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Investigation of Superhydrophobic/Hydrophobic Materials Properties Using Electrospinning Technique

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Abstract:

The aim of this research is to study the surface alteration characteristics and surface morphology of the superhydrophobic/hydrophobic nanocomposite coatings prepared by an electrospinning method to coat various materials such as glass and metal. This is considered as a low cost method of fabrication for polymer solutions of Polystyrene (PS), Polymethylmethacrylate (PMMA) and Silicone Rubber (RTV). Si were prepared in various wt% of composition for each solutions. Contact angle measurement, surface tension, viscosity, roughness tests were calculated for all specimens. SEM showed the morphology of the surfaces after coated. PS and PMMA showed superhydrophobic properties for metal substrate, while Si showed hydrophobic characteristics for both metal and glass substrate. Polymer solution of (15%Si/Thinner (Th)) owned best roughness for glass substrate and polymer solution of (4%PMMA/Tetrahydrofuran (THF)) owned best roughness for metal substrate.

Keywords: Contact Angle, Polymethylmethacrylate, Polystyrene, Scanning Electron Microscope, Silicon Room Temperature Vulcanizing, Tetrahydrofuran

Introduction:

Recently, people have devoted great attention to study of super-hydrophobic materials and have made significant progress. Studying the surface with special wettability on research and development of functional super-hydrophobic surface are significantly important. Hydrophobic coatings mainly relate to the wettability of coatings, usually characterized by the hydrophobic angle of liquid on the solid contact plane. Solid surface wetting is one of the most important properties of solid surfaces(1).

Hydrophobic coating is measured by adding a drop of water over the concerned surface and measuring the contact Angle, which will provide a rating of the substance's hydrophobicity. A contact angle that give hydrophobicity properties it's in range of an angle between 90^o - 150^o in which equal or higher than 90^o and equal or lower than 150^o. Coated surfaces that show a contact angle more than 150^o known as a superhydrophobic coating (1). Figure 1 shows different ranges of contact angle.

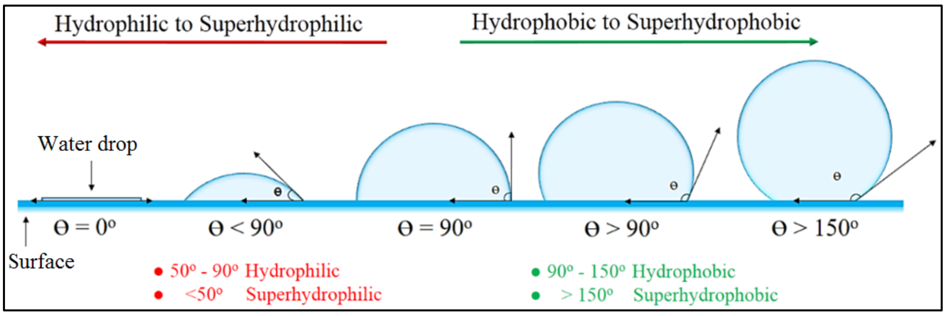

Figure 1. Ranges of Contact Angle.

Electrospinning technique is considered as the most efficient process to fabricate nanofibers and nanocomposite hydrophobicity coatings, which are common in nanotechnology due to the manufacture of nanofibers with diameter 2nm-5µm. This type of process mainly contains a syringe pump, high voltage root and a roller or constant collector. The solution of polymer prepared is inserted with a syringe pump and boosted in steady flow and the

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needle is linked to a high voltage root in the range of 3KV - 30KV (2).

There are many factors which effect electrospinning including solution parameters such as viscosity, surface tension and molecular weight, instrumental parameters like feed rate, needle-collector distance and voltage source and ambient parameters including humidity, temperature and weathering effect. Each of these previous parameters has special effect that changes the properties of the production (3).

Viscosity of the polymer solution has a very important effect on manufactured coating by the electrospinning method, which depends on the amount of polymer to the solutions or polymer concentration, and on the molecular weight of polymer used. Other factor affecting on electrospinning technique which effect by the composition of solution of polymer amount is surface tension which effect on decreasing the surface area of the fluid (4).

Roughness of the surface is tested in this article on all coated specimen to define the changes alter the concerned substrate and how they interact to the ambient conditions. The high amount of roughness is unwanted and would be expensive to produce. This also gives undesirable properties for the manufacturing of hydrophobic coating, which in general have very smooth surface characteristics (5). This research focused on the fabrication of superhydrophobic/hydrophobic nanocomposites coating by electrospinning technique and aimed to study the surface morphology of coated surface.

Materials and Methods:

Materials used were polystyrene PS granules with its solvent N,N-dimethylformamide DMF solution, silicon rubber R.T.V resin with its solvent thinner solution, polymethylmethacrylate PMMA powder with its solvent tetrahydrofuran THF solution, epoxy resin and ethanol ethyl alcohol.

Electrospinning

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

Contact angle

The contact angles 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.

Viscometer

Digital LCD rotary viscometer tester NDJ-8S type were used consisting of rotary rod and the speed of rotor was determined by its screen. Prepared polymer solution were placed with the rotary rod to determine the viscosity.

Surface Tension

Torsion balance surface and interface tension O ring model type were used. The polymer solution was placed in a petri dish, a ring was dipped in the solution and the handle was moved up very slowly until arc bubble of solution is obtained and results recorded on the gauge.

Roughness

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.

Scanning Electron Microscope

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

Preparation Technique

Glass and metal specimens were have been cleaned with distilled water and alcohol and then dried them in an oven at 30-40^{o} C to obtain a smooth surface without contamination or scratches (6). 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. 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 (7).

The electrospinning process, requires a syringe pump, voltage source and a roller or constant collector. Initially, this method contained 2 electrodes, with the positive electrode set to 6.5KV for Si and PMMA solution and 8.5KV for PS solution. The electrode is connected to the tip of needle of the syringe pump, which boosted in constant feed flow. The other negative electrode was connected to the roller collector that placed the specimen substrate on it, and a ground was connected to prevent electrical fault shock.

When an electrical current was applied, it flowed to the tip of needle it arise from it electro static force that changed the surface tension of polymer solution and changed the shape of splatter on the collector and when the voltage increment to deform the shape of the splatter to make it spherical or Tylor cone shape. When the voltage stabilized, it evaporated the solute and only the polymer stayed on the coated specimen substrate. Figure 2 show electrospinning process preparation and installation.

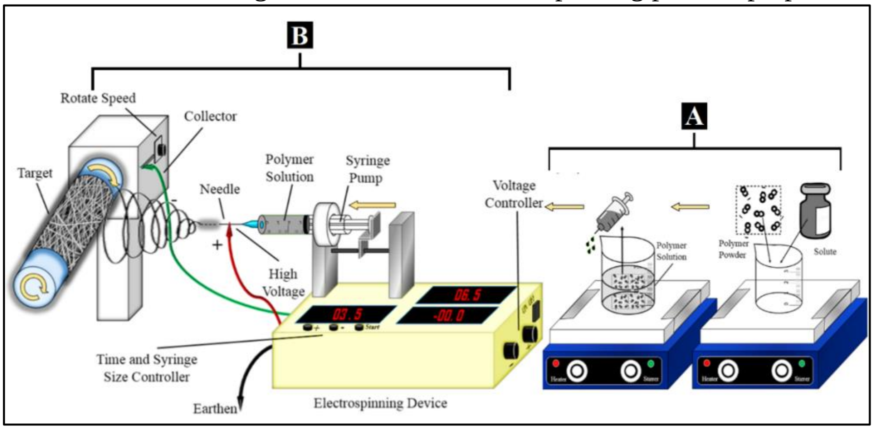

Figure 2. Electrospinning Process Preparation and Installation; A. homogeneity process using magnetic stirrer, B. Electrospinning set up and fiber prepared.

The prepared specimens were placed on collector for coating, and tested for contact angle CA measurement to calculate the wettability of the surface and to show its superhydrophobicity/ hydrophobicity properties.

For metal specimens coated with 20% PS/DMF solution, larger contact angle results of 160.739^o were obtained compared to 5%, 10% and 15% PS/DMF solution. This type of coating cannot stick with the surface directly, so epoxy was used as matrix for PS/DMF to force the layer of PS/DMF to coat the substrate surface of the specimen. Epoxy resin was prepared by ratio of 90:10 EP:Hardener, and was diluted with ethanol in percentage of 25%wt. It was diluted to reduce viscosity of the solution and all it to pass through the hole of the needle syringe pump easily (7).

