Utilization of bamboo leaf silica as a superhydrophobic coating using trimethylchlorosilane as a surface modification agent

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Abstract. In recent years, there has been an increasing research interest regarding the development of superhydrophobic coating for various purposes with tetraethyl orthosilicate (TEOS) as the source of silica. Unfortunately, TEOS is hazardous as an alkoxide and need long step as well as time consuming to synthesize it. Typically, previous researches using fluoroalkylsilane (FOK) as the surface modification agent is containing fluoro compound which is not safety to use. This paper is aimed to develop a cost-effective and environmental-friendly superhydrophobic coating by utilizing bamboo leaf silica. This work was particularly conducted to develop the method of purification of bamboo leaf ash as the source of silica to produce superhydrophobic coating material. This method could be an effective and efficient way of preparing a superhydrophobic coating using silica bamboo leaf with eco-friendly solvent exchange agents. This observation used n-hexane, cyclohexane, isoctane as a solvent exchange, and trimethylchlorosilane (TMCS) as a surface modification agent which is not containing fluoro component. The initial bamboo leaf silica and purified silica were examined using XRD, BET, XRF, and SEM EDX Mapping to obtain essential information such as structure, porosity, purity, and surface topography. Also, the coated zinc plat with different solvents was assessed hydrophobicity by contact angle measurement and surface morphology by SEM. The efficient and effective formulation of the superhydrophobic coating was attained by applying n-hexane solvent, 13 %-v/v TMCS, 1.75 %-w/v of bamboo leaf silica was the highest of contact angle.

1. Introduction
Materials are susceptible to various types of corrosion and/or degradation, especially in most tropical countries. Degradation can proceed by distinguished as physical, chemical, and biological. Water plays a central role in many of those processes of degradation [1]. Since material durability is considered a vital concern in modern society, corrosion protection has been denoted as a general topic with tremendous aspects. Not only to assure for constructions and vehicles safety but also to approach the commercial aspect of industrial [2]. One attempt to protect materials from corrosion is efficiently carried out by using a chromium-containing coating. Meanwhile, this coating does not have a benign environmentally. Therefore, many utilizations of this coating were banned due to the toxicity of chromium (IV) ions [3].
Environmental-friendly corrosion protective coatings have been developing over the past few years. Coating industries have been introducing outstanding water repellency properties with oxide/polymer-based superhydrophobic coatings [4]. Silica or silicon dioxide (SiO\textsubscript{2}) denotes a potential approach to developing superhydrophobic coating due to magnificent intrinsic properties such as harmless, good stability in thermal and mechanical [5]. Although silica is naturally hydrophilic, by subjecting silica to a silane substance, the particles would be functionalized, and they wouldn’t be wetted by water [4]. This property helps the material to be able to have self-cleaning property by letting water and contaminants slide through its surface.

Previous researches regarding the synthesis of superhydrophobic coating have been studied with various silica resources, such as tetraethyl orthosilicate (TEOS) [6], organically modified silica aerogel [7]. However, nanostructures preparation requires more effort, especially in the economic path of the production cost of hydrophobic materials [4]. Other researches about superhydrophobic coating were carried out using geothermal solid waste as the raw material. Unfortunately, heavy metal contents such as Zr, Pb, and Cr reach up to 1% and may defect the product's superhydrophobic property [5]. A relatively cost-effective and environmental-friendly silica synthesis was studied using bamboo through pyrolysis [8], followed by a sol-gel method [9]. As fast-growing grass and native plant in Asia, bamboo denotes the potential as a natural silica source since bamboo leaf consists mostly of silica, about 17 – 23% by weight. It means silica in bamboo leaf consists of higher content than in other natural sources such as rice husk with 9.3 – 13.5 %-w [9]. This silica may be utilized as a water glass (Na\textsubscript{2}SiO\textsubscript{3}), an intermediate product widely used in industries [10], and silicic acid (Si(OH)\textsubscript{4}) as the precursor for the preparation of superhydrophobic silica coating [11]. Another factor contributing to the formation of superhydrophobic property is the surface modification agent. Previous research used fluoroalkylsilane (FOK) with TEOS as a silica source, resulting in a contact angle of 152° [6]. However, there is a health risk from utilizing the fluorocarbon compound due to its toxicity. Another method of preparing superhydrophobic coating has been investigated using TEOS and non-fluorocarbon compounds as the surface modification agent, such as trimethylchlorosilane (TMCS) resulted in a contact angle of 110° [4]. TMCS causes this lower contact angle to not react significantly with TEOS because of the difference in the solvent's polarity. Polar solvent might decrease the superhydrophobic property of coatings [5].

Nevertheless, all the mentioned methods require more than one step process during superhydrophobic surface preparation experiments. Other research utilizes methyltrimethoxysilane (MTMS) based silica sol on different substrates using polymethylmethacrylate (PMMA) as a surface modifier to increase its superhydrophobicity resulting in a contact angle of 153° by a dip-coating method to apply the superhydrophobic solution to the material [6]. Therefore, this method requires such expensive equipment, reducing their applicability while showing low resistance when exposed to the environment. Thus, in this paper, a new and simplified technique to create superhydrophobic coