

This research investigates Alumina (Al_2O_3) and Magnesium nano membrane layers using hybrid technology. Hybrid is a concept of combining two or more materials/elements to achieve something better. Hybrid technology was developed because of the possibility of combining materials/elements which, if used simultaneously, has more advantages than if used independently. The problem to be solved is to find the best composition of Alumina and Magnesium hybrid membranes. Superhydrophobic properties of the membrane are achieved at a percentage of Mg:50 %, Al_2O_3 :50 %. At a composition below 50 % Mg, the small surface roughness has a low surface tension, while the H_2 production reaction by Mg is also low, so the surface tension carrying capacity of the gas and the roughness of the droplets is not strong, which causes the hydrophobicity to be low. In compositions above 50 % Mg, H_2 production by high Mg makes bubbles cover the roughness peaks so that the surface tension is lower and changes the superhydrophobic to hydrophobic properties. At a high Mg percentage, H_2 production is very large, while surface roughness decreases due to minimal Al_2O_3 . As a result, the roughness grooves are unable to accommodate H_2 gas bubbles, the bubbles completely cover the roughness peaks which are the source of surface tension so that the hydrophobic properties become hydrophilic. The results of this best hybrid composition can be used as a guide in making superhydrophobic membranes on Alumina (Al_2O_3) and Magnesium alloys. This membrane application is used as a filtration membrane in the water purification process. Superhydrophobic membranes are widely applied in membrane distillation, membrane gas absorption and pervaporation

Keywords: hybrid technology, superhydrophobicity, surface roughness, hybrid composition, membranes

UDC 532
DOI: 10.15587/1729-4061.2023.286391

IDENTIFYING THE FEATURES OF SURFACE ROUGHNESS AND H_2 BUBBLE PRODUCTION ON THE SUPER-HYDROPHOBIC PROPERTIES OF Al_2O_3 AND MG MEMBRANES

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Received date 10.08.2023

How to Cite: Subagyo, R., Wardana, I. N. G., Widodo, A. S., Siswanto, E., Nugraha, A., Fadilah, M. M., Agusnaedi, Ramadhani, A. F. (2023).

Accepted date 20.08.2023

Identifying the features of surface roughness and H_2 bubble production on the super-hydrophobic properties of Al_2O_3 and Mg membranes.

Published date 30.10.2023

Eastern-European Journal of Enterprise Technologies, 5 (6 (125)), 36–48. doi: <https://doi.org/10.15587/1729-4061.2023.286391>

1. Introduction

The surface roughness of superhydrophobic materials and the self-cleaning ability of their surfaces inspire a wide range of applications. Various kinds of superhydrophobic surfaces have been produced on a laboratory scale and some have even been produced commercially. Like paint, roofs, textiles and window panes that are self-cleaning. Surfaces having properties between superhydrophobic and hydrophilic have also been developed for photo-responsive surfaces with inorganic oxides and photo-reactive organic molecules; copolymer films are sensitive to pH or electric fields.

Superhydrophobicity is a very unique and interesting property to study. Many studies have been conducted to

unravel the mysteries of superhydrophobicity. These studies include examining the surface roughness [1], examining the droplet volume when in contact with the leaf surface [2]. In fact, recent research has been carried out to explore the potential of superhydrophobic properties as a generator of electrical energy [3, 4]. The mystery of superhydrophobicity begins to be solved by making membranes from nanoparticles [5]. The results of this invention are capable of making membranes that have superhydrophobic properties. The superhydrophobic nature is created from the combination of two nanoparticles, each of which has mutually beneficial properties or is often referred to as a hybrid.

Hybrid is a concept of combining two or more ingredients/elements to achieve something better. Hybrid technol-

ogy was developed because of the possibility of the combination of materials/elements when used together has more advantages than when used independently. The advantage of the element Al_2O_3 is that it has hydrophobic properties and its ability to react with H_2O to form O_2 gas bubbles on its surface [6]. The weakness is not being able to increase its hydrophobicity to become super-hydrophobic which is expected to be a perfect membrane. While the advantage possessed by Magnesium is its ability to react with H_2O to form Hydrogen gas bubbles which can have the effect of gas being trapped on a surface so that it can increase its super-hydrophobic properties [7]. The weakness is that when used independently it generates excessive hydrogen gas which causes a more dominant bubble effect [8]. When these two elements are hybridized, they have good super-hydrophobic properties where the trapped gas formed in the grooves can be increased to reach optimal limits. The application of the Mg hybrid surface with Al_2O_3 above is in membrane technology (hydrophobic properties) [9].

It is necessary to increase the hydrophobicity of the material to become superhydrophobic, one of the methods used is the hybrid method [10]. This method is carried out by conditioning the proper composition of Magnesium. At the right composition the membrane is able to increase its hydrophobicity. Membrane hydrophobicity has a very important role in reducing fouling on the filtration membrane. Therefore, research on superhydrophobic membranes becomes relevant in the field of filtration development which is very necessary at this time.

2. Literature review and problem statement

There are many studies related to hydrophobic membranes, such as that carried out by [11], but this research has not been able to increase the properties of the membrane to reach superhydrophobicity. Membrane research that has been carried out requires more expensive costs and results are less than optimal because it uses a membrane contact system between gas and liquid. The new method offered in this research can clearly increase the very beneficial superhydrophobic properties of membranes by using a hybrid method of combining two mutually beneficial nanoparticles. This method of making membranes also uses simple technology and is not too difficult to do. By increasing the properties of the membrane to become superhydrophobic, the efficiency and performance of the membrane becomes more optimal, resulting in better filtration results. Another advantage of superhydrophobic membranes is that the level of use of the membrane is much more durable than before.

Research on gas bubbles began with research on hydrogen gas in membranes ($\text{Al}_2\text{O}_3+\text{Mg}$) [5]. This research succeeded in finding membranes that have hydrophobic and hydrophilic properties. Further research carried out to investigate the physical and chemical mechanisms of the hydrophobic properties of nanoparticle membranes ($\text{Mg}+\text{Al}_2\text{O}_3$) [9] succeeded in finding nano-sized bubbles which are the main actors in the physical and chemical mechanisms in determining hydrophobic properties. Previous research on nanobubbles has also found the influence of hydrophobic and hydrophilic properties on alumina surfaces. Research on membranes that has been carried out was initially inspired by research into the mechanism of hydrogen bubbles on the surface of taro leaves when droplets contact. The research above is research

that is interrelated and supports each other so that the secret of superhydrophobic properties is discovered.

To determine the role of bubbles in hydrophobic properties, it is necessary to carry out further research on different nanoparticles to form hybrid technology. By carrying out experimental methods to measure contact angles and analyzing the effect of bubbles on their superhydrophobic properties.

The influence of the gas layer on the surface of the material is also able to provide a hydrophobic and hydrophilic effect on the material. Research on coating materials with oxygen, hydrogen and fluorine gas has been carried. This research carried out a coating on diamond nanocrystal material so that it has a hydrophobic surface. The results of the hydrophobic properties test show that: the layer of particles with oxygen gas shows hydrophilic properties with a contact angle ($42.3-51.4^\circ$), while the layer using hydrogen gas ($78.5-83.9^\circ$) and fluorine gas ($101.8-103.9^\circ$) exhibits hydrophobic properties. The results of this research show that hydrogen gas has the potential to change the properties of a material to become hydrophobic.

Many studies have been carried out previously on the superhydrophobic properties of taro leaves, but there is still little research on the influence of gas bubbles trapped on the surface. In general, superhydrophobic properties are caused by gas bubbles trapped on the leaf surface. Emitting the trapped gas is the key that influences the superhydrophobic properties. With these superhydrophobic properties, taro leaves are able to reduce the contact angle and maintain the surface so that it is not wetted by air. The droplet phenomenon when it comes into contact with the surface of Taro leaves will be observed in more detail so that the secret of this superhydrophobic nature can be revealed.