While for metal specimens that coated with 4% PMMA/THF showed a contact angle of 151.856^o as compared to 3% and 5% PMMA/THF solution, and for metal specimens that were coated with 15%Si/Th solution, which show a contact angle of 110.173^o as compared to 10% and 20%Si/Th solution. Both types of PMMA and Si don't need EP as matrix to adhesion with substrate. Figure 3 shows coated specimens for metal substrate.

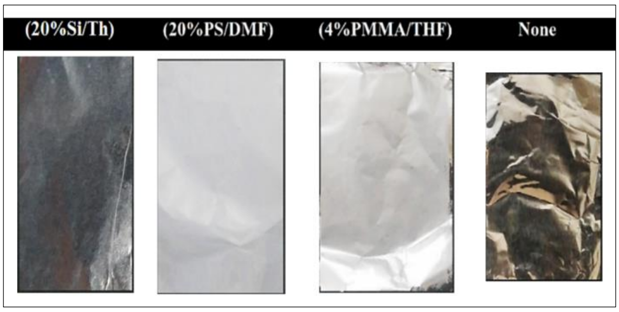

Figure 3. Prepared samples of metal substrate before and after coating.

For the glass substrate, PS specimen shows larger CA at percentage of 20% PS/DMF solution about 146.137^o, and the PMMA specimen shows larger CA at a percentage of 4% PMMA/THF solution about 141.629^o and Si specimen shows larger CA at percentage of 15%Si/Th solution, about 107.491^o. Figure 4 shows coated specimen for glass substrate.

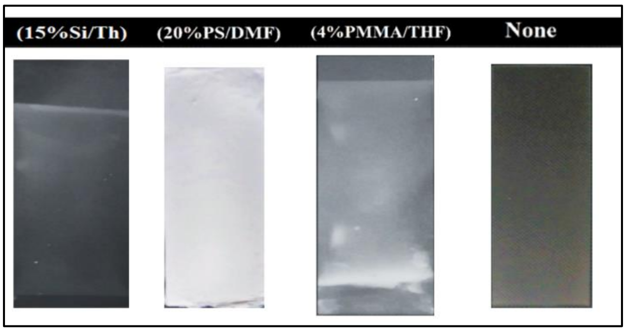

Figure 4. Prepared samples of glass substrate before and after coating.

Result and Discussion:

Viscosity and surface tension tests were measured for the polymer solution, and the results showed that higher viscosity of polymer solution was 27m^2.sec^{-1} for 5%PMMA/THF and lowest viscosity was 5.93m^2.sec^{-1} for (5%PS/DMF), due to the amount of polymer concentration added to its solute. Higher viscosity gives a high amount of bead and low viscosity of polymer solution gives coating with less beads that created at the coated surface.

The results for surface tension test shows that higher surface tension was 32.53N.m^{-2} for 20% PS/DMF and lowest surface tension was 10.55 N.m^{-2} for 10% Si/Th, was due to two factors. First, there is high ratio of free solvent molecules, the molecules will mixed to each other and form beads and that what appears in SEM test images for 20% PS/DMF coated specimen containing high amount of beads. The second reason is the molecular weight and the concentration of the polymer used in polymer solution which effect on the results for viscosity and surface tension tests (9). Table 1 shows the data of viscosity and surface tension test of prepared polymer solution. Figure 5 shows the relation between viscosity and surface tension is in direct relation as explained by M. Forouharshad in 2010 (10).

Table 1. Viscosity and surface tension tests of prepared polymer solution.

