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Hydrophobic Surface Coating on The Surface of Ship Hulls and Structures

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A B S T R A C T

In this research, a hydrophobic layer has been successfully created on the surface of a steel plate using natural mineral silica modified with MTMS (Methyltrimethoxysilane) precursor. The synthesis process begins with the process of purifying silica sand, titration and calcination to obtain mineral silica in the cristobalite phase. This research used three variations of calcination holding time for silica minerals. Variations in the calcination holding time for the mineral silica used were 8 hours, 12 hours and 16 hours using the same temperature, namely 950°C. Each variation of silica mineral that has been synthesized is then modified with MTMS precursors. The names of the modified silica samples are modified MTMS/SiO2 V1, modified MTMS/SiO2 V2, and modified MTMS/SiO2 V3 with a mineral silica calcination holding time of 8 hours, 12 hours, and 16 hours respectively. The synthesized silica powder is then mixed with steel ship paint and applied to the surface of the steel plate as a topcoat layer. The coating method used is the brush coating method. Increasing the concentration of silica powder and the calcination holding time of silica minerals affect the roughness and hierarchical structure of the steel plate surface. Surface roughness and hierarchical structure are important indicators of the formation of a hydrophobic surface. Roughness on the surface of a steel plate can be identified by performing AFM (Atomic Force Microscope) characterization. The AFM characterization results show that the highest roughness is found in the MTMS/SiO2 modified V3 sample. Hydrophobicity on the surface of the steel plate can be identified from the WCA (Water Contact Angle) test. WCA testing is carried out using two different types of liquid, namely fresh water and sea water. The highest water contact angle produced in this study was 128° using fresh water and 134° using sea water.

Keywords: Hydrophobicity, MTMS, Silica, Water Contact Angle.

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1. Introduction

As technology develops, multifunctional material innovation becomes a general need. One of the multifunctional material innovations is hydrophobic material. This hydrophobic material has attracted the attention of researchers both in the academic and industrial worlds. Hydrophobicity is an innovation by researchers for a material that has other functions or is multifunctional which can support the main function of a material. Hydrophobic materials are materials that repel water or in other words don't like water. When water is dropped on the surface of a hydrophobic material, what will happen is that the water will form dots which then slide and carry dirt and dust on the surface of the material so that this hydrophobic material is often known to have self-cleaning capabilities. Self-cleaning ability is the ability to clean itself on a surface through hydrophobic mechanisms or the lotus effect produced by certain chemical compounds. Properties such as self-cleaning are highly desirable for many industrial applications such as anti-biofouling paint for ships.

On ships, being able to maneuver well is greatly influenced by the geometric design of the ship's building and the surface performance of the ship's walls. The surface of the ship's walls must have a minimum sea water resistance force. Hydrophobic paint coatings based on silica material can be used as a water quenching material and have self-cleaning capabilities and are very suitable when applied to ship walls.

Much research has been carried out to understand the function, structure and working principles of superhydrophobic surfaces that have self-cleaning properties. There are many ways to obtain a superhydrophobic surface on a material. One of them is using silica material. Silica has strong bonds and high thermal stability so that this material can be used to form superhydrophobic layers. Silica can be found in natural materials, namely silica sand. Apart from that, silica can also be found in synthetic materials, such as MTMS (Methyltrimethoxysilane). MTMS is a precursor of silica and can easily be used to modify the surface of materials to make them superhydrophobic. Therefore, a hydrophobic layer was made by modifying steel ship paint mixed with MTMS-based silica powder which serves to determine its effect on the hydrophobicity of the steel plate. In this research,

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steel plate coating media is used because ship walls generally use steel material.

1.1. Ship

Ships are a technology whose existence is increasingly needed in this increasingly advanced era. Many ships. Many ships are used as a means of transportation or transporting goods from one place to another. Ships are also a means of national defense from external threats. Considering that most of Indonesia's territory is sea and Indonesia is a country with hundreds of islands, of course the presence of ships is very important.

