

SiO₂-FATTY ACIDS AND TiO₂-FATTY ACIDS WITH THE ROLE OF BASED HYDROPHOBIC COATINGS FOR THE PRESERVATION OF ANDESITE STONE

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Abstract

This study explains the innovation of self-cleaning material and preservation agent for andesite stone by consecutively layering the surface with SiO₂ and fatty acid through dip coating method. SiO₂ and TiO₂ behaved as surface roughness agent, while palmitic acid and stearic acid were functioned to create hydrophobic layer by lowering the surface tension. The performance of the surface was defined as the hydrophobicity indicated by the contact angle formed by the water droplet. The influence of dip coating parameters was investigated including SiO₂ or TiO₂ and stearic acid or palmitic acid concentration, contact time, drying temperature as well as pH of hydrolysis. The highest contact angles were obtained by TiO₂-stearic acid coatings with the water contact angle about 136.6±0.9°. These maximum values were obtained over dip coating condition as follow: TiO₂ 0.04 M, stearic acid 0.16 M, 30 minutes of contact time, 95 °C of drying temperature and acid hydrolysis.

Keywords: Innovation; Andesite stone; SiO₂; TiO₂; Stearic acid; Palmitic acid; Hydrophobicity; Preservation

Introduction

Indonesia has a large number of heritage buildings. One of them is Borobudur Temple, one of the greatest Buddhist monuments in the world. This temple was constructed using andesite stone. Andesite is a type of igneous rock which contains 52-63% of silica. Andesite stone has plain and speckled motif. One of the weathering problems in Borobudur temple is the high humidity which trigger the growth of moss. Interaction between moss and other endolithic microorganisms such as actinomycetes can enhance the rate of biodegradation [1]. The humidity of stone can be decreased through applying hydrophobic coating on the stones.

Hydrophobic self-cleaning technology has been widely applied on material not only to reach the water resistant, but also to remove contaminant on particle surface. High efficiency is the main reason since self-cleaning surface exhibited long durability and lower maintenance cost. Basically, the self-cleaning principal involves the removal of dirt particle without any external interventions. The water droplet easily eliminated the dust material from the self-

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cleaning surface, excluding the application of detergent or other cleansing chemicals. This removal can be carried out through the dust pick up or dirt slide by rolling droplet. Mechanism of self-cleaning is categorized into two types, namely hydrophilic and hydrophobic mechanism. Hydrophilic self-cleaning had been conducted through the photocatalytic technology [2]. However, hydrophilic technology is not suitable to decrease the moisture of surfaces.

Hydrophobicity of a surface is determined by the roughness level and surface tension. Increase in roughness leads to higher hydrophobicity where the water feasibly reeling on. Rough surface can be prepared from metal oxides including SiO_2 , TiO_2 and ZnO . Meanwhile, lower surface tension enhances the hydrophobicity that improves the surface ability to reject water. Some materials are naturally embodied with lower surface tension such as silane, polymers and long chain fatty acid. Untreated polypropylene films showed a WCA of about 110° , hydrophobicity increased at 160° when is modified with TiO_2 [3]. Hydrophobic functionalization also can be performed through perfluoro-silanes [4]. However, perfluorinated chemicals bad issue on the health and environmental since they are stable, do not biodegradable, and toxic [5].

Previous studies reported that superhydrophobic marble stone had resulted by growing self-assembled polydopamine (PDA) as the adhesive layer on the stone surface, followed by depositing Al_2O_3 nanoparticles derivatized by self-assembled monolayers of a fluorophosphonic acid (FPA) on the natural marble produced [6]. Combination of TiO_2 and commercial polymer have been tested as self-cleaning protective agent on the stone surface in temple [7]. This coating successfully prevents dirt accumulation on the surfaces.

High hydrophobicity and high permeability of water vapour are the most important requirements of a protective film. In fact, many coated stone give high water contact angle but low permeability of water [8]. The limited breathability could be negative impact of coatings because it was thick and closed the pore of stones. Stones with low breathability are difficult to evaporate so that the moisture is trapped. This condition causes serious problems like salt crystallization and growth of moss which would accelerate the loss of solidity or cracking the stones. Applying thin hydrophobic coating and controlling the hydrophobicity to prevent the diffusion of water can solve this problem.