Polymer Solution	Viscosity $m^2.sec^{-1}$	Surface Tension $N.m^{-2}$
10%Si/Th	12.15	10.55
15%Si/Th	13.68	12.9
20%Si/Th	19.06	17.38
5%PS/DMF	5.93	28.47
10%PS/DMF	11.86	30.17
15%PS/DMF	17.79	31.16
20%PS/DMF	23.72	32.53
3%PMMA/THF	9.7	20.7
4%PMMA/THF	15	20.59
5%PMMA/THF	27	20.2

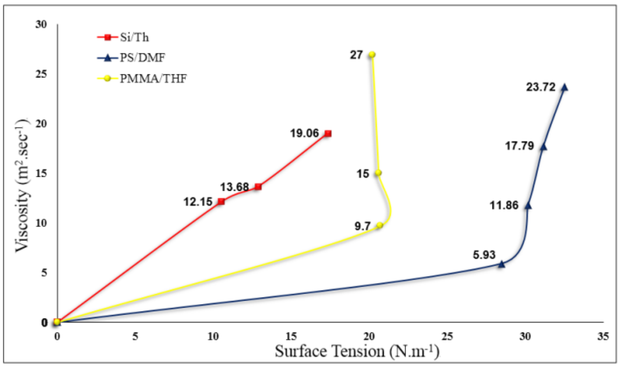

Figure 5. Relation between viscosity and surface tension of prepared polymer solution.

Contact angle test were examined for coated specimen in Figs 3 and 4 and shows that metal substrate achieved good enhancement to the surface after coating as compared before coating by change its properties from hydrophilic to superhydrophobic surface.

Figure 6 shows contact angle results for metal substrate before and after coating, Fig 6 A. is determined contact angle results for metal surface before coating that owns hydrophilic contact angle of 60.493°. Figure 6 B. shows contact angles results equal to 110.173° for 20%Si/Th coated specimen, 4%PMMA/THF coated specimen owns contact angle of 151.856° as in Fig 6 C. and 20%PS/DMF coated specimen owns contact angle of 160.739° as in Fig 6 D. .

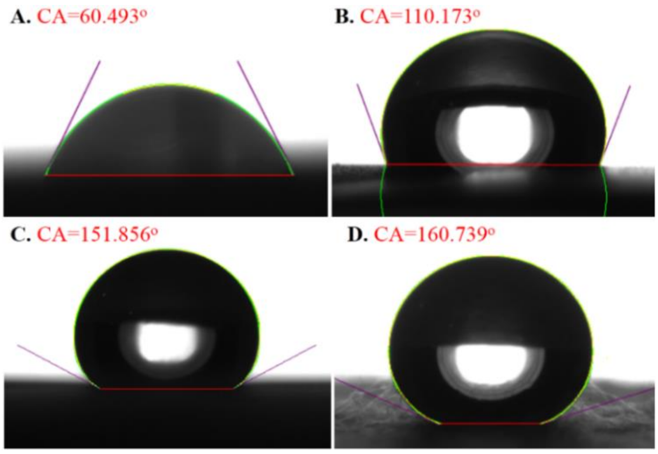

Figure 6. Contact Angle Results for Metal Substrate.

The glass substrate also obtained good improvement by mutating its properties from hydrophilic to a hydrophobic surface, which owns hydrophilic contact angle of 47.647° before coating as shown in Fig 7 A. and the value of contact angle increased to 107.491° after coating with 15% Si/Th as shown in Fig 7 B.

The angle was improved after coating with 4% PMMA/THF to 141.629° as shown in Fig 7 C., and to 146.137° after coating with 20% PS/DMF as in Fig 7 D. . Table 2 show complete data for contact angle for both glass and metal substrate (11).

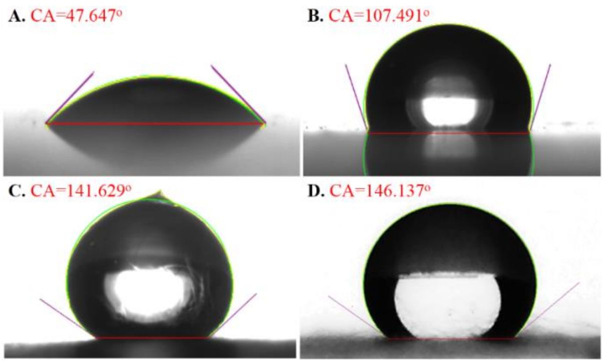

Figure 7. Contact Angle Results for Glass Substrate.

Table 2. Complete Data of Contact Angle Test.