A ship moves using a thrust which is simply called thrust. The thrust power is generated by an engine which is transmitted through a shaft and then the power is distributed to the propeller. The thrust that is transmitted in moving the ship is greatly influenced by the ship's resistance. Ship resistance is a fluid force that acts at such a time as to result in resistance to the ship's movement. The ship's resistance is equal to the fluid force acting parallel to the ship's axis of motion. A ship's resistance is related to hydrodynamic forces. Hydrodynamic forces are caused by the relative movement of the ship relative to the water.

Ship resistance is divided into two, namely those above the water surface and those from below the water surface. Resistance above the water surface is the force that acts on the part of the ship's hull that is visible above the water surface. In general, ship resistance is influenced by ship friction resistance. Friction resistance occurs due to the movement of the ship through a fluid that has a viscosity such as sea water. This fluid is in direct contact with the submerged surface of the ship's hull when the ship is moving and will cause friction along that surface. Friction resistance occurs due to friction between the surface of the ship's body and the medium through which it passes. Whether this friction is important or not depends on the type of fluid and flow pattern.

Friction resistance is greatly influenced by the roughness and type of ship surface. By modifying the surface of the ship's walls using hydrophobic materials to produce hydrophobic ship walls in areas that interact with sea water, it is able to reduce the resistance of the ship, making it easier for the ship to move and maneuver in all its activities. In addition, modifying the ship walls with hydrophobic materials can reduce the occurrence of corrosion on the ship walls, thereby minimizing the cost of maintaining the ship walls.

1.2. Hydrophobicity

Hydrophobicity of a material is a resistance to the flow of water on its surface. A material is said to have high hydrophobic properties if it is difficult for water to flow on the surface of the material. The hydrophobicity of a material can be explained using the contact angle on the material surface (Amiruddin, 2022).

A surface can be said to be hydrophobic if the surface does not get wet if the surface is exposed to water and the surface always looks clean. If there is dirt attached to a surface then when the surface is exposed to water, the dirt attached to the surface will be dispelled by the water rolling on the surface (Ensikat, 2011). This has been researched by scientists through biomimetics, namely a technological development that imitates the way nature works (Bhusan, 2009).

In simple terms, surfaces that attract water are called hydrophilic, while surfaces that repel water are called hydrophobic. The degree to which an internal surface attracts or repels water can be called, respectively, hydrophilicity or hydrophobicity. Polar liquids such as water and alcohol interact more strongly with hydrophilic surfaces. Likewise, nonpolar fluids such as petroleum-based solvents interact more strongly with hydrophobic surfaces. On hydrophobic surfaces, water droplets form small clumps with relatively large contact angles. In contrast, on a hydrophilic surface, water droplets spread out to form even clumps with a smaller contact angle. In the scientific community, a surface is hydrophobic when the static contact angle of water is $\theta > 90°$ and is hydrophilic when $\theta < 90°$ (Lag et al., 2008; Law, 2014).

The contact angle depends on several factors, such as surface energy, surface roughness, and cleanliness. Surfaces with high energy are formed by polar molecules, which tend to be hydrophilic, while surfaces with low energy are formed by nonpolar molecules, which tend to be hydrophobic.

1.3. Silica

Silica is a compound that has the characteristics of a high melting point, is resistant to acids and bases and is insoluble in water (Katsuki et al., 2005). Silica is often found in nature, such as sand or quartz, as well as diatom cell walls. The existence of silica is not free, but is bound to other compounds both physically and chemically (Faisal, 2009). Because of its characteristics, the use of silica has been widely developed in several fields. One of them is the industrial sector. Silica is used primarily in the production of glass for windows, drinking glasses, glasses, mirrors, and many other uses.

Silica has three crystalline phases and one non-crystalline phase. The crystalline phases of silica are quartz, cristobalite and tridymite (Apriliana, 2015). Meanwhile, the non-crystalline phase is amorphous silica (R E Smallman, 2000). Most of the methods used to purify silica produce amorphous silica, so it needs to be given other treatment to change the crystal structure into crystals. To get the crystal structure from amorphous to crystalline phase, it is given calcination treatment. Where calcination at a temperature of 800°C has an amorphous phase with a steeper structure than silica that has not been calcined. At a temperature of 1000°C it has tridymite and cristobalite phases. Meanwhile, at a calcination temperature of 1200°C, the intensity of the tridymite phase decreases and cristobalite increases, so that at this temperature it can be said that a phase transformation occurs from tridymite to cristobalite (Latif, 2014).