Research on the hydrophobicity of hybrid surfaces was initiated by [7]. Hybrid surfaces consisting of an array of hydrophobic and hydrophilic sites were designed and fabricated in an attempt to better understand the wettability effect of chemical and micro-scale surface features. Models based on energy minimization were developed to design and predict hybrid surface wettability. The increase and decrease in the contact angle is measured at equilibrium conditions in order to obtain an appropriate model. This experiment shows that the level of hydrophobicity is equivalent to increasing the contact angle and inversely proportional to the decreasing micro-pillar distance (b/a).

Subsequent research on hydrophobic and hydrophilic hybrid surfaces was carried out with a micropillar-array designed and fabricated to understand the unique effects of surface morphology and chemistry on condensation droplets [8]. The droplet test revealed that the hybrid surface exhibited a high contact angle, which is characteristic of a hydrophobic surface. However, little is known about the wetting behavior of atom-containing droplets growing on hybrid surfaces during condensation. In this study, hybrids with three different spacing ratios were subjected to a condensation test using environmental scanning electron microscopy (ESEM) at ambient conditions. For hybrid surfaces with spacing ratios below 2, droplets form on the top and sides of the micro-pillars, where they grow, coalesce with adjacent droplets, and overflow once they reach a certain size. After overflow, the upper surface remains partially dry, which allows for droplet growth. For a hybrid surface with a spacing ratio equal to 2, the wetting behavior becomes different, in that the droplets essentially coalesce

and form a thin liquid film which is eventually pushed into the micro-valleys. The process of liquid shedding causes re-nucleation of droplets especially over dry hydrophilic sites. To better understand the nature of the droplets on the hybrid surface, a surface energy-based model was developed to predict the transition between the two wetting behaviors observed at different distance ratios. The experimental and analytical results show that the micro-pillar spacing ratio is a key factor supporting the different wetting behavior of hybrid surface-condensed droplets.

Hybrid surfaces in membrane technology that are processed with environmentally friendly energy as a separator for mixed liquid molecules, are increasingly playing an important role among various membrane technologies. Membrane applications in the world of engineering have a very important role, including: Membrane distillation (MD) is a non-isothermal separation process using a membrane [9], Membrane gas absorption technology combines conventional techniques for gas absorption into solution and a contactor membrane as a mass transfer device [10], Pervaporation is a membrane separation process whose working principle is based on the relative solubility and diffusivity of each component in the membrane material [11].

The weakness of these three studies is that they still use micro membranes which result in the filtration process seeming slow so the best membrane is needed that can replace them. Environmentally friendly nature is a technology that is highly favored at the moment, because in the long term this technology does not cause environmental damage. The application of nanoparticles to membranes is very useful because the contact process is faster and results are more optimal. The advantage of environmentally friendly membrane technology is that it does not pollute the environment, so it is very good in Kembangan for the future. Environmental pollution due to chemicals is very dangerous nowadays. The strong and complex interactions in liquid molecular mixtures impose stringent requirements on the design and preparation of membrane materials to achieve high separation performance and long-term stability. Hybrid membranes, which have 4M features (multiple-interactions, multiscale-structures, multiphase and multiple-functionalities), have been extensively exploited in pervaporation processes. This study aims to provide an overall picture of hybrid membranes for pervaporation separations.

The membrane is a selective barrier between two phases, which has the ability to transfer one component of the feed mixture better than the other components, so that separation can be achieved. The surface properties of the membrane are divided into two, namely hydrophilic and hydrophobic properties.

Research on the use of hydrophobic membranes shows that even though the membrane is hydrophobic, wetting of the membrane by absorbent liquid still occurs [12], which causes an increase in mass transfer resistance, and as a consequence a decrease in membrane performance in long-term operation. Research to extend membrane life was carried out by simultaneously modifying CO₂ and SO₂ in a polypropylene hollow fiber membrane contactor [13]. The weakness of this membrane is that the rate of fouling still occurs because of the relatively large surface energy. To overcome this, research was carried out on the development of membranes with low surface energy to reduce the fouling in ultrafiltration applications [14].

Three basic things in the three researches that must be addressed are the relatively short lifespan of the membrane. This is because the membrane is made from only one element so there is no recovery process when the membrane begins to decline in function. The discovery of hydrophobic membranes that are durable and have better efficiency is very necessary in the increasingly advanced world of filtration. Hybrid technology is one solution to overcome this. Weaknesses that occur in the membrane need to be overcome so that the membrane performance can be maximized. Membranes that experience decreased performance need to be repaired, at least the time can be extended. Based on research sources, superhydrophobic membranes have the advantage of longer use time and better results. To improve the separation performance of hydrophobic membranes, studies are increasingly being developed to increase the hydrophobicity of membranes towards superhydrophobicity.

One of the modifications for superhydrophobic properties is mixing hydrophobic additives or hydrophobic polymers into polymer solutions in a phase inversion technique which is a popular method for increasing the hydrophobicity of membranes. Membrane manufacturing can be done by direct processing, namely by increasing phase separation hydrophobicity with increased surface roughness through increased phase separation [14], mixing with additives mixing hydrophobic additives or hydrophobic polymers into polymer solutions in the phase inversion technique is a popular method to increase membrane hydrophobicity [15] and electrospinning a process for producing nano and micro scale fibers that uses electrostatically charged polymeric solutions under varying conditions [16]. The second way is to use surface modification methods, namely: Plasma treatment generally is used to increase membrane hydrophobicity by fluorination of the membrane surface [17], rough polymer film coating made by adding non-solvents or nanoparticles into the coating solution [18], chemical vapor deposition is a process in which a thin solid film is deposited on a substrate through a gaseous chemical reaction [19], sol-gel method. The precursor is converted to a glass-like material through a series of hydrolysis and polycondensation reactions where the surface roughness can be controlled by varying the system conditions and reaction mixture [20], grafting method. Widely used for surface modification of ceramic membranes, where fluorosilane compounds are generally used [21] and other methods. The weakness of modifications to macromolecules is that the filtration process seems slow because the contact and cleaning process with the membrane surface takes quite a long time. This affects the cleaning results with a small capacity. To overcome this, the best technology currently is to apply nanoparticles to increase the superhydrophobic properties of the membrane. The nanoparticle method has more advantages compared to other methods, this is because nanoparticle has the advantage of a wide contact area so that the filtration process will be faster. Superhydrophobic nanoparticles have better advantages compared to macromolecules, this is because they are supported by the surface energy that occurs in the nanoparticles. Increasing membrane superhydrophobicity is very necessary nowadays, because of several advantages it has. The short membrane usage time and less than optimal filtration results are membrane deficiencies that must be corrected. The use of superhydrophobic membranes with low surface energy properties can minimize the forces between impurity molecules and the

surface. This causes foulants to be removed with low hydrodynamic shear forces.

Hybrid technology on nano-alumina (Al_2O_3) and Magnesium (Mg) can increase the superhydrophobic properties of a membrane. To find out more about how the superhydrophobic process occurs and the correct percentage of the mixture in the membrane layer, this research was carried out.

Research on the use of hydrophobic membranes shows that even though the membrane is hydrophobic, wetting of the membrane by the absorbent liquid still occurs, which causes an increase in mass transfer resistance, and as a consequence, a decrease in the performance of the membrane in long-term operation. To improve the separation performance of hydrophobic membranes, studies are increasingly being developed to increase the hydrophobicity of membranes towards superhydrophobicity. It is generally recognized that hydrophilic membranes are less susceptible to fouling than hydrophobic membranes. Several studies have shown that hydrophobic membranes with low surface energy have a low tendency to fouling.

The low surface energy property of hydrophobic surfaces minimizes the intermolecular forces between the foulants and the surface, so that the foulants are removed by low hydrodynamic shear forces or by simple mechanical cleaning, exhibiting fouling-release properties. Foulants on hydrophobic surfaces are easier to clean than hydrophilic membranes. Previous research results show that hydrophobic membranes are more beneficial than hydrophilic membranes. The latest breakthrough that needs to be done is to increase the hydrophobic membrane to become superhydrophobic so that foulants can be minimized or even eliminated. By cleaning the foulant attached to the membrane, the membrane becomes durable and long-lasting, making it more economical.