Coated Specimen	Contact Angle Left CA_L	Contact Angle Right CA_R	Contact Angle Average CA_AV
(None) - Metal	60.493	60.493	60.493
(20%Si/Th) - Metal	99.314	100.386	99.850
(4%PMMA/THF) - Metal	151.856	151.856	151.856
(20%PS/DMF) - Metal	158.019	163.459	160.739
(None) - Glass	47.647	47.647	47.647
(15%Si/Th) - Glass	107.491	107.491	107.491
(4%PMMA/THF) - Glass	145.758	137.501	141.629
(20%PS/DMF) - Glass	146.137	146.137	146.137

Surface roughness was tested for glass and metal substrate before and after coating as a comparison to see roughness effect on the surface. The results shows good enhancement to roughness for metal specimen after been coated. Metal substrate before coating owns 1.115µm amount of roughness and appear excellent improvement after coating with 4% PMMA/THF which shows of 0.534µm roughness result and for metal specimen that coated with 20% PS/DMF showed 0.614µm of roughness, Fig 8 show roughness results for metal substrate.

Glass substrate before coating owns 1.115µm amount of roughness and showed good enhancement in roughness after coating with 15% Si/Th which is equal to 0.010µm.

Figure 9 shows roughness result for glass substrate. The changes in surface roughness is due to the formation of beading on the surface and the environment of the coating procedure's effect led to some irregularly to coated surfaces (12).

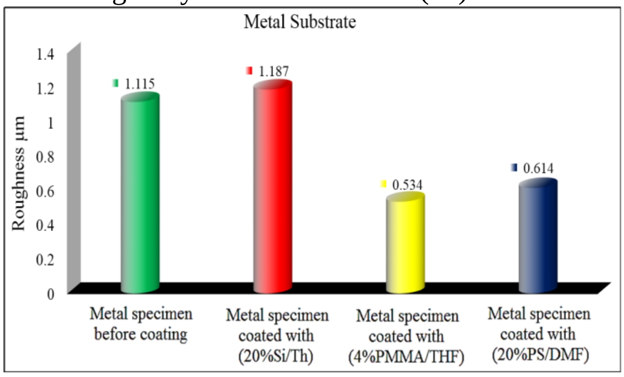

Figure 8. Relation between roughness and polymer solution used as coating for metal substrate.

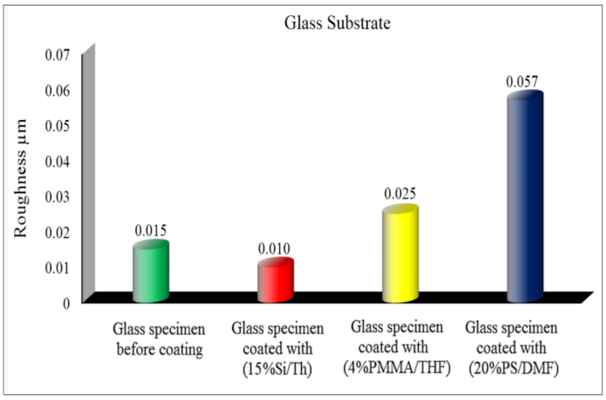

Figure 9. Relation between roughness and polymer solution used as coating for glass substrate.

The **scanning electron microscope SEM** images for coated specimen were examined. Among the solvents used; tetrahydrofuran THF, N,N-Dimethylformamide DMF and Thinner Th, for electrospinning of PMMA, PS and Si respectively, DMF was found to be the optimal solvent producing bead uniform electrospun PS fibers. SEM images showed that the DMF solvent yielded bead PS fibers but fibers with irregular structures were obtained when THF and Th were used as solvents. Figure 10 shows coated specimen using DMF solvents for 20%PS/DMF (13).

These results are in very good accordance with the literature findings where DMF was reported to be the most favorable solvent yielding uniform PS fibers due to its solution conductivity, high dielectric constant and high boiling point (12). This result indicated that the conductivity of the polymer solution is one of the key factors in the production of uniform electrospun PS fibers (14).