2. Research Methods

The synthesis of natural mineral MTMS/SiO2 is made using the main material, namely silica mineral, obtained from the previous process and using a silica precursor, namely MTMS (methyltrimethoxysilane). Synthesis began by mixing 9.5 ml MTMS and 48.14 ml methanol. Then the two ingredients were stirred at room temperature for 24 hours using a magnetic stirrer. After 24 hours had passed, 9 ml of distilled water was added and stirred at a constant speed for 15 minutes. Then 3 ml of NH4OH 3M was added drop by drop. Next, 1 gram of mineral silica was added to the mixture and stirred for 1 hour at room temperature. Then the sample was dried at a temperature of 100°C using a hot plate while still being stirred using a magnetic bar. The dry sample is then crushed and sieved to obtain uniform particles. The dried sample is in the form of silica powder.

The silica powder is then coated on the surface of the steel plate using a coating medium, namely paint. Before the coating process is carried out, the steel substrate is first cleaned using soap and rinsed with water. Then the steel plate is sanded using a grid of 120, 240, 400 to remove dirt that is still attached and rust that is stuck to the steel surface. Next, the steel plate is cleaned again using acetone and dried.

Then the steel plate is coated using 3 layers of paint, namely the primary layer, secondary layer and top layer. The primer layer functions to slow down the occurrence of corrosion. The secondary layer is an intermediate layer that functions to provide a good bond between the primary layer and the top layer. Meanwhile, the top layer is the top layer which is the first line of defense in the coating system. In this top layer, the paint is mixed with previously synthesized silica powder. This silica powder acts as a hydrophobic material which functions to increase the hydrophobicity of the surface of the steel plate. After the silica powder is mixed with the top coat of paint, then these two ingredients are stirred until even and homogeneous. Then this paint mixture is coated on the surface of the steel plate and dried at room temperature for 24 hours. After the steel plate is dry, the steel plate is characterized by WCA (Water Contact Angle) and AFM (Atomic Force Microscope). WCA testing is carried out to determine the contact angle of water droplets with the material surface and to determine the wettability of the material surface. Meanwhile, AFM testing was carried out to analyze the surface topography of the layer in three dimensions and to determine the surface roughness of the steel plate.

3. Discussion

The basic material used in this research is silica. The silica used in this research was two different types of silica which were then mixed together. The silica materials used are mineral silica and MTMS precursors. The silica used is natural sand originating from the Bangka Belitung Islands. The mineral silica is then mixed with the MTMS precursor.

In mineral silica, in mineral silica, the synthesis process begins with the process of refining silica sand to produce powder with a high level of purity. This purification process is carried out by mixing mineral silica with 2M HCl. After the sand purification process is carried out, it continues with the titration and calcination process. The calcination process is carried out using a high temperature, namely 950°C. This research uses variations in the calcination holding time of mineral silica. There are three types of variations, namely 8 hours, 12 hours and 16 hours. This research uses variations in calcination resistance time with the aim of determining its effect on the hydrophobicity produced after being applied to the surface of a steel plate.

Each variation of silica mineral is then mixed with the MTMS precursor to modify the morphology of the silica particles. Mixing between silica minerals and MTMS precursors is carried out by mixing MTMS and methanol. The modified materials that have been synthesized are then named sequentially, namely modified MTMS/SiO2 V1, V2, and V3.

The synthesized MTMS/SiO2 modified V1, V2, and V3 were then subjected to AFM testing to analyze the surface topography of the layer in three dimensions to determine the surface roughness of the steel plate. AFM characterization is carried out after the sample forms a layer (coating). The modified MTMS/SiO2 powder that has been synthesized is then applied to the surface of the steel plate using paint media. The results of AFM characterization on the surface of a steel plate that has been modified with silica powder can be seen in Figure 1. - Figure 4.