Nowadays, fatty acids have been demonstrated as hydrophobic self-cleaning. Fatty acids are promising candidate as a coating agent [9,10]. They are also known as natural antifungal, which is makes them suitable for functional coatings [11]. The antifungal properties have synergistic effect with hydrophobicity. However, applying fatty acids as a single component did not expose hydrophobic properties [12]. Modification fatty acids with SiO_2 particles with long carbon chain fatty acids produced superhydrophobic coatings [9]. As it is known, particle of silica increased the roughness of surfaces [13]. Many efforts have been developed to increase the surface roughness, such as self-assembled fatty acid crystalline coatings.

This study aims to combine fatty acids and metal oxide (SiO_2 and TiO_2) to modify hydrophilic andesite stone towards hydrophobic material. This research hopes to solve the preservation self-cleaning application through dip coating method. Fatty acid was applied as coating material. Amorphous SiO_2 would be applied to enhance the hydrophobicity of andesite surface owing to its roughness. In addition, long aliphatic chain of stearic acid and palmitic acid will be used because possessed low water solubility and surface tension. Furthermore, this study includes the investigation on the influence of several parameters of dip coating process such as concentration of coating solution, deposition time, drying temperature and solution acidity. The sample with maximum contact angle attained from the optimum parameters were characterized by FTIR and SEM techniques.

Experimental part

Materials

Andesite stone was acquired locally. Tetraethyl orthosilicate (99%), titanium tetra isopropoxide (98%), ammonia (32%), acetic acid (100%) and ethanol (99%) were purchased from Merck KGaA, Darmstadt, Germany. Palmitic acid (97%) was attained from Tokyo Chemical Industry and stearic acid (99%) was obtained from Fujifilm Wako Pure Chemical Corporation.

Methods

Preparation of SiO₂ and TiO₂ solution

In terms of 0.09 M SiO₂ solution, 6.95 mL of ethanol was mixed with 0.05 mL TEOS as SiO₂ source under stirring condition. Acetic acid was then added until the acidity of the mixture reached the value of pH = 2. The SiO₂ in the form of solution was achieved after three hours. This procedure was repeated with various proportions of the precursors to synthesize the SiO₂ solution with concentration of 0.02, 0.04, 0.45, 0.90 and 1.80M.

The 0.02M TiO₂ sol was prepared from titanium tetra isopropoxide, ethanol and glacial acetic acid. A total of 0.05 mL of titanium tetra isopropoxide was added glacial acetic acid dropwise as much as three mL (pH = 2) then was added ethanol until the volume becomes 10 mL. The mixture was stirred for three hours. The similar procedure was also conducted to prepare TiO₂ with various of concentration of 0.04, 0.06, 0.14, 0.28, 0.34 and 0.68M.

Preparation of fatty acids

To obtain 0.035M stearic solution, 100mg of stearic acid was diluted into 10 mL ethanol and stirred for 30 min. Following the same procedure, the amount of stearic acid was altered to prepare stearic solution with concentration of 0.0175, 0.070, 0.140 and 0.210M. The same method was applied for palmitic acid with varied concentrations of 0.02, 0.04, 0.08, 0.16 and 0.23M.

Dip coating process

Prior to coating process, the andesite stone (dimension: 1.0 × 2.0 × 1.0cm) was sonicated in methanol for three hours. The coating process was carried out by layering andesite stone with SiO₂ and fatty acid consecutively. Andesite stone was dipped into SiO₂ solution for desired amount of time, followed by drying at room temperature for 15 minutes and at 90°C for 30 minutes.

This step was reproduced for the second layer using fatty acid solution. The influence of dipping time, SiO₂ concentration, fatty acids concentration, deposition time and drying temperature were thoroughly investigated and reported in the following chapter. The acidity of the dip coating solution was investigated by changing the pH to the value of 2 and 10.