Many studies on membranes have not been able to find the best superhydrophobic membrane. In the filtration process, a superhydrophobic membrane is needed which is capable of cleaning itself so that impurities do not stick to the membrane. The weakness of the existing membrane is that it is still hydrophobic so that the rate of fouling occurs more quickly. Most membranes still use only one material to increase their hydrophobicity. This has several weaknesses, including that the membrane is only hydrophobic, there is no collaboration between two or more materials that can increase its hydrophobic properties. It is these weaknesses that need to be corrected and resolved in order to obtain an ideal membrane according to the needs and application.

3. The aim and objectives of the study

The aim of this research is to find a membrane that has superhydrophobic properties like taro leaves. This membrane is made by combining Alumina (Al_2O_3) and Magnesium (Mg) nanoparticles. The expected advantages of superhydrophobic membranes include their ability to recover, self-clean and their durability. With ideal membrane conditions, it is hoped that it will be possible to improve the weaknesses of the filtration membrane so far, so that filtration efficiency and results can be increased.

To achieve this aim, the following objectives are accomplished:

- to find a superhydrophobic membrane that can be used as a filtration membrane, easy to recover and more durable;
- to carrying out SEM-EDX tests to determine the composition distribution of Alumina and Magnesium nanoparticles;
- to measure the contact angle of the H_2O droplet when it contacts the membrane layer;
- to observe gas trapped in the membrane layer when it comes into contact with H_2O droplets.

4. Materials and methods of research

The object of research is Alumina (Al_2O_3) and Magnesium (Mg) nanoparticles.

If gas bubbles affect the hydrophobicity of a material, there will be an increase in the superhydrophobic properties of the hybrid membrane.

That the superhydrophobic properties of a membrane are influenced by the presence of nano or micro bubbles covering its surface thereby increasing the surface tension of the droplet which creates hydrophobic or superhydrophobic properties.

The mechanism for hydrophobic properties is the presence of surface roughness and nanobubbles that fill the gaps between particles which are able to create very high surface tension so that they are able to support the droplets so that they have superhydrophobic properties.

The synthetic material used to research the Hybrid Effect is: Magnesium nanoparticles, with size (800 nm), made by US Research Nanomaterials, Inc (USA). Alumina nanoparticles (Al_2O_3), size (52.45 nm), brand Merck, made in Germany, processed to the size of nano-materials in the UM Advanced Materials laboratory. These two materials were mixed with the following percentages of Mg: (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 %). A simple hybrid technology schematic is shown in Fig. 1.

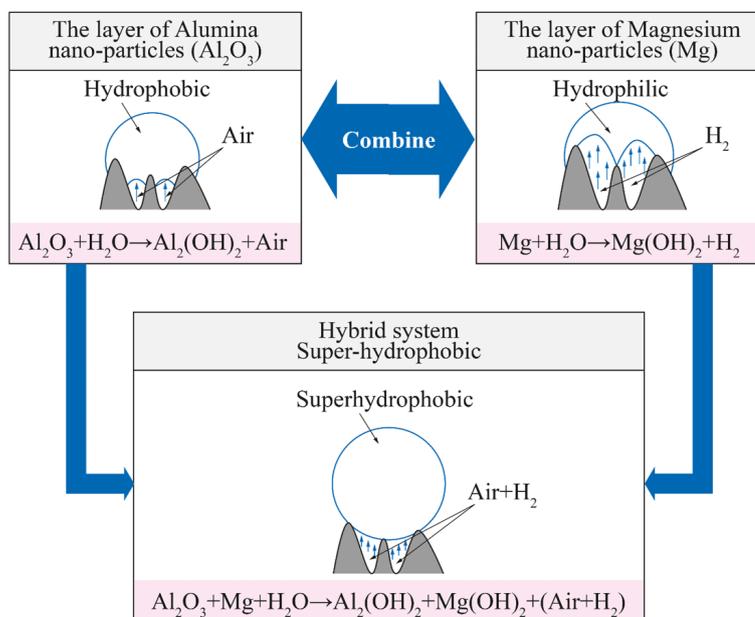


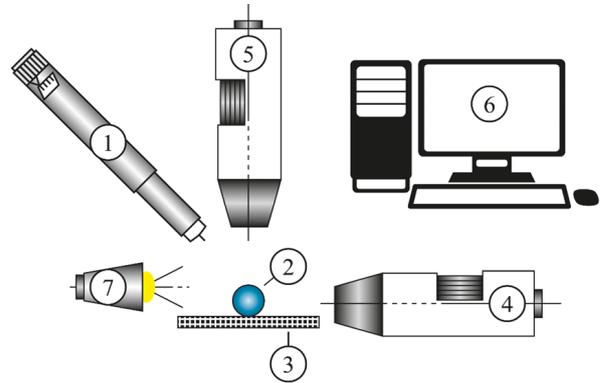
Fig. 1. Hybrid technology schematic on a super-hydrophobic surface

This hybrid technology is made by combining a layer of Alumina (Al_2O_3) nanoparticles in Fig. 2, *b* (White arrow) with a layer of Magnesium (Mg) nanoparticles in Fig. 2, *a* (red arrow). Fig. 2, *c* mixed results, producing gas bubbles (trapped air and Hydrogen) which will strengthen the pressure in the mixed layer nano-gaps when in contact with H_2O droplets. Fig. 2, *d* is the result of the mapping of the surface of the mixed nano-particle layer consisting of particles Alumina (green color) and magnesium particles (blue color) The results of this combination can increase the superhydrophobic properties of a coating.

The droplet volume measurement was carried out as shown in Fig. 3, using tool (1), the droplet volume was varied (1–5 ml). The droplet contact angle was measured using the microscope position (4). Before taking the picture, adjust the lighting using the lamp (7). The results of the images are displayed on the notebook (6), then with measurement software the droplet contact angle is measured (2).

The droplet volume measurement was carried out as shown in Fig. 3, using the tool (1), the droplet volume was varied (1–5 ml) dripped onto the nano-particle hybrid layer (3). Take pictures vertically on droplets when contact is made with the microscope position (5). The results of the images are displayed on the notebook (6), then the image-J software is displayed with a mm scale.

using Image-J software, to determine the Mg fraction in the Alumina layer.



1. Droplet measurement tool
2. Droplet
3. The layer of Mg, Al_2O_3 and mix nanoparticles ($Mg+Al_2O_3$)
4. The position of microscope 1
5. The position of microscope 2
6. Notebook
7. Lamp

Fig. 3. Technique for measuring droplet contact angle and observing magnesium bubbles in the hybrid layer

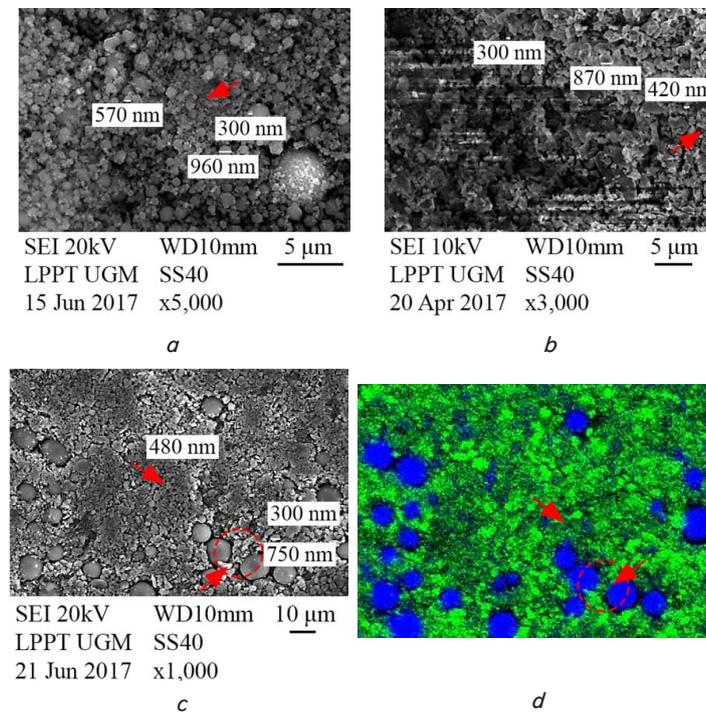


Fig. 2. SEM Test Results on Hybrid coating on: *a* – Magnesium-layer; *b* – Alumina-coating; *c* – Hybrid-mixed layer (Al_2O_3+Mg); *d* – Mapping results on the mixed layer