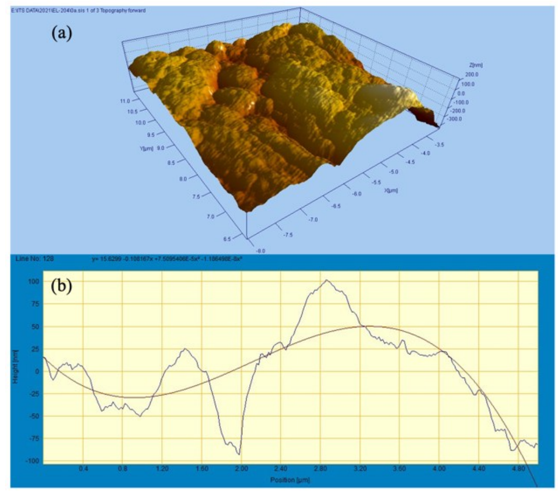

Figure 1. AFM characterization results on the surface of a steel plate without the addition of powder (a) 3-dimensional top view (b) 2-dimensional topography

Figure 1 (a) shows the three-dimensional top view surface morphology of the surface layer of a steel plate without the addition of silica powder or only consisting of paint and thinner. The surface of the plate without the addition of silica powder has several quite low peaks distributed on the surface of the layer. On this surface, the roughness formed tends to be low as shown in Figure 4.1 (b). Figure 4.1 (b) is the result of AFM testing in 2 dimensions. The peaks on the plate surface without the addition of silica powder have an average height of around 80 - 100 nm and the distance between the peaks is around 0.15 µm. Peak height and distance between peaks were measured using image-J software. The peaks formed do not come from silica particles. However, the peaks formed are structures produced by steel ship paint particles.

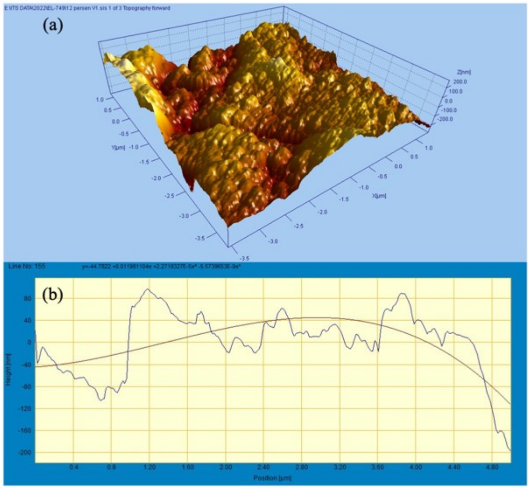

Figure 2. AFM Characterization Results on the Plate Surface with the Addition of V1 Modified MTMS/SiO2 Powder (a) 3 Dimensional Top View Topography (b) 2 Dimensional Topography

Figure 2. is a three-dimensional surface morphology on the surface of a steel plate mixed with MTMS/SiO2 modified V1. If you pay attention, the surface of the steel plate has succeeded in forming a hierarchical structure. The coating shows increased roughness compared to the coating without silica powder. Based on Figure 4.2 (b), the average peak height is around 70 – 104 nm and the average distance between peaks is around 0.19 – 0.30 µm.

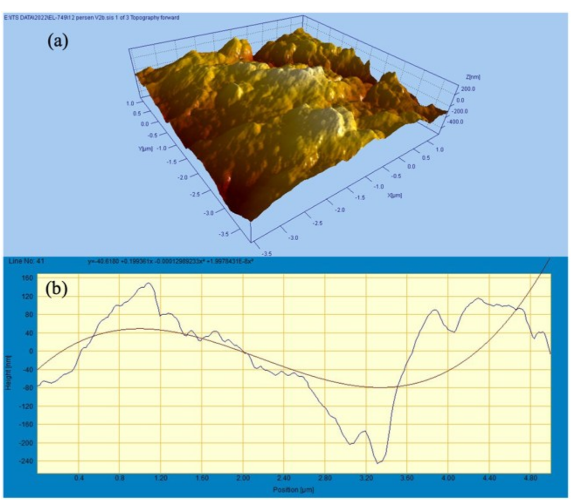

Figure 3. AFM Characterization Results on the Plate Surface with the Addition of V2 Modified MTMS/SiO2 Powder (a) 3 Dimensional Top View Topography (b) 2 Dimensional Topography

Figure 3 (a) is a three-dimensional surface morphology on the surface of a steel plate mixed with MTMS/SiO2 modified V2. The surface morphology shows the formation of a hierarchical structure. The hierarchical structure formed has a higher peak shape than the previous sample. This can be proven from Figure 4.3 (b) which shows the average peak height is around 100 – 115 nm and the average distance between peaks is around 0.08 – 0.22 µm.