Characterisation

FTIR was applied to investigate the functional group of SiO₂ and fatty acid which the sample was prepared in KBr pellet method. The morphology of SiO₂-fatty acid coated andesite surface was studied by Scanning Electron Microscopic (SEM) technique. The sample was positioned on carbon tape and treated with gold/paladium (60:40) sputtering. The contact angle formed by the water droplet on coated andesite surface was measured using image J software.

Stability test

The stability of SiO₂-fatty acid coating on the andesite surface was carried out by open-air exposure for one month. The influence of the ambient air was checked by measuring the contact angle every week. This method was adopted from the previous research [14] This test was adapted to determine the weather durability of the coatings.

Results and discussion

Characteristic of SiO₂-fatty acid coated andesite

SiO₂-fatty acid coated andesite have been characterized using FTIR to investigate the functional group and potential bonding formation between SiO₂ and fatty acid. Figure 1 elaborates the FTIR spectra of SiO₂, fatty acid, SiO₂-fatty acids and TiO₂-fatty acids. Two kinds of fatty acids, namely stearic acid and palmitic acid have been used as coating agents. The presence of SiO₂ was confirmed by several functional group features including Si-O at 798.53cm⁻¹, Si-O-Si at 1629.85cm⁻¹ and Si-OH at 1629.85cm⁻¹. Various features represented the functional groups of fatty acid. A peak at 2916.3 cm⁻¹ was related to the symmetrical vibration of aliphatic group and 2848.86cm⁻¹ was the asymmetric one. A peak 1701.22cm⁻¹ was assigned to the carbonyl group. The characteristics of palmitic acid can also be demonstrated by absorption at a wavelength of 1471cm⁻¹ which indicated the presence of a COO- bond. At wavelength 1294cm⁻¹ indicated the presence of -CH₂ bending bonds [15].

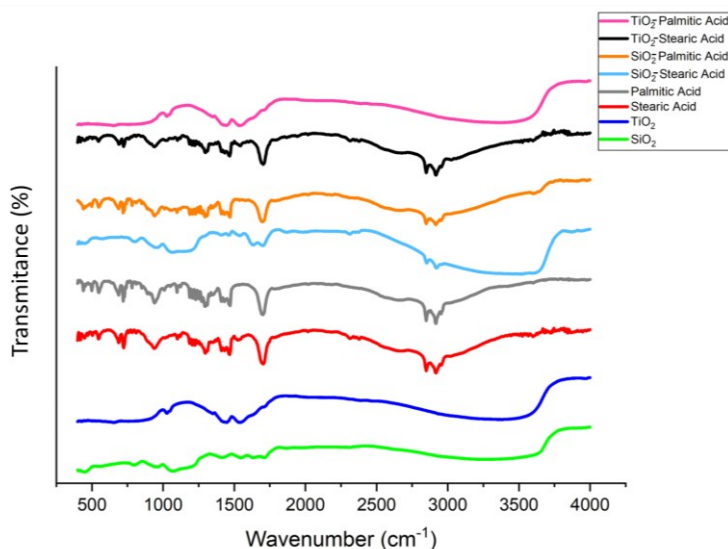


Fig. 1. FTIR spectra of SiO₂, fatty acid, SiO₂-fatty acids and TiO₂-fatty acids

In the case of SiO₂-palmitic acid, the Si-O-Si feature was shifted from 1074.42 to 1097.50cm⁻¹ as a result of hydrogen bonding. It is commonly known that hydrogen bonding was responsible for peak shift or broadening [16]. On the other hand, the existence of peak shift was not observed in SiO₂-stearic acid indicating the absence of hydrogen bonding between SiO₂ and stearic acid. Presumably, the interaction of SiO₂ and stearic acid was the weaker dipole bonding. This weak bond influenced the stability of SiO₂ and stearic acid layering. Subsequently, the SiO₂-stearic acid produced an inferior outcome compared to SiO₂-palmitic acid.

The absorption bands of TiO₂-palmitic acid and TiO₂-stearic acid existed at a wavelength of 653cm⁻¹ indicated the presence of Ti-O-Ti bonds. The peak was found at wavelength 1348cm⁻¹ which showed the Ti-OH bonds. The absorption band of Ti-O-Ti shifts from 653cm⁻¹ to 688cm⁻¹ due to the presence of hydrogen bonds between TiO₂ and fatty acids.