To adjust the amount of the Mg fraction in Fig. 2, *c* (red arrow) in the alumina layer Fig. 2, *c* (white arrow) is carried out by varying the amount of Mg/mm^2 in the Alumina area. Alumina and Magnesium nanoparticles were weighed according to their percentage: (0:100 mg, 10:90 mg, 20:80 mg, 30:70 mg, 40:60 mg, 50:50 mg, 60:40 mg, 70:30 mg, 80:20 mg, 90:10 mg and 100:0 mg). Calculation of the percentage of hybrid (Al_2O_3+Mg) is done by first taking an image with a digital microscope position (5). Then the image results were analyzed

Research steps:

- optimum composition conditioning was carried out by making eleven membrane samples with composition ratios (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100);
- conducted a superhydrophobic property test on samples to determine the best hydrophobic properties of the eleven membranes. Measurements were made by measuring the contact angle formed on each membrane;
- studying the superhydrophobic mechanism that occurs so that it can be developed for engineering in other engineering applications.

5. Results of research on superhydrophobic properties of nanoparticle hybrid membranes (Al_2O_3+Mg)

5.1. Relationship between droplet volume and contact angle nano-particles of Alumina, Hybrid ($Mg+Al_2O_3$), Magnesium and Taro leaves

The results of the droplet contact angle measurement (1–5 ml) are shown in Fig. 4. It can be seen that the contact angle of the hybrid layer ($Mg+Al_2O_3$) is greater than the contact angle of Taro leaf, Alumina and Magnesium layers. This phenomenon indicates that the Hybrid technology ($Mg+Al_2O_3$) provides a significant increase in superhydrophobic properties. The contact angle formed on the Taro leaves, the Alumina and Magnesium layers are under the hybrid-mixed layer. This indicates that there are interesting events in the hybrid-mixed ($Mg+Al_2O_3$). The excess of hybrid ($Mg+Al_2O_3$) can increase the trapped gas on the surface roughness of the layers (grooves). When in contact with H_2O droplets, Al_2O_3 produces O_2 gas which is trapped on its surface which helps the hydrophobic process occur when testing the contact angle. When Mg is added, the volume of trapped gas increases due to the additional reaction of Mg with H_2O which pro-

duces hydrogen gas. The trapped gas volume continues to increase until it reaches the optimal value. The increase in droplet contact angle of the mixed-layer hybrid compared to Alumina nanoparticles ranged from (58–88 %), with Magnesium nanoparticles ranging from (85–89 %) and with Taro leaves (5–10 %). These results indicate that the increase in the super-hydrophobic properties of the mixed layer hybrid was able to surpass the super-hydrophobic properties of taro leaves.

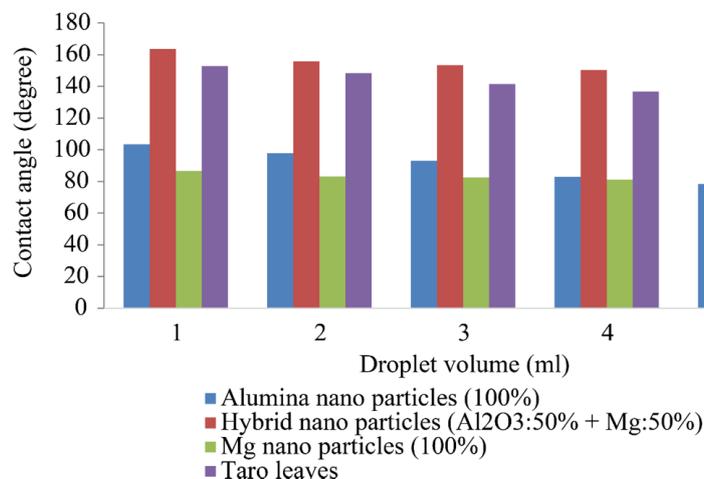


Fig. 4. Graph of the relationship between droplet volume and contact angle nano-particles of Alumina, Hybrid (Mg+Al₂O₃), Magnesium and Taro leaves

Fig. 5 shows changes in the surface hydrophobic properties of Alumina mixed with various compositions of Mg. In the composition of Alumina: 100 % interesting things happen. When the droplet volume is varied from 1 to 5 ml, the surface properties of Alumina change from hydrophilic to hydrophobic. At a volume of 1–3 ml it is hydrophobic and 4–5 ml is hydrophilic like the droplet photo shown in Fig. 6 (A1–A5). This happens because of the surface tension on each droplet. Small droplet sizes (1–3 ml) have high surface tension because of their small radius, whereas large radius droplets have low surface tension. Research conducted by [23] showed that Alumina has hydrophilic and hydrophobic properties. Both of these properties can be formed when there are nano bubbles on the surface. This study found the effect of nano bubbles on hydrophobic and hydrophilic Alumina. When the droplet has a small radius the surface tension is high which helps the process of forming O₂ nano gas bubbles which are trapped on the Alumina surface and produce hydrophobic properties.

It is clear from Fig. 5 that the increase in the contact angle continues with the increase in the percentage of Mg. At 50 % Mg the surface condition reaches maximum super-hydrophobicity with a contact angle of 166°. The hybrid effect (O₂+H₂) is very effective in creating super-hydrophobic properties as shown in Fig. 6 (A11–A15). The 100 % Alumina coating is only able to form a contact angle between 78–108° as shown in Fig. 6 (A1–A5). While the

100 % Magnesium layer is only able to form a contact angle between 70–76° as shown in Fig. 6 (A26–A30).

The decrease in contact angle is clearly seen when the percentage of Mg=80 % and Al₂O₃=20 %. In these conditions the growth of H₂ gas is increasing and O₂ gas is low. This is shown visually by the growth of bubbles that begin to appear at the droplet base of Fig. 6 (A21–A25), which results in a decrease in the contact angle. The completely hydrophilic region is shown in Fig. 6 (A26–A30), Fig. 5 (point 4) (Magnesium:100 %) where the bubble growth is more and more obvious at the droplet bottom and the decrease in the contact angle is more obvious. From this visualization it is clear that excessive hydrogen gas bubbles reduce the contact angle of the droplets. The hybrid effect appears at Mg percentages from 10 to 80 %, and the effect starts to disappear at Mg percentages from 80 % and above.

Besides the contact angle, another factor that determines the hydrophobicity of a surface is roughness [24]. On a nano-hydrophobic surface, an increase in roughness causes an increase in the contact angle, whereas on a nano-hydrophilic surface the opposite occurs. Fig. 7, 8 show that the roughness of the hybrid-mixed (Mg: 50 %, Al₂O₃: 50 %) is higher than that of 100 % Alumina and 100 % Magnesium. The shape of the texture is more spiky as shown in the blue circle in Fig. 7. The higher surface tension on the more spiky texture supports the occurrence of very good super-hydrophobic properties. The sinusoidal graph in Fig. 7, b shows a stable shape when the number of Magnesium nanoparticles is equal to that of Alumina. However, when the entire layer is composed of Alumina or Magnesium, the roughness level is smaller than in the hybrid condition (Mg: 50 %, Al₂O₃: 50 %). This shows that the nano-mixed particles increase the roughness value.

