrophilic to superhydrophobic and hydrophobic, and the coated surfaces possess a high ability to repel the water and give anti-wetting properties. Another

improvement was discovered in this work is the roughness of the surface which resulted in good enhancement for all nanocoating that gives anti-dust and anti-smudge properties to the surface due to its high smoothness; also under weathering effects, PS/ZrO₂ specimens maintained their high hydrophobic properties.

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