The morphology of andesite surface was studied by SEM as illustrated in figure 2. The uncoated andesite surface was smooth as the water droplet enabled it to cover thoroughly. The SiO₂-fatty acid coating caused the andesite morphology to become rough with the present of

some agglomeration dispersed on the surface. As presented in the following points of this paper, the rough hydrophobic surface was confirmed by the greater contact angle formed between the droplet and the surface.

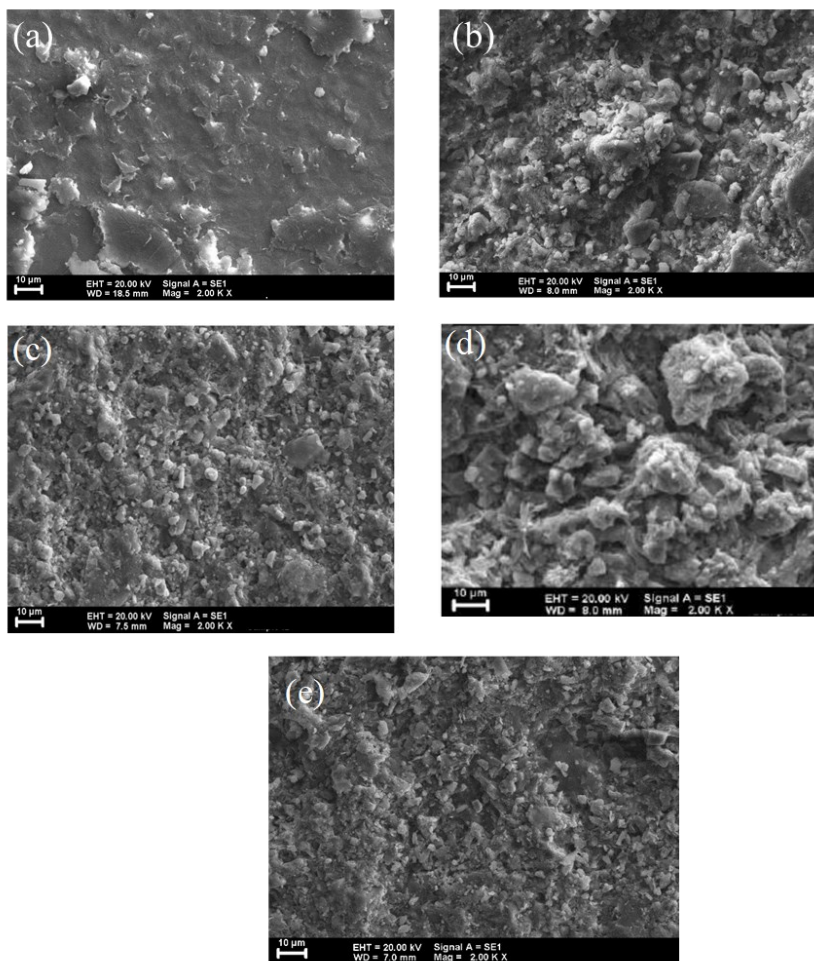


Fig. 2. Morphology of: (a) uncoated andesite stone surface, (b) SiO₂-palmitic acid coated andesite, (c) SiO₂-stearic acid coated andesite, (d) TiO₂-stearic acid coated andesite, (e) TiO₂-palmitic acid coated andesite

