THE INFLUENCE OF SILICA CALCINATION TEMPERATURE VARIATION TO THE HYDROPHOBICITY AND TRANSMITTANCE ON GLASS SUBSTRATE

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ABSTRACT

The hydrophobic surface can be self-cleaning. The hierarchy of surface roughness affects the hydrophobic surface. In this research, the hydrophobic surface was fabricated by modification of surface roughness from the composite filler. Natural silica was used as a filler and was done a variation of calcination temperature to modify the hierarchy of roughness formed. The variation of calcination temperature was 800°C, 1000°C, 1200°C, and 1400°C. The coating method was a dip-coating method by 30-second long immersion. A glass as coating media was coated by $PVDF/SiO_2$ composite. The hydrophobic surface could be known from the value of the water contact angle (WCA) formed. If a water contact angle more than 90°, the surface could be called the hydrophobic surface. In this research, the hydrophobicity aspect cause of variation of calcination temperature was known from the value of water contact angle formed on the surface of $PVDF/SiO_2$ composite coating 800°C, 1000°C, 1200°C, and 1400°C was 117,12° ± 0,98°, 107,80° ± 0,91°, 121,31° ± 1,45°, and 111,75° ± 1,47°, respectively.

Keywords: Dip Coating; Hydrophobic Surface; Silica; Water Contact Angle

Introduction

Adding filler in the composite can increase the hydrophobicity of the surface. Composite filler in this research is silica. Silica particles will form roughness that can increase the water contact angle on the surface. Rougher hydrophobic surface, more increase the hydrophobicity. The surface is called a hydrophobic surface if the water contact angle formed on the surface more than 90°. If it can more than 150°, the surface becomes super-hydrophobic. While if the surface has a water contact angle less than 90°, the surface is called a hydrophilic surface or wet. The hydrophobicity is had the surface is very many advantages. In addition to anti-corrosion, the hydrophobic surface also can keep the surface from dust. Because when the water can roll perfectly on the surface, the dust stick on the surface will be lift by water and follow to roll. Hence if this coating is coated on the surface of the solar cell, it can help the surface of the

solar cell to avoid dust that blocks the entry of sunlight in the solar cell.

Silica from natural sand has a Quartz phase with other mineral impurities. However, after silica is purified, it has a pure Quartz phase. If silica is synthesized next, it will be obtained an amorphous phase. In this research, amorphous silica is given variation of calcination temperature was 800°C, 1000°C, 1200°C, and 1400°C. Calcined silica is used as filler in the fabrication of composite for coating of hydrophobic surface. The matrix of composite is Polyvinylidene (PVDF) with water contact angle ±75°. Based on research was done by Basu and Paranthaman (2009), super-hydrophobic material was fabricated from PVDF and HMFS (Hydrophobically Modified Fumed Silica).[1] The material produced increasing in water contact angle when the concentration of HMFS was increased. Besides that, Efome et al. (2015) also done research about the super-hydrophobic membrane from PVDF and SiO_2

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nanoparticle.[2] The membrane produced the highest water contact angle was on the membrane, with the content of filler 10%. Hence in this research, we also fabricated hydrophobic coating from PVDF as a matrix. However, the filler is used in silica-based nature. It did not modify and was not nanoparticle. The variation is calcination of silica from 800°C to 1400°C, so that is known as the effect of hydrophobicity.

Methods

Materials

Silica sand from the Beach Bancar was purified, *hydrochloride* (HCl) 2M, *Sodium hydroxide* (NaOH) 7M, aquadest, epoxy, alcohol, *Polyvinylidene Fluoride* (PVDF), and *Dimethyl Acetamide* (DMAc).

### Preparation of hydrophobic surface

Natural sand was synthesized to produce amorphous silica. Leaching with HCl and coprecipitation with NaOH used synthesis. Next, amorphous silica powder was calcined by temperature variation of 800°C, 1000°C, 1200°C, and 1400°C. To obtain hydrophobic coating was done synthesis of PVDF/silica composite. PVDF 0.2 gr, DMAc 2 ml, and alcohol 10 ml mixed by ultrasonic-cleaner for 30 minutes. Next, silica powder 0.05 gr added to the PVDF solution and mixed for 30 minutes. PVDF/silica composite solution was coated to the glass substrate with a dip-coating method (immersion for 30 s). The composite coating was dried in a lamp oven.