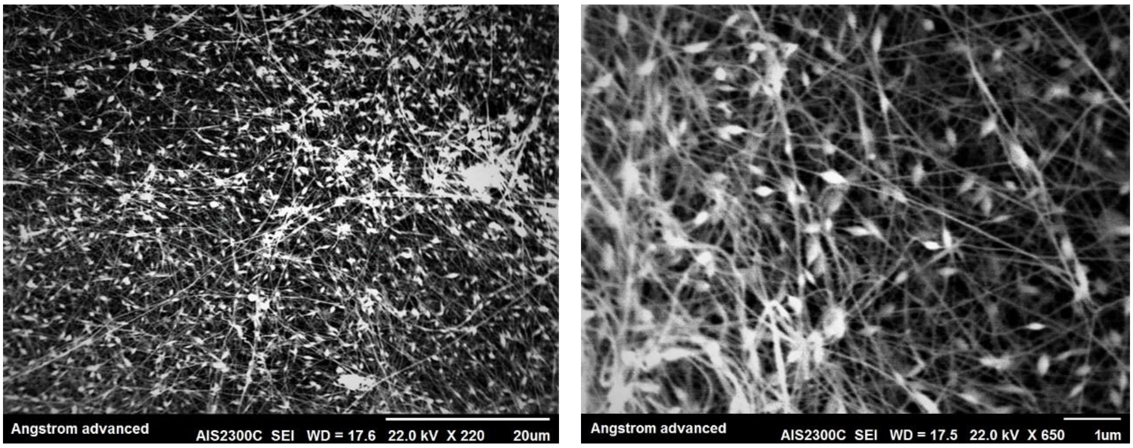

Figure 10. SEM Images for Specimen Coated with 20% PS/DMF.

SEM images depicted in Fig. 11 showed that beaded structures were obtained at lower polymer concentrations of 4% PMMA unlike of 20% PS which yielded bead fibers, which indicating that a high viscosity is required to obtain uniform PMMA fibers coating. These findings are consistent with previous findings in the literature where bead PS fibers were obtained only at the high viscosity.

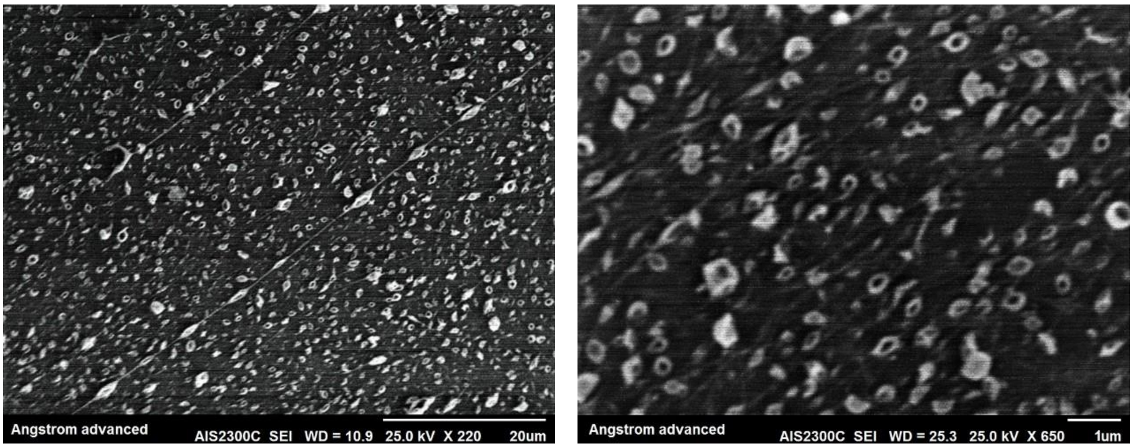

Figure 11. SEM Images for Specimen Coated with 4% PMMA/THF.

Figure 12, it depicted how the viscosity varies as a function of the Si concentration prepared by using Th solvent, showed that 20%Si/Th coated specimen owns less beads and defect. It is observed that the measured viscosities for same concentration of Si solutions are basically very close when different grades of Th 10%, 15% and 20% are used. Figure 12 shows 15%Si/Th coated specimen.