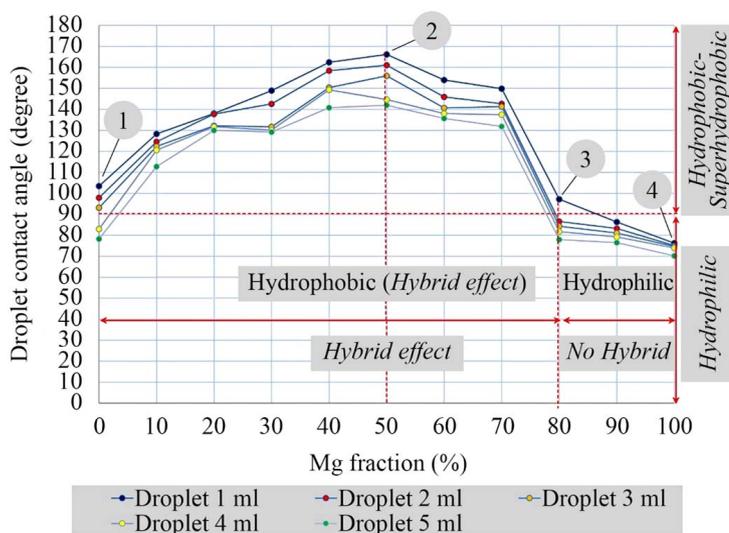


Fig. 5. Graph of the relationship between variations in the percentage of Magnesium to droplet contact angle

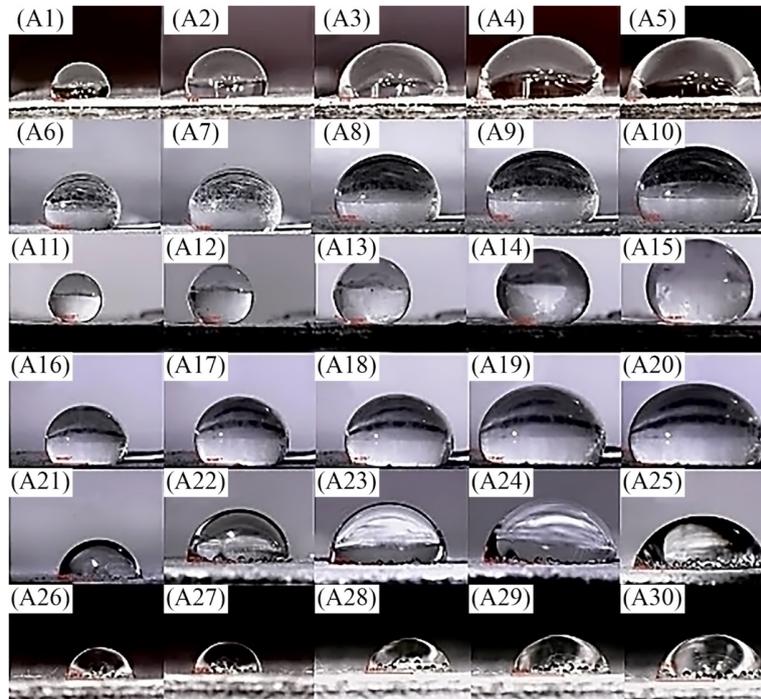


Fig. 6. Droplets on the hybrid layer at the percentage of Mg: 0 % (A1–A5); Mg: 30 % (A6–A10) Mg: 50 % (A11–A15); Mg: 70 % (A16–A20); Mg: 80 % (A21–A25) and Mg: 100 % (A26–A30) in droplet volume (1–5 ml)

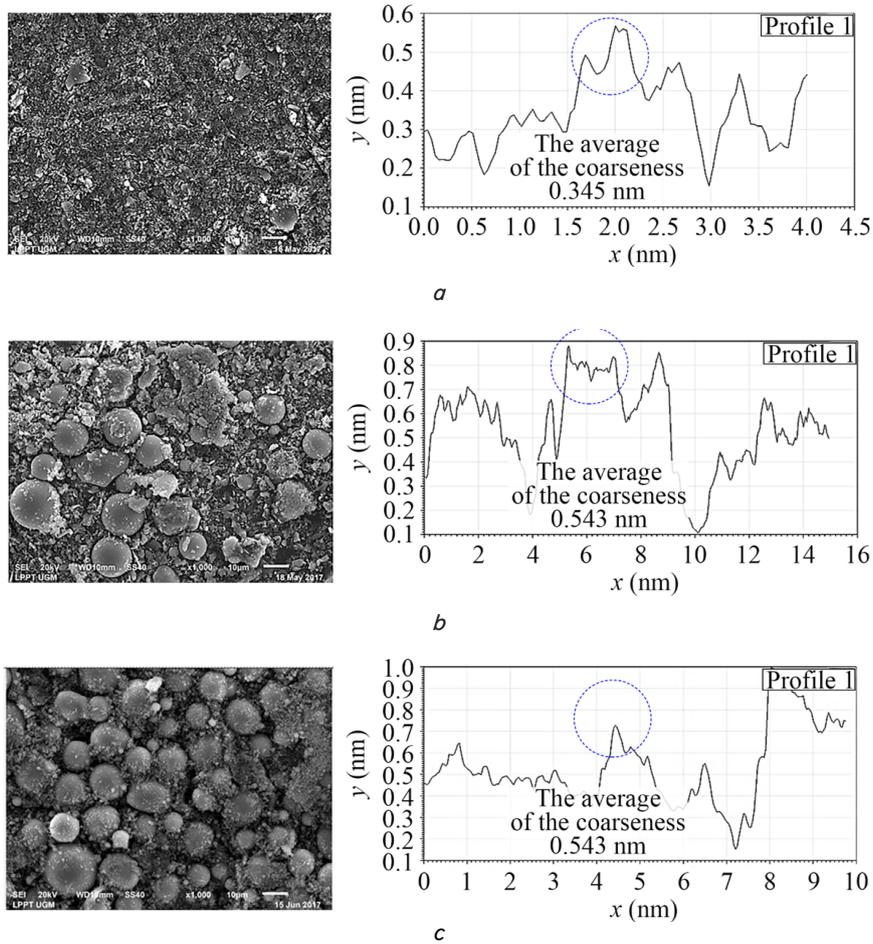


Fig. 7. Surface roughness measurement on: *a* – Alumina Coating (Mg: 0 %, Al₂O₃: 100 %); *b* – Hybrid (Mg: 50 %, Al₂O₃: 50 %); *c* – Magnesium coating (Mg: 100 %, Al₂O₃: 0 %)

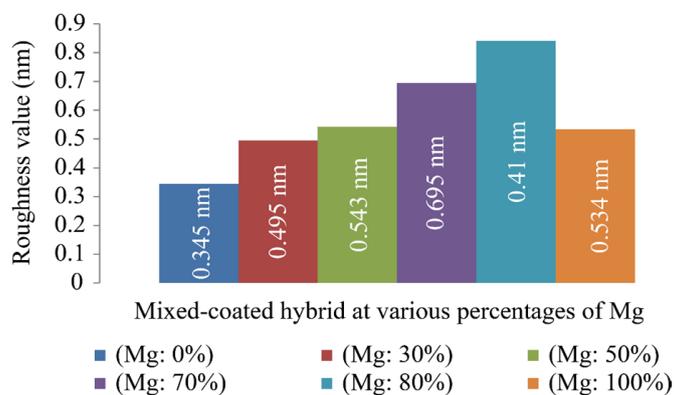


Fig. 8. The surface roughness value of the mixed-coated hybrid at various percentages of Mg

Fig. 8, shows the surface roughness of 5 varying Mg fractions (0–100 %) against the Alumina layer. It appears that increasing the percentage of Mg increases the surface roughness from (6.12–11.29 μm). The hydrophobic nature of a material is largely determined by its surface roughness. The Wenzel model predicts that hydrophobic surfaces ($\theta_0 > 90^\circ$) become more hydrophobic with increasing roughness values, while hydrophilic surfaces ($\theta_0 < 90^\circ$) become more hydrophilic with increasing roughness values. Which means that the hydrophobic properties of a material increase if the roughness value is high. In mixed layer conditions (Mg+Al₂O₃) the role of hydrogen gas bubbles is more dominant than the influence of roughness on the surface in creating hydrophobic properties. This is proven by the fact that the highest contact angle does not occur at the maximum roughness but at the roughness number: 7.60 μm. This shows that the effect of hydrogen bubbles is more dominant than the effect of surface roughness.