Result and Discussion

Analysis of Natural Silica Sand Powder

Natural sand from Bancar has content 83.3% of silica.[3] After done purifying with the leaching process obtained 93.5% of silica compound. Silica powder after purifying is known that the Quartz phase with trigonal of crystal structure was a=b=4,91 Å and c=5,41Å (ICSD (*Inorganic Crystal Structure Database*) Quartz phase Code 79634). After the coprecipitation process, the silica powder has an amorphous phase. The amorphous silica formed is a cause of the heat treatment coprecipitation method. In that method, has a hydrothermal process, the temperature used is 225°C. Hence, phases previously crystalline transformed into amorphous. This is due to the movement of atoms randomly at heat treatment.
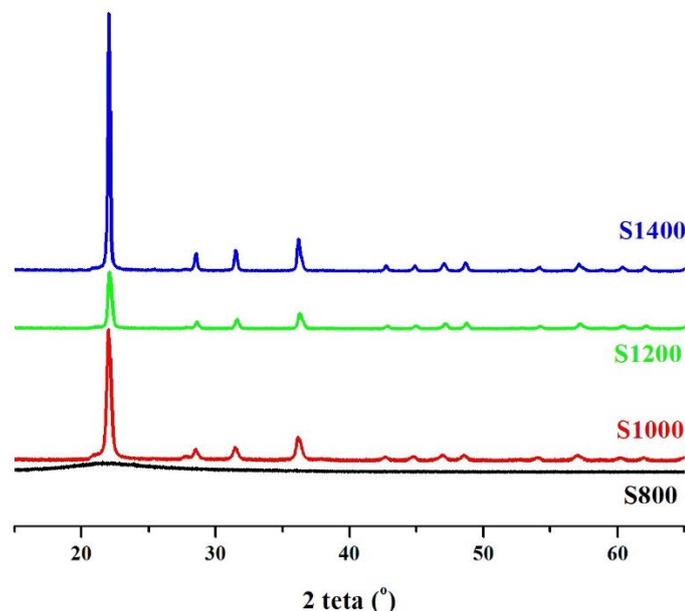
Figure 1. XRD of silica powder

*S800 = surface composite layer of PVDF/SiO$_2$ calcined 800°C, S1000 = surface composite layer of PVDF/SiO$_2$ calcined 1000°C, S1200 = surface composite layer of PVDF/SiO$_2$ calcined 1200°C, and S1400 = surface composite layer of PVDF/SiO$_2$ calcined 1400°C.

Table 1. The result of calculation of the fraction of contact area between the air-air interface and the solid water

Surface	θ (°)	D (cm)	f_{LA}	f_{SL}
S800	117.12 ± 0.98	0.299	0.7300	0.2700
S1000	107.80 ± 0.91	0.320	0.6540	0.3460
S1200	121.31 ± 1.45	0.278	0.7600	0.2400
S1400	111.75 ± 1.47	0.321	0.6876	0.3124

The results of x-ray diffraction testing on calcined silica 800°C indicate that the silica powder still has an amorphous silica content. Calcined silica powder 1000°C is qualitatively known to have β-tridymite and α-cristobalite silica phases. The weight percentage of the β-tridymite and α-cristobalite silica phases in 1000°C calcination powders of 0.5 wt% and 99.5 wt%. In the preceding calcination, 800°C, the crystal structure has not yet formed. This is in accordance with research done by Rizka (2014), which states that the crystal phase has not been formed at calcination of 800°C.[4] However, at 1000°C calcination in this study, two crystal phases have been formed. The β-tridymite silica phase is an intermediate phase. Thus the β-tridymite silica phase in the 1000°C calcined silica powder is only a small percentage. By using reference data Kihara K (1978) Z. Kristallogr. 148 237-253, the β-tridymite phase has a hexagonal-shaped crystal structure, with its lattice parameter a= b≠c. In this result, the β-tridymite silica has a=b=4.93820 Å and c=8.62210 Å. While α-cristobalite silica phase with reference data CIF (crystallographic information file) 9001578 has a tetragonal crystal structure. The lattice parameter is also a=b≠c. The results of data processing in the quantitative value obtained a=b=4.99370Å and c=6.97920Å. Silica 1200°C has a silica α-cristobalite content of 100%. The values of lattice parameters obtained are a=b=4.97082 Å and c=6.93899 Å. Calcined silica of 1400 ° C qualitatively has an α-cristobalite silica phase. Quantitatively, using different CIF data with reference data for silica 1200°C i.e., CIF 9008225 obtained lattice parameter a=b equal to 4.97510 Å and c equal to 6.94450 Å.