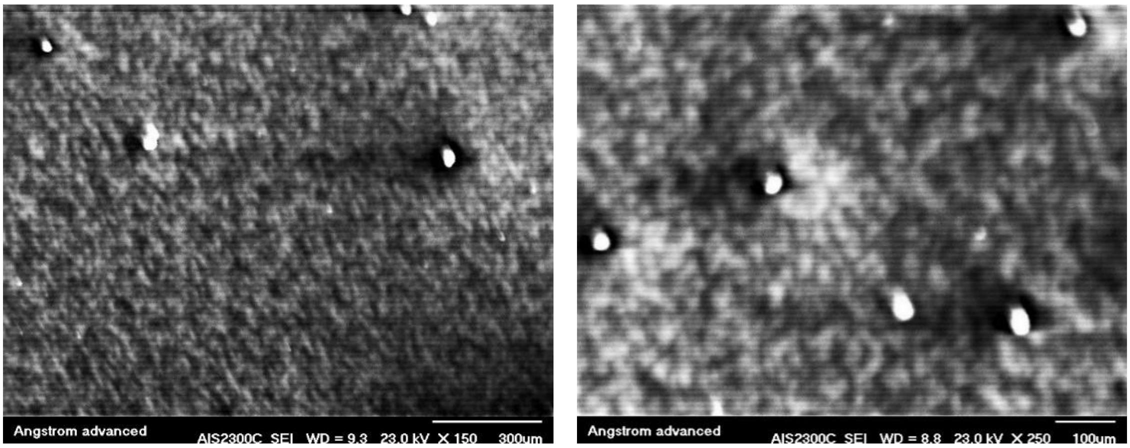

Figure 12. SEM Images for Specimen Coated with 20% Si/Th.

Conclusion:

- It is revealed that different grades of solvents for DMF, THF and Th have slightly different solution conductivities. Consequently, the polymer solutions prepared with the same polymer concentration have different conductivities, which are shown to influence the morphology of coating obtained under otherwise identical electrospinning conditions.
- Obtained superhydrophobic/hydrophobic coating with micro/nano structure and good roughness property from polymer solutions by using electrospinning techniques.
- Demonstrated that metal substrates can be easily altered into superhydrophobic metals stable with water hatred. The selection of precursor, PMMA-composition, yielded coatings found adhesive, water-repellent, hydrophobicity, and effective at preventing corrosion of coated metal substrates. While glass demonstrates very good improvement to the surface that use for self-cleaning.
- The result also implied that glass and metal substrates, before coating has a hydrophilic property and after coating changed their surface properties from hydrophilic to superhydrophobic/hydrophobic properties which is considered as excellent enhancement for both surfaces.

Conflicts of Interest: None.

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التحقق من خصائص مواد نافرة للماء/كاره للماء بأستخدام تقنية البرم الكهربائي

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الخلاصة :

الهدف من هذا البحث هو دراسة خصائص التغيرات الحاصلة على السطح لطلاءات متراكبة نانوية طارده للماء محضرة بطريقة البرم الالكتروني والتي تعتبر كطريقة غير مكلفة للتصنيع. تم طلاء اسطح مختلفة من الزجاج والمعدن حيث تم تحضير المحلول البوليمري لكل من البوليمرات البولي ستايرين، بولي مثيل ميثا كريليت والسيليكون بنسب مختلفة لكل محلول. تم اجراء اختبار مقياس زاوية التماس للاسطح قبل وبعد الطلاء لغرض معرفة الترطيب الحاصل على السطح . واختبار الشد السطحي واللزوجة وخشونة السطح لجميع النماذج المحضرة. تم الفحص بالمجهر الالكتروني الماسح أيضا لإظهار مورفولوجيا السطح بعد الطلاء. أظهرت النماذج بعد الطلاء بمادة البولي ستايرين ومادة البولي مثيل ميثا كريليت خصائص طارده للماء للسطح المعدني بينما اظهرت النماذج بعد الطلاء بمادة السيليكون خصائص طارده للماء للسطحين المعدن والزجاج. امتلاك المحلول البوليمري المحضر بنسبة 15%Si/Th افضل خشونة لسطح الزجاج وامتلاك المحلول البوليمري المحضر بنسبة 4%PMMA/THF افضل خشونة لسطح المعدن.

الكلمات المفتاحية: PMMA بولي مثيل ميثا اكريليت ، THF تيترا هايدرو فيوران , Si سيليكون المطاط , TH ثنر.