The influence of SiO₂ and TiO₂ concentration

The effect of SiO₂ and TiO₂ concentration on the contact angle is shown in figure 3. Both SiO₂-palmitic acid and TiO₂-palmitic acid have similar trends of water contact angle during the increase of SiO₂ and TiO₂ concentration. The increase of SiO₂ concentration up to 0.45M, enlarged the contact angle of liquid on the surface of SiO₂-palmitic acid coated andesite and TiO₂-palmitic acid coated andesite stone to the maximum value of 116.49±1.4° and 129.6±3.2°, respectively. SiO₂-stearic acid and TiO₂-stearic acid coated andesite stone also exposed higher water contact angle in the concentration of metal oxide about 0,04M. The water contact angle of SiO₂-stearic acid and TiO₂-stearic acid coated andesite were 124.2±2.5° and 128.4±1.4°, respectively. The increasing of hydrophobicity was due to the increasing of surface roughness of coated stone. Deposition of metal oxide on the stone surfaces produced agglomeration particle on the surfaces as shown by the image of SEM at figure 2. As a comparison, the water

contact angle of uncoated andesite stone, SiO₂ coated andesite stone, TiO₂ coated andesite stone, palmitic acid coated andesite stone and stearic acid coated andesite stone were found at 66.95±0.5, 87.57±0.38°, respectively. This data showed that the addition of metal oxide, SiO₂ or TiO₂ to the fatty acids is able to improve the hydrophobicity water contact angle of andesite stone.

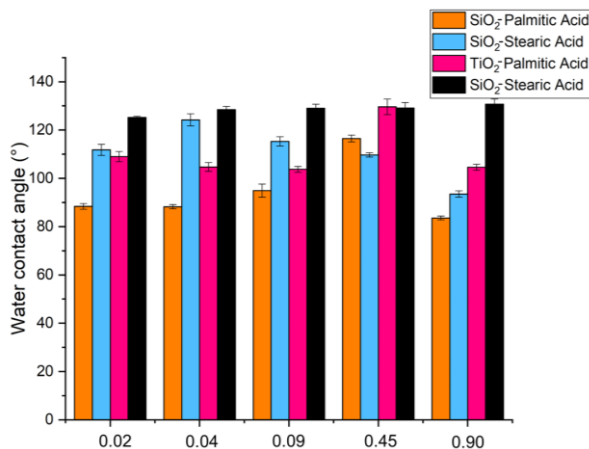


Fig. 3. The effect of SiO₂ and TiO₂ concentration on the contact angle of droplet on the SiO₂ or TiO₂-fatty acid coated andesite

Meanwhile, higher SiO₂ concentration caused a continuous decline of contact angle for all samples. In terms of SiO₂-palmitic acid coated andesite and TiO₂-palmitic acid coated andesite, the addition of SiO₂ concentration of about 0.9M only caused a negligible increase to the contact angle. It also happened at SiO₂-stearic acid coated stone coated in the concentration of SiO₂ from 0.09 to 0.04M, the contact angle was dropped to 93.5±1.3°. The constant value of water contact angle about 128-130° was shown in TiO₂-stearic acid with concentration of TiO₂ about 0.04-0.9M. The addition of SiO₂ increased the hydrophobicity of the surface owing to its roughness effect. However, this effect remained at certain point due to the formation of hydrophilic hydroxyl group (Si-OH). Subsequently, water droplets would be easily dispersed on the surface of the andesite. Therefore, the maximum SiO₂ concentration was 0.45M for SiO₂-palmitic acid and TiO₂-palmitic acid and 0.04M for SiO₂-stearic acid and TiO₂-stearic acid, respectively.

The influence of fatty acid concentration.

The fatty acid concentration was varied to investigate the influence hydrophobicity on the contact angle, as it shown in figure 4. These experiments were conducted using optimum concentration of SiO₂ or TiO₂ in each of samples. The palmitic acid concentration of 0.04M produced the largest contact angle for SiO₂-palmitic acid, SiO₂-stearic acid and TiO₂-palmitic acid, while the TiO₂-stearic acid produced largest water contact angle at 0.16M of TiO₂ concentration. Fatty acid possessed nonpolar characteristics due to the long chain aliphatic hydrocarbon which decreased the surface tension. It was expected that the higher fatty acid concentration would raise the hydrophobicity properties which leading to the higher roughness of the andesite surface as well as larger contact angle. However, there was a certain limit of the concentration of fatty acid to reach the optimum water contact angle. At higher concentration, fatty acid as second layer of coating covered the layer of SiO₂ or TiO₂, therefore the surface roughness was decreased and presented a low contact angle [8].