Analysis of Hydrophobic Properties of PVDF/SiO₂ Composite Layers

A layer is called to be hydrophobic if it has low wetting properties. The properties can be known from the contact angle values formed between water and solids (surface layers). A hydrophobic surface will have no great surface contact to water. Figure 2 is the result of the measurement of the water contact angle of the sample in this study by using ImageJ software. The critical water contact angle occurs at an angle of 90°, i.e., the lowest angle of the hydrophobic surface. Because the surface is said to be hydrophobic if the water contact angle formed is ≥ 90° and its maximum angle is 150° if it is more than 150°, it is said to be a super-hydrophobic surface.

From the measurements of the water contact angle, it can be seen that the fraction of contact between the air-water and the solid-water interface, symbolically represented by f_{LA} (fraction contact area of liquid-air interfaces) and f_{SL} (fraction contact area of solid-liquid interfaces).[5] In Figure 2, we can find the diameter value of the water droplets and the results obtained in Table 1. The diameter of the water droplet is measured at a critical point of 90°.

Based on the calculation of the contact area fraction in Table 1, it can be seen that the f_{LA} value of all surface variations is greater than the f_{SL} value. This means that the contact area between water and air is more dominant than the contact area between water and solids. So the surfaces in this variation of the study tend to have hydrophobic properties rather than hydrophilic (wetted). If the result is closer to 1 f_{LA} value on the hydrophobic surface, the lower the wettability, and the vice versa. The closer to the value of f_{LA} on the hydrophobic

surface, the greater the wettability becomes hydrophilic.[5]

One of the factors that influence the hydrophobic nature of a surface is the presence of surface roughness. In this study, the roughness formed in the coating was modified from the variation of calcined silica powder. The silica powder in this study acts as a filler in a PVDF/SiO$_2$ composite and as surface roughness. From each powder, the variation obtained a hierarchy structure of different roughness.

The existence of a hierarchical structure of roughness on the hydrophobic surface can increase the angular contact value of water formed. The hierarchical structure of roughness is a large particle structure surrounded by smaller particles. The description of the hierarchical structure of roughness can be seen from the illustration in Figure 3. These smaller particles greatly affect the value of the roughness formed because a hydrophobic surface will be increasingly hydrophobic if it has a great roughness.[5]
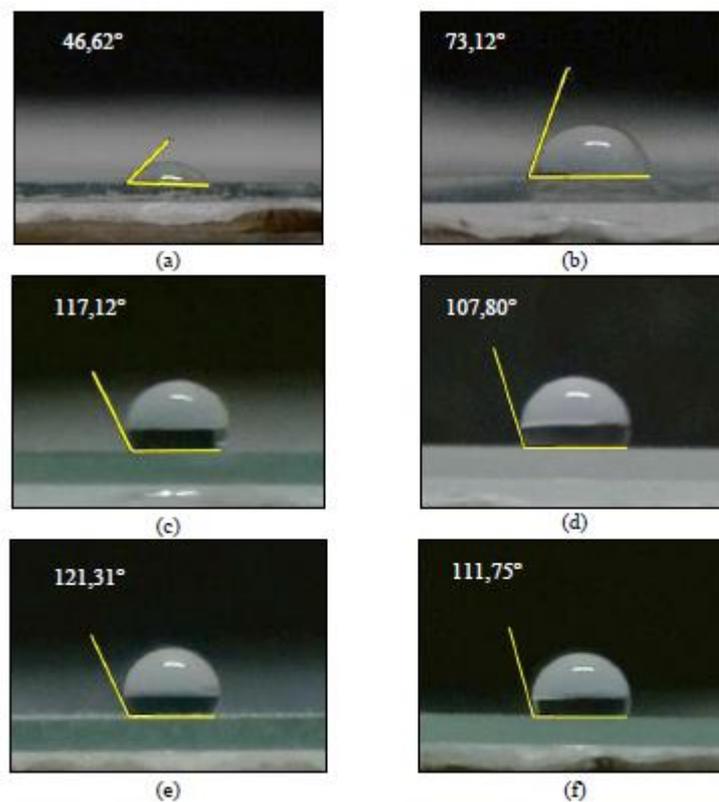