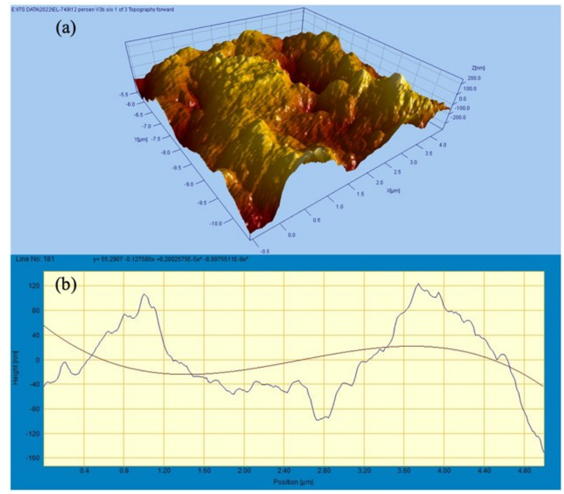

Figure 4. AFM Characterization Results on the Plate Surface with the Addition of V3 Modified MTMS/SiO2 Powder (a) 3 Dimensional Top View Topography (b) 2 Dimensional Topography

Figure 4 (a) is a three-dimensional surface morphology on the surface of a steel plate mixed with MTMS/SiO2 modified V3. If you pay attention, the surface of the steel plate has formed a hierarchical structure. Based on Figure 4.2 (b), the average peak height is around 108 – 126 nm and the average distance between peaks is around 0.03 – 0.175 µm.

The surface of the steel plate mixed with MTMS/SiO2 modified V3 has the largest average peak height and the lowest average distance between peaks compared to the other samples. The smaller the distance between peaks results in greater surface roughness. The rougher the surface, the more hierarchical structures are formed and the narrower the empty space between two adjacent structural peaks.

The addition of modified silica powder to the surface of steel plates using ship paint media has a significant effect on surface roughness. This can be seen from the AFM analysis results in Figure 2, Figure 3, and Figure 4. The addition of silica powder to the surface of the steel plate causes the formation of a hierarchical structure on the surface of the steel plate with peaks that tend to be blunt with a distribution that tends to be homogeneous. Based on references, the formation of a hierarchical structure causes surface roughness to increase. If the roughness of a surface increases, the resulting hydrophobicity will get better.

Apart from paying attention to surface roughness, the level of hydrophobicity on the surface of the steel plate can be determined by measuring the water contact angle. The higher the contact angle value indicates that the surface of the steel plate is more hydrophobic. Therefore, a WCA test was carried out to measure the water contact angle formed on the surface of the steel plate by dripping water on the surface of the steel plate. The water droplets that have stuck to the surface of the steel plate are called the water contact angle. The water contact angle formed was taken using a digital microscope. Then the image results obtained were analyzed using image-J software to determine the water contact angle formed. The liquid used in this WCA test is fresh water and sea water. The WCA test using fresh water can be seen in Figure 5 and the WCA test using sea water can be seen in Figure 6.

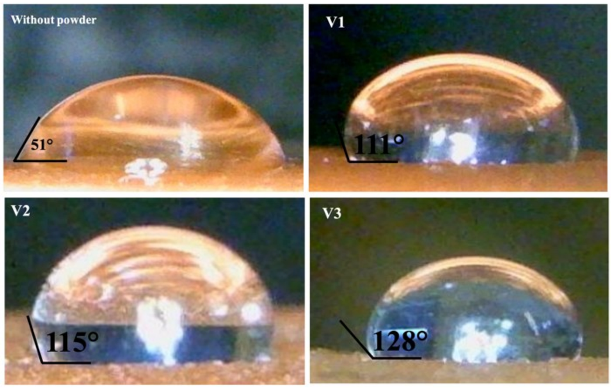

Figure 5. Water contact angle using fresh water on the surface of a steel plate (a) without powder (b) V1 (c) V2 (d) V3