5. 2. Effect of Magnesium percentage on contact angle and surface roughness

Fig. 9 shows the relationship between surface roughness and contact angle at various percentages of Mg. It appears that the surface roughness is strongly correlated with the contact angle. It means that the contact angle is determined by the surface roughness. But above 50 % Mg the contact angle actually decreases with increasing surface roughness. This happens because the increase in surface roughness actually increases the surface tension which triggers a very high hydrogen gas formation reaction so that the grooves formed by the roughness are unable to accommodate gas bubbles so that the peaks of the roughness which are the source of surface tension sink and reduce the contact angle formed.

The results of droplet observations when in contact with the Mg layer with a percentage (0–100 %) are shown in Fig. 10. At the percentage of Mg: (0–50 %) no gas bubbles are visible which are formed due to the very small size of the gas bubbles on the nano-scale. In this condition the gas is trapped and the roughness effect has a very good effect on the hydrophobicity that occurs as shown in Fig. 9 where the droplet contact angle continues to increase until it reaches superhydrophobicity. In Mg: (70–100 %) it is clear that bubbles appear on the surface due to the capacity of the grooves not being able to accommodate the gas formed. The formation of bubbles on the surface covers the roughness peaks causing the carrying capacity of the droplets above it to become weaker so that the contact angle decreases until it reaches hydrophilicity.

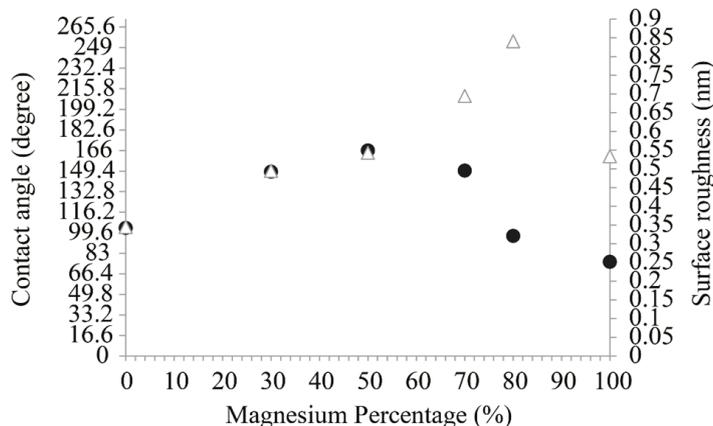


Fig. 9. Effect of Magnesium percentage on contact angle and surface roughness

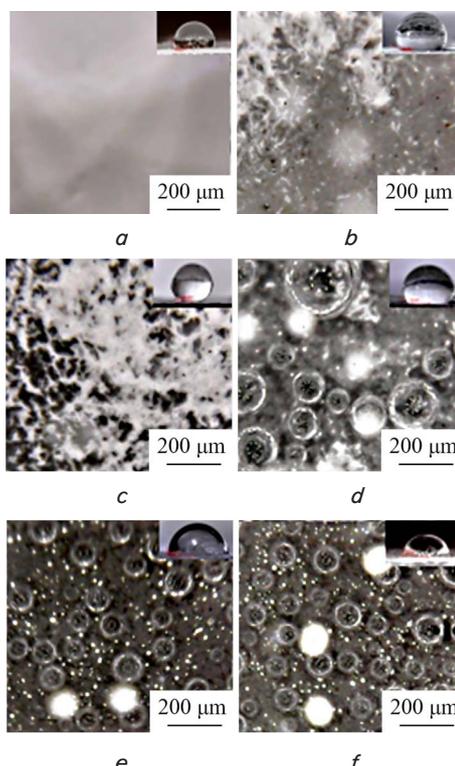


Fig. 10. Coating of nano-particles in contact with H₂O droplets: a – Alumina (Mg:0 %); b – Mixed (Mg:30 %); c – Mixed (Mg: 50 %); d – Mixed (Mg: 70 %); e – Mixed (Mg: 80 %); f – Magnesium (Mg: 100 %)

The hydrophobicity condition of the membrane is determined by the number of bubbles that form on the surface when in contact with the droplet. In mixed conditions between 0–50 % Fig. 10, *a–c*. There are no large bubbles visible, this is very effective in creating hydrophobic properties. This is different in mixed conditions (50–100 %) Fig. 10, *d–f* visible bubbles forming. In this condition, the hydrophobicity condition decreases until it becomes hydrophilic.

5. 3. Mechanism of occurrence of superhydrophobic and hydrophilic properties in membranes

Surface tension causes the surface of the liquid to appear to be covered by an elastic stretch of membrane, so that it is able to withstand the buoyancy of the gas trapped in the Alumina grooves as shown in Fig. 11, *b*. When Alumina comes in contact with droplets (H₂O) in Fig. 11, *a*, with the help of high surface tension, a reaction occurs and produces gas (O₂) which is trapped in the grooves as shown in the blue circle in Fig. 11, *c*. The contact angle of Alumina does not reach superhydrophobicity because the carrying capacity of gas trapped in the grooves is not maximum, as shown in Fig. 11, *d*. This is caused by the capacity of the grooves which are not completely filled with air, causing empty gaps which reduce the carrying capacity of the droplets above them.

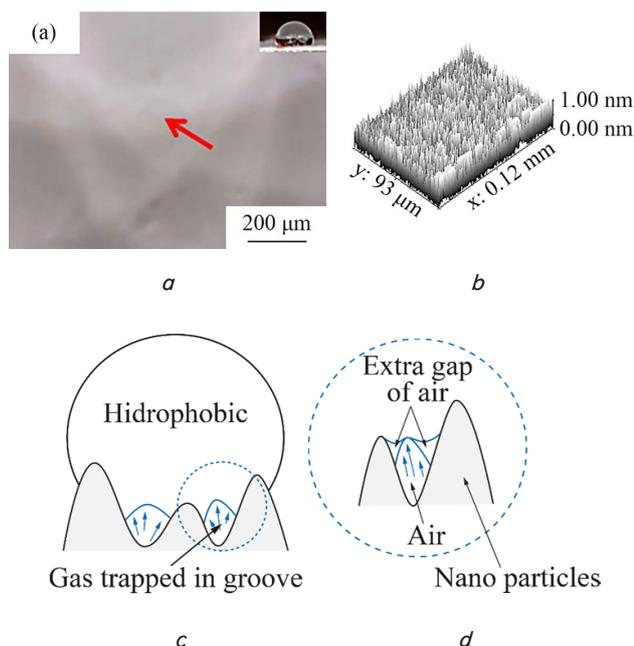
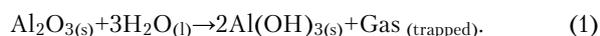


Fig. 11. The process of droplet contact with the membrane surface: *a* – Alumina coating when in contact with H₂O; *b* – 3D analysis of nano Alumina surface; *c, d* – Schematic of trapped air

The reaction that occurs in Alumina follows the following equation:



A different thing happens when additional hydrogen bubbles (hybrid effect) appear as shown in Fig. 12, *a*. When the droplet comes into contact with a rough surface, Fig. 12, *b* creates a very high surface tension that triggers the following reaction:

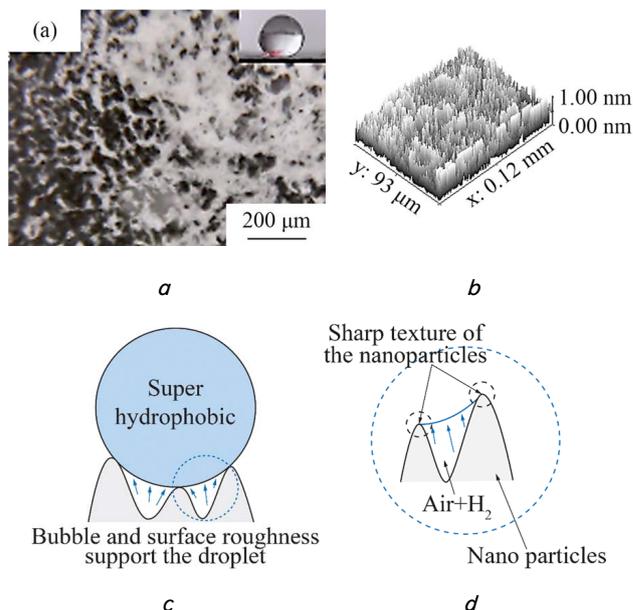
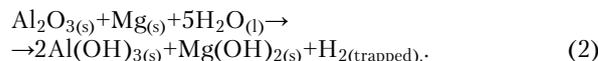
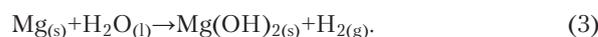