Figure 2. The water contact angle on the coated glass surface (a) epoxy, (b) PVDF, composite layer PVDF/SiO$_2$ (c) 800°C, (d) 1000°C, (e) 1200°C, and (f) 1400°C
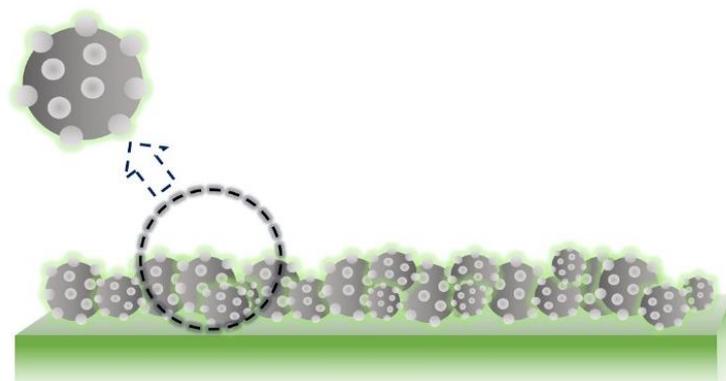
Figure 3. Illustration of the hierarchy of roughness on the surface

The theory used in this research in the analysis of the water contact angle is the theory expressed by Cassie-Baxter. Both scientists claim that water droplets formed on a rough surface do not enter or wet the sidelines between the roughnesses. However, there is air trapped between the roughnesses of the surface. Where the water surface only touches or contacts against the ends of roughness. Therefore, in theory, it has been noticed the presence of roughness factors for hydrophobic surfaces. Roughness factor is symbolized by R_f.[5]

(a)

(a)