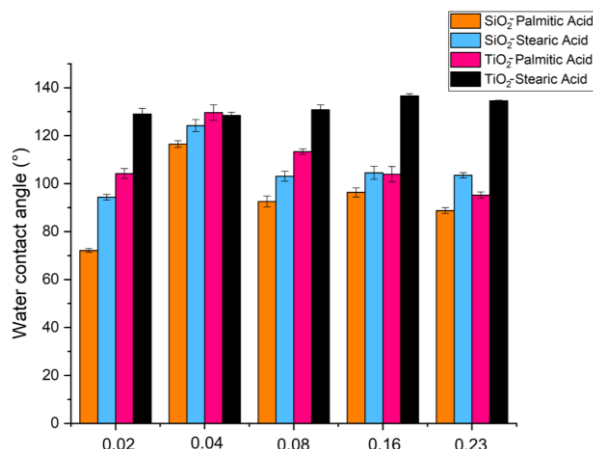


Fig. 4. The effect of fatty acid concentration on the water contact angle on the SiO₂ or TiO₂-fatty acid coated andesite

The influence of deposition time

Figure 5 illustrates the water contact angle as a function of metal oxide and fatty acid deposition time. Overall, the varied SiO₂ and TiO₂ deposition time generated the same trend of contact angle for all of samples. The contact angle continuously rose as the deposition was prolonged from 5 to 30 minutes. This point was the maximum SiO₂ or TiO₂ deposition time with the highest contact angles of 116.5±1.4, 124.2±2.5, 129.6±3.2 and 136.6±0.9° for SiO₂-palmitic acid, SiO₂-stearic acid, TiO₂-palmitic acid and TiO₂-stearic acid, respectively, as depicted in figure 5a. The trend of contact angle over different fatty acid deposition time is also revealed in figure 5b. The influence of fatty acid deposition time on the contact angle was comparable to the SiO₂ and TiO₂. Both fatty acids resulted the optimum contact angles after 30 minutes of deposition, the andesite surfaces were well coated by fatty acid.

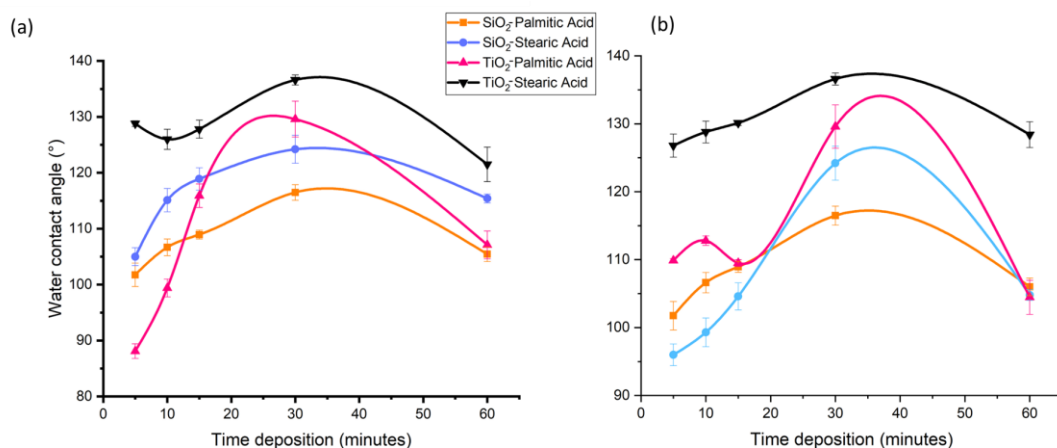


Fig. 5. The water contact angle as the function of (a) SiO₂ or TiO₂ and (b) fatty acids deposition time

Extended deposition time allowed high adsorption on the surface of stones until the optimum adsorption capacity was fulfilled. Above the optimum time, the adsorption was no

longer proceeded while desorption began to take place, implicated the contact angle to become smaller.

The influence of drying temperature

Drying temperature affected the properties of the coated andesite surface as well as the hydrophobicity (Fig. 6). In terms of SiO₂-palmitic acid, the contact angle of 101.7±0.8° was generated from drying temperature at 70°C. This contact angle inclined to 116.5±1.4° when the layers were heated up to 90°C and lessened significantly to 108.9±1.2° as the drying process was conducted at 105°C. In addition, SiO₂-stearic acid, TiO₂-palmitic acid and TiO₂-stearic acid also performed a similar trend.