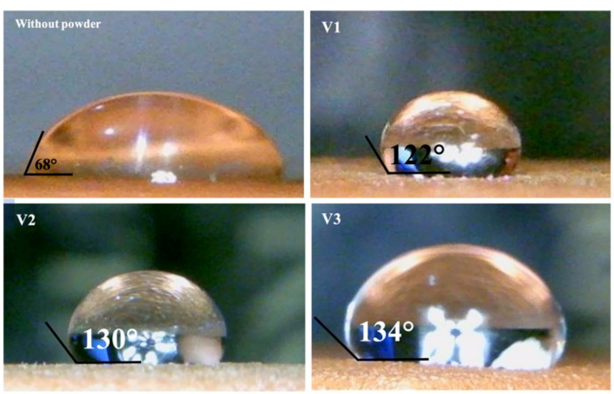

Figure 6. Water contact angle using sea water on the surface of a steel plate (a) without powder (b) V1 (c) V2 (d) V3

If a surface shows a water contact angle of more than 90° then the surface has hydrophobic properties. Meanwhile, if the water contact angle formed is more than 150° then the surface is superhydrophobic. However, if the water contact angle formed is less than 90° then the surface has hydrophilic properties. If you pay attention to the water contact angle test using fresh water and sea water on the surface of the steel plate without the addition of silica powder to the paint medium which can be seen in Figure 5 and Figure 6, the water contact angle formed on the surface of the steel plate without the addition of silica powder is 51° and 68°. The water contact angle formed on the surface of the steel plate without the addition of silica powder indicates that the surface of the steel plate is hydrophilic, whether using fresh water or using sea water.

Then pictures of the water contact angle were taken using fresh water on the surface of the steel plate modified with MTMS/SiO2 modified V1, V2 and V3 which can be seen in Figure 5 (b), (c), (d). Meanwhile, the results of taking pictures of water contact angles using sea water on the surface of steel plates modified with MTMS/SiO2 modified V1, V2 and V3 can be seen in Figure 6 (b), (c), (d), respectively. If you look at the data above, the surface of the steel plate that has been modified with MTMS/SiO2 modified V1, V2 and V3 results in an increase in the water contact angle. The water contact angle formed shows a value of more than 90°, whether using fresh water or sea water. So the addition of silica powder to the surface of the steel plate causes the surface of the steel plate to become hydrophobic. The hydrophobic surface of the steel plate shows the shape of liquid droplets which tend to be round. The increasingly round shape of the liquid drop indicates a high cohesive force between the water and the surface of the steel plate so that the force created between the two will repel each other so that the liquid that is dropped will not wet the surface of the steel plate.

From the WCA data that has been obtained, the addition of silica powder affects the water contact angle formed. Apart from that, the calcination holding time also influences the water contact angle formed. From these data, MTMS/SiO2 modified V3 shows a higher water contact angle compared to MTMS/SiO2 modified V2 and MTMS/SiO2 modified V1. MTMS/SiO2 modified V3 is a silica mineral that is calcined using a calcination holding time of 16 hours mixed with MTMS precursor. Increasing the calcination holding time also causes the water contact angle formed to increase.

In this research, water contact angle measurements were carried out using two different liquids, namely fresh water and sea water. After analysis, water contact angle measurements using sea water show that the water contact angle value is greater than using fresh water. This is because the salinity of sea water has a greater value than fresh water. Salinity is the total concentration of salt ions dissolved in water. The higher the salinity value of water in a liquid, the more polarity it will have. If a liquid with high polarity hits a non-polar hydrophobic surface, the two will repel each other and produce a large water contact angle. Thus, using sea water to measure the water contact angle on the surface of a steel plate is more efficient than using fresh water.

4. Conclusions

Based on the results of the research that has been carried out, the conclusion is that the addition of modified MTMS/SiO2 to the surface of the steel plate using ship paint media has a significant influence on surface roughness. The addition of modified MTMS/SiO2 to the surface of the steel plate causes the formation of a hierarchical structure on the surface of the steel plate. With the formation of a hierarchical structure, surface roughness will increase. If the roughness of a surface increases, it will cause the resulting hydrophobicity to get better. In addition, the calcination holding time of silica minerals has a significant impact on the hydrophobicity of the steel plate surface. The longer the calcination holding time used, the greater the water contact angle formed.

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