(b)
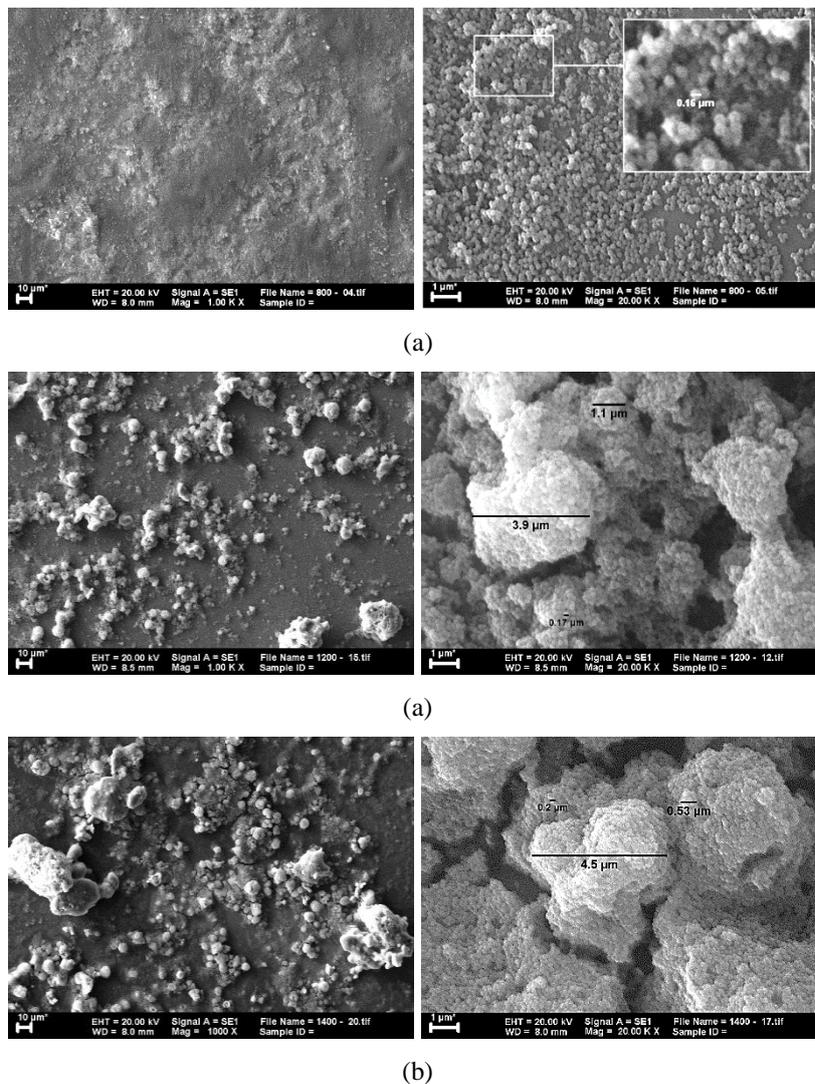
Figure 5. Morphology of hierarchical structure of surface roughness of composite layer PVDF/SiO$_2$ calcination (a) 1200°C and (b) 1000°C
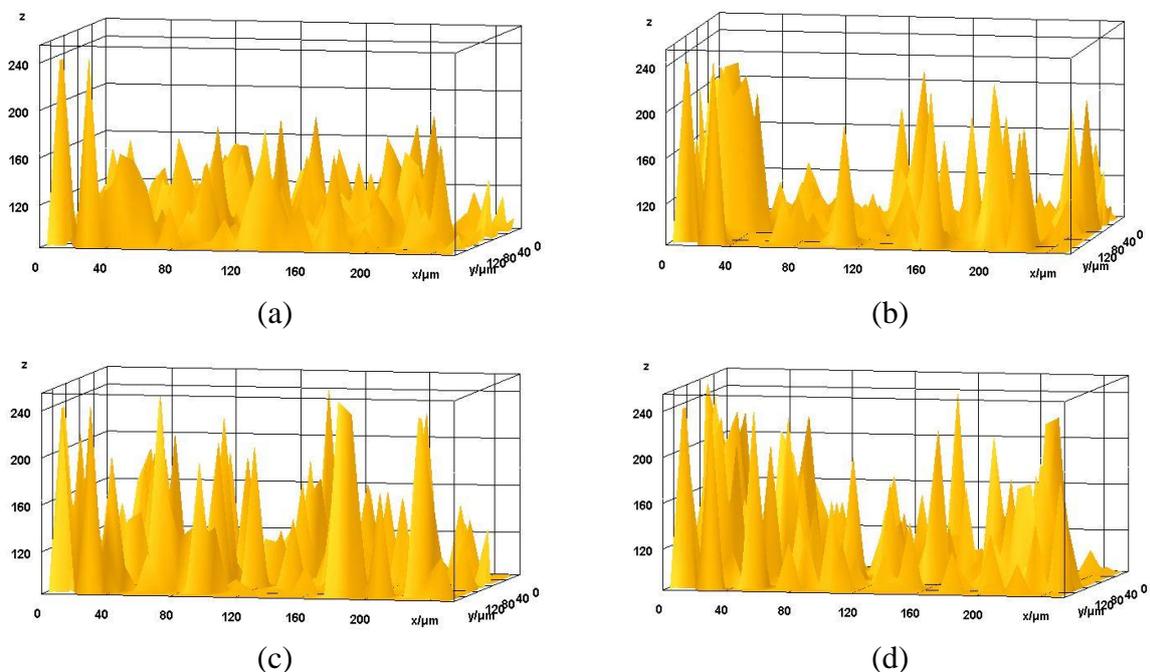
The composite surface of PVDF/SiO$_2$ 800°C has a flatter surface morphology than a 1200°C PVDF/SiO$_2$ composite. Filler or powder of 800°C calcined silica has an amorphous phase, which causes the powder size to tend to be small. So when it becomes composite, then PVDF will coat all the silica powder. When superimposed onto the surface of the glass, it will tend to flat, or in other words, the role of powder as a hierarchy of roughness is a little. While on the surface of the composite PVDF/SiO$_2$ 1200°C, the surface morphology was seen spreading of evenly distributed silica powder. The α-cristobalite silica powders provide a hierarchy of surface roughness and are enhanced by the size of the powders composed of PVDF of $\pm$ 0.17 μm. From the morphological results of

the composite surface of PVDF/SiO$_2$ 800°C and 1200°C can be known as the effect of the silica powder phase used as filler. Silica powder with an amorphous phase will result in flat surfaces, and silica powder with crystalline or α-cristobalite phases will produce surfaces that have more hierarchy of roughness.