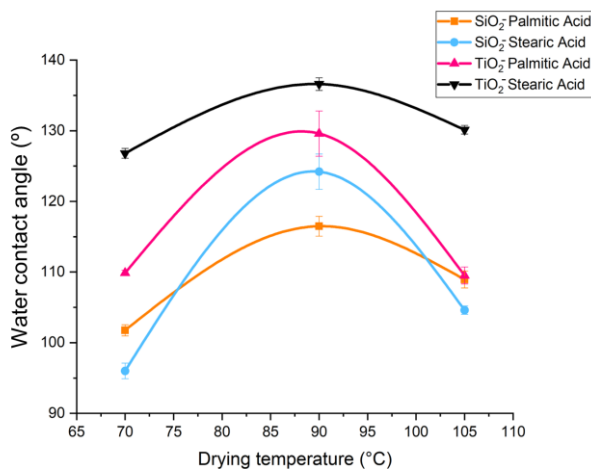


Fig. 6. The contact angle generated from coated andesite stone over various drying temperatures

At 70°C, ethanol was not completely removed from the coated andesite since ethanol boiling point was above the drying temperature (78.3°C). The remaining ethanol-initiated hydrolysis and condensation occurred. This process created hydrophilic hydroxyl group that depleted the contact angle value. The complete removal of ethanol occurred when the drying temperature were incremented at 90°C. Subsequently, the contact angle reached maximum at this point. In addition, the layers cracked and were feasibly released from the andesite surface when the drying temperature was higher than 90°C.

The influence of hydrolysis pH

The influence of hydrolysis condition of SiO₂ and TiO₂ were addressed by the addition of acetic acid until pH = 2 and sodium hydroxide for pH 10 during hydrolysis reaction of SiO₂ and TiO₂. The influence of acidity/basicity on the contact angle was described in figure 7. As the pH was changed to pH = 2, resulted a contact angle of 136.6±0.9° on the surface of TiO₂-stearic acid coated andesite. In contrast, basic solution (pH = 10) reduced the contact angle to 111.4±2.0°. Similar trends occurred over SiO₂-stearic acid, SiO₂-palmitic acid and TiO₂-palmitic acid coating with slightly lower value.

The base catalyst promotes condensation reactions while keeping the hydrolysis reaction under control. Base catalyst produced larger particles than acid catalyst of hydrolysis, however the larger particle size tends to have low surface roughness and low hydrophobicity [17]. This information correlate with the data which basic hydrolysis of SiO₂ or TiO₂ modified with

hydrophobic agent produced lower contact angle. Therefore, acidic hydrolysis was beneficial for the hydrophobicity of the surface.

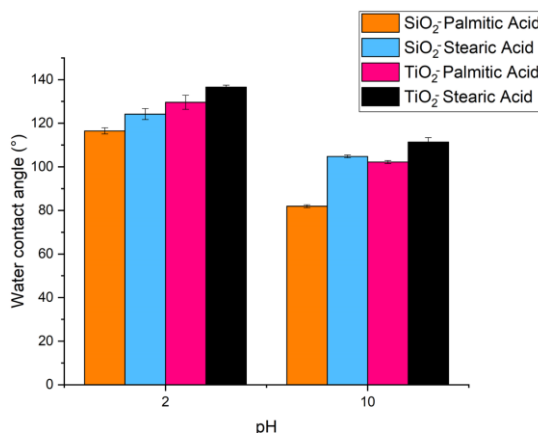


Fig. 7. Effect of hydrolysis pH of SiO₂ and TiO₂ on the contact angle of SiO₂-fatty acids and TiO₂ fatty acids coated andesite stones

Comparison performance of SiO₂ and TiO₂ in same condition showed that TiO₂ produced higher hydrophobicity than SiO₂. Previous research stated that TiO₂ resulted in lower particle size than SiO₂ under similar conditions [18]. The agglomeration of small particles could produce hierarchical morphology and lead to high surface roughness. These properties synergistically combined with low surface tension of hydrophobic agents and presented the high hydrophobicity.