Fig. 12. The process of droplet contact with the membrane surface: *a* – Hybrid layer (Al₂O₃+Mg) when in contact with H₂O; *b* – 3D analysis of hybrid surface (Al₂O₃+Mg); *c, d* – Schematic of trapped air

Hydrogen gas pressure in the grooves continues to increase as the percentage of Mg increases and vice versa for the oxygen gas formed as shown in Fig. 12, *c*. When ideal conditions are achieved as shown in Fig. 12, *d*, all grooves are filled with hybrid gas at optimum conditions so that the spiky texture of the nanoparticles still contributes optimally. This condition is able to create perfect superhydrophobic properties due to the collaboration between the spiky texture of the nanoparticles and the hybrid gas present in the grooves. The very sharp peak point of the nanoparticles creates a very high surface tension effect on the droplet while the trapped gas exerts pressure evenly on the contact droplet surface so that it becomes superhydrophobic. The ideal Hybrid condition is achieved at the percentage of Mg: 50 % as shown in Fig. 5 (point 2). This phenomenon is supported by [25] in his research on the superhydrophobic properties of taro leaves (*Colocasia esculenta*).

The gas bubbles in the grooves continue to increase so that the pressure increases to the droplet surface tension strength limit. When the grooves are no longer able to accommodate gas bubbles, bubbles form outside the grooves with an increasingly large size. The large bubble size causes the surface tension to weaken so that it is easy to join with other bubbles to form a larger diameter as shown in Fig. 13. The bubbles on the surface cover the entire hybrid layer so that the effect is more dominant than the surface roughness effect. When the bubble effect is more dominant, the droplet contact angle decreases and changes the superhydrophobic nature to become hydrophilic.

Hydrogen gas formation increases with increasing percentage of Mg following the following reaction:



The gas formed is accommodated in the grooves in Fig. 14, *b*, when the gas volume continues to increase some of the gas is no longer accommodated as shown in Fig. 14, *c, d* so that bubbles are formed outside the grooves with an ever-increasing diam-

eter. The surface tension of the bubbles decreases with increasing diameter, this causes the droplet contact angle to decrease resulting in a change in properties from superhydrophobic to hydrophobic as shown in Fig. 14, *c, d*.

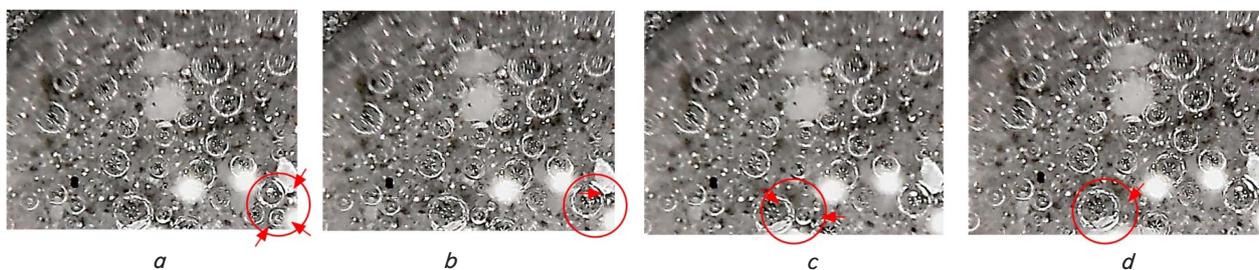


Fig. 13. The process of incorporating gas bubbles at an increasing percentage of Mg: *a, b* – the process of merging 3 bubbles into one; *c, d* – the process of merging two gas bubbles into one

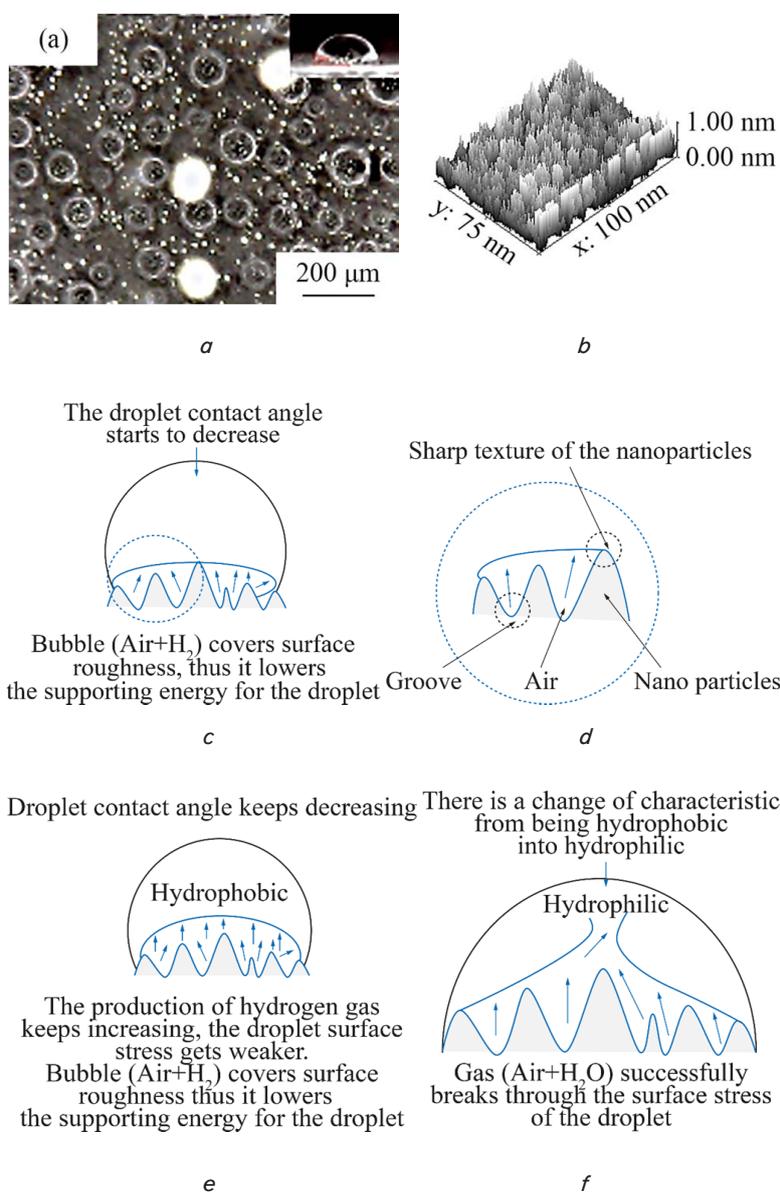


Fig. 14. The process of changing hydrophobic to hydrophilic: *a* – Magnesium coating when in contact with H_2O ; *b* – 3-D analysis of the surface of the Magnesium layer; *c, d* – Initial schematic of the decrease in droplet contact angle; *e, f* – Schematic of the change in hydrophobic to hydrophilic properties

As Mg increases to 100 %, the amount of hydrogen gas that is formed increases as shown in Fig. 14, *e* and the diameter of the bubbles that are formed increases due to the merger between the bubbles as shown in Fig. 13, so that the surface tension weakens. When the bubble surface tension weakens, it affects the contact angle and the droplet surface tension decreases. The stronger pressure of hydrogen gas along with the lower droplet surface tension causes the gas to break through the droplet surface tension and change its hydrophobic nature to become hydrophilic as shown in Fig. 14, *f*.