3D topography on the surface of the composite layer of PVDF/SiO$_2$ 1000°C, 1200°C, and 1400°C almost has the same roughness. However, for silica of 1200°C, it further forms roughness with relatively equal roughness distance. Therefore, in the presence of relatively equal roughness level distributions, the 1200°C PVDF/SiO2 composite coating layer forms the highest water-contact angle between the surfaces of the other layers. This is due to the hierarchical structure influenced by a single-phase, i.e., α-cristobalite. Whereas the roughness formed in the composite layer of PVDF/SiO$_2$ 1000 ° C and 1400°C has an uneven roughness height between roughness. Some are low, and some are high. The roughness height distribution formed on the surface of the PVDF/SiO$_2$

1000°C composite layer is uneven due to the impurities phases of β-tridymite. The impurities phase leads to the uneven formation of the hierarchy of roughness in silica powder. So from the surface morphology of the PVDF/SiO$_2$ 1000°C composite layer, the presence of smaller powder is dominant evenly, and there is a large one. This large-size powder causes unevenness of roughness. While on the surface of the PVDF/SiO$_2$ 1400°C composite layer, the uniformity of roughness is attributed to the large size powder. That can be shown by the distribution of particles formed on the surface (Figure 4, Figure 5). Therefore, the water contact angles formed on the surface of the composite layer of PVDF/SiO$_2$ 1000°C and 1400°C were lower than the surface of the 1200°C PVDF/SiO$_2$ composite layer. Because of even distribution on fillers in the composite, which makes water contact angle different (Figure 6). On the surface of the composite layer of PVDF/SiO$_2$ 800°C was different from the others because the filler had an amorphous phase. So, even distribution on the fillers in the composite more uniform

Figure 6. Topography 3D surface roughness of the composite layer of PVDF/SiO$_2$ (a) 800°C, (b) 1000°C, (c) 1200°C, and (d) 1400°C
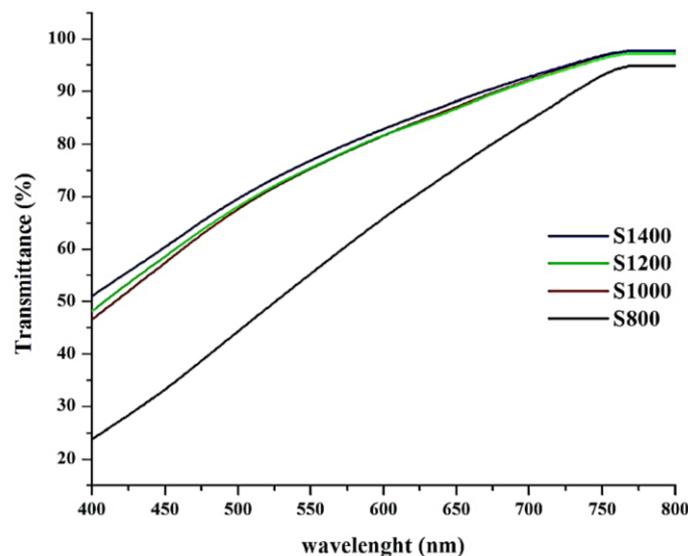
Figure 7. Transmittance surface of PVDF/SiO$_2$ composite coating

Test results with UV Visible were performed at 400-800 nm wavelengths (Figure 7). For the surface of the 800°C PVDF/SiO$_2$ composite layer, it can transmit visible light from 400 nm wavelength of 23.825 % and rise significantly until the wavelength of 768 nm is 94.826 %. As for the light transmitted by the surface of the composite layer of PVDF/SiO$_2$ 1000°C, 1200°C, and 1400°C is almost the same. When viewed from the whole, UV Vis test results from the four surface variations obtained by the highest transmittance results on the surface of the composite layer of PVDF/SiO$_2$ 1400°C. Transmittance is closely related to the gap energy possessed by the surface. In this study, the calcined silica 1000°C, 1200°C, and 1400°C had the same phase, i.e., α-cristobalite. The energy gap of α-cristobalite is 5.525 eV.[6] With an energy gap of 5.525 eV, then at a wavelength of ± 224.6 nm, the energy from that ray going to the surface will be absorbed, or nothing is transmitted. Therefore, the greater the wavelength or > 224.6 nm starting to have transmitted. And the bigger, the greater the transmission percentage. In addition, the surface area produced from calcined powder also influences the transmittance results. The higher the calcination temperature, the smaller the surface area of the resulting powder. Because this study used silica mass composition in each of the same variations, then the amount of powder that is in the layer of surface variation is not the same. So as to obtain the results of variations of transmittance as well.

Conclusion

From the analysis that has been done in this research, it can be concluded that the hydrophobicity aspect due to the variation of silica calcination temperature is known from the contact angle value formed on the surface of the composite layer of PVDF/SiO$_2$ 800°C, 1000°C, 1200°C and 1400°C respectively of 117.12° ± 0.98°, 107.80° ± 0.91°, 121.31° ± 1.45°, and 111.75° ± 1.47°.

Acknowledgment

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