The stability test of coated stones

The data of coating stability was obtained through the water contact angle measurement of coated andesite samples after were placed under the ambient air for one month. Figure 8 elaborates the stability of all of samples which was determined by the change of water contact angle.

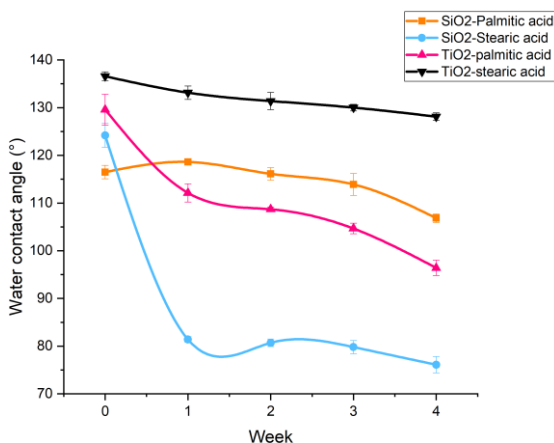


Fig. 8. The stability test of metal oxide-fatty acid coated andesite stone

The TiO₂-stearic acid coating showed excellent stability with a small reduction of contact angle for four weeks under outdoor exposure, with a relative humidity of between 38 and 76% and a temperature of between 23 and 35 °C. The decline of contact angle was the consequence of decreased hydrophobicity due to the reaction between SiO₂ or TiO₂ with the air to form Si-OH or Ti-OH. This phenomenon was also affirmed by other studies [17, 19].

Overall, the performance of TiO₂-stearic acid is better than others. Figure 9 shows the water droplet on coated andesite stone.

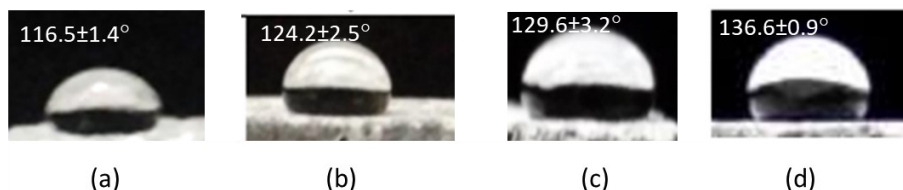


Fig. 9. The water droplet on (a) SiO₂-palmitic acid, (b) SiO₂-stearic acid, (c) TiO₂-palmitic acid, and (d) TiO₂-stearic acid coated andesite stone

As the previous explanation, TiO₂ tends to produce higher surface roughness than SiO₂. Meanwhile, stearic acid with long chain alkyl-C18 presented higher non-polar properties than palmitic acid (C-16 of chain alkyl). It can be concluded that TiO₂-stearic acid was the best coating solution for andesite stone than SiO₂-palmitic acid, SiO₂-stearic acid and TiO₂-palmitic acid. It produced water contact angle of coated andesite stone about 136.6±0.9°. The TiO₂-stearic acid coated andesite stones were predicted could reduce the moisture of stones; therefore, it could be minimizing the growth of moss. Because the hydrophobicity was not reached super hydrophobicity, the coating was also predicted to still have good breathability of stones, so that the crack of stones and salt crystallization could be avoided.

Conclusions

Self-cleaning material of SiO₂-fatty acid and TiO₂-fatty acid coated andesite was successfully prepared by dip coating method on layering SiO₂ or TiO₂ as surface roughness agent and the hydrophobic stearic acid/palmitic acid alternatively. TiO₂-stearic acid andesite stone exposed high water contact angle about 136.6±0.9° and good stability of coating. The formulation of TiO₂-stearic acid as coating solution potentially to be applied as preservation agent on andesite stone. The issue of weathering on the stone is predicted can be avoided using this coating. The coated stone had high hydrophobicity but did not reach the superhydrophobicity categories. Therefore, the problem of low breathability in the coating stones could be overcome.

Acknowledgments

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