6. The inner membrane mechanism achieves superhydrophobic properties

Fig. 11 shows the phenomenon of hydrophobic properties that occur in alumina membranes. When alumina comes into contact with droplets (H_2O), with the help of high surface tension, a reaction occurs and produces gas (O_2) which is trapped in the grooves. The contact angle of alumina does not reach superhydrophobicity because the carrying capacity of gas trapped in the grooves is not maximum. This is caused by the capacity of the grooves not being completely filled with air, resulting in empty gaps which reduce the carrying capacity of the droplets above them. This is supported by [23] who has conducted previous research that Alumina has nanobubbles scattered on its surface which supports hydrophobic properties. The hydrophobicity of this membrane cannot be increased because the number of nanobubbles remains constant.

When the droplet contacts a rough surface, a very high surface tension occurs, triggering a reaction in the magnesium nanoparticles (Fig. 12). The pressure of Hydrogen gas in the grooves continues to increase as the percentage of Mg increases and the opposite applies to the Oxygen gas that is formed. When ideal conditions are reached, all grooves are filled with hybrid gas at optimum conditions so that the spiky texture of the nanoparticles still contributes optimally. This condition is able to create perfect superhydrophobic properties due to the collaboration between the spiky texture of the nanoparticles and the hybrid gas in the grooves.

The gas bubbles in the grooves continue to grow so that the pressure increases to the limit of the droplet surface tension strength (Fig. 14). When the grooves are no longer able to accommodate gas bubbles, bubbles form outside the grooves with increasingly larger sizes. The large size of the bubble causes the surface tension to weaken so that it easily combines with other bubbles to form a larger diameter. Bubbles on the surface cover the entire hybrid layer so that the effect is more dominant than the effect of surface roughness. When the bubble effect is more dominant, the droplet contact angle decreases and changes the superhydrophobic nature to hydrophilic.

Fig. 5 shows a comparison of the hydrophobicity of the membrane and *Colocasia esculenta*. These results show that the best superhydrophobic properties occur in the mixed alumina + magnesium membrane. Based on the results of this test, it shows that the new membrane created has the best superhydrophobic properties so it is highly recommended for use in filtration. Research on nanoparticle membranes was carried out to improve previous research [5], where this study was unable to create a superhydrophobic membrane that exceeded the superhydrophobic properties of taro leaves.

The main parameters that characterize the hydrophobic properties of a material are: the results of measuring the contact angle of the droplet when it comes into contact with the leaf surface. The contact angle depends on several factors, namely: surface energy, surface roughness and surface cleaning. If a surface is wetted by a liquid, it is called a hydrophilic surface, the static contact angle value is between $0^\circ \leq 90^\circ$, whereas if the liquid cannot wet the surface, it is called a hydrophobic surface, the contact angle value is from $90^\circ \leq 180^\circ$.

Based on the results of research conducted the surface elements of taro leaves consist of papillose epidermal cells which form papillae or micro-bumps on the surface. As well as an additional layer of three-dimensional epicuticular wax which is a mixture of very long chain fatty acid molecules (compounds with chain atoms >20 carbons) and creates a nanostructure on the entire surface.

Further research was to observe Lotus leaves when they came into contact with water. An interesting thing that was discovered was that there were gas bubbles trapped on the surface of the Lotus leaves. The roughness factor on the surface of superhydrophobic leaves has the effect of gas bubbles being trapped on the surface of the leaf. The presence of gas bubbles trapped on the surface of lotus leaves greatly influences its superhydrophobic properties. The results of this research concluded that the trapped gas was air.

The conducted research and found that the topography and elemental content on the surface of taro leaves greatly influenced its superhydrophobic properties. This is in accordance with the latest research carrying out EDS (Energy Dispersion Spectroscopy) spectrum tests on Lotus leaves and Lotus leaves (bamboo-like surface). The element content test of lotus leaves consists of: Carbon (C), Potassium (K), Oxygen (O) and Calcium (Ca) while lotus leaves (like bamboo surface) consist of the elements: Carbon (C), Oxygen (O). From the test results above, it shows that there are differences in the content of elements on the two leaf surfaces.

From the results of the description of the theoretical framework above, it can be concluded that: there are two things that greatly influence the superhydrophobic properties of lotus leaves, namely: the combination of chemical elements and their physical properties. The effect of this chemical element is caused by a layer of crystalloid wax contained on its surface, making the surface hydrophobic. The contribution of physical properties is derived from the topology of the surface, and when combined with chemical attributes, makes the surface superhydrophobic.

There are two things that really influence superhydrophobic leaves, namely: the combination of chemical elements and physical properties. The influence of chemical elements is caused by a layer of crystalloid wax contained on the surface, making the surface hydrophobic, while the contribution of physical properties is obtained from the surface topography. When both topography and chemical attributes are combined, the surface becomes superhydrophobic.

The main parameters that characterize the hydrophobicity of a material are: the results of measuring the contact angle of the droplet when it comes into contact with the leaf surface. The contact angle depends on several factors namely: surface energy, surface roughness and surface cleaning. The surface energy in superhydrophobic leaves is caused by roughness effects at the nanoscale. When superhydrophobic leaves come into contact with H_2O droplets, they generate very high surface energy, this affects the water molecules on the surface which have very strong intermolecular bonds. In

H₂O molecules there are two bonds that occur, namely the covalent bond that occurs in the Oxygen-Hydrogen (O–H) molecule and the weaker hydrogen bond. These bonds are what support the occurrence of surface tension in the droplets when they come into contact with taro leaves.

The surface tension that occurs in superhydrophobic droplets is equivalent to the surface energy divided by the contact cross-sectional area between the droplet and the surface ($\gamma \approx E/A$). When the cross-sectional area is very small (on the scale of nano particles), the energy becomes infinite. This large energy is transferred to the nanoparticles on the surface of the superhydrophobic leaves so that these particles will vibrate violently and break through the surface tension of the droplets, triggering Brownian motion. Brownian motion is the random movement of particles in a fluid caused by the collision of solid particles with fluid molecules. The smaller the particle, the greater the energy and speed of Brownian motion. The browning motion indicates that a reaction occurs between the particles in contact with the superhydrophobic H₂O droplet.

Evidence of a reaction between the superhydrophobic leaf surface and H₂O droplets is characterized by the appearance of bubbles and trapped gas when the droplets contact the surface of the taro leaves. This statement is supported by research conducted which found that air was trapped on the surface of Lotus leaves. Trapped gas bubbles are the key influencing hydrophobicity a material.

The method used is experimental, the results obtained are able to explain the mechanism of superhydrophobic properties physically and chemically. The previous method based on the superhydrophobicity occurs due to physical properties.

The limitation of this study is that it has not been able to apply it to membrane applications that can be used immediately, it takes time to arrive at the application.

The drawback of this research is that it has not been able to be applied to materials, especially in technology to form surface roughness at the nanoscale and to look for materials that are able to react continuously.

The development of this research is to write in mathematical equations the process of adding hydrogen gas and air which makes the nano surface have superhydrophobic and hydrophilic properties.

7. Conclusions

1. Conditions for optimal superhydrophobic properties occur in the composition of Alumina nanoparticles: 50 % and 50 % Magnesium have the best superhydrophobic properties on membranes.

2. The results of the hydrophobic properties test found three conditions of hydrophobicity of the material, namely: hydrophilic (72–89°), hydrophobic (98–108°) and superhydrophobic (119–144°), this is influenced by the magnesium composition.

3. The hydrophobicity of the material is determined by the gas trapped in the gaps of the nanoparticles where this gas can increase in number due to the reaction between H₂O and magnesium in the membrane

Conflict of interest

That we guarantee that there is no conflict of interest with respect to this research, whether financial, personal, authorship or otherwise, which may affect the research and the results presented in this paper.

Financing

This research was funded by Lambung Mangkurat University through the Compulsory Research Lecturer Program.

Data availability

Data will be made available on reasonable request.

Acknowledgments

The author would like to thank Lambung Mangkurat University for funding this research through DIPA funding from Lambung Mangkurat University for the 2023 Fiscal Year with Number: SP-DIPA – 023.17.2.677518/2023 dated 30 November 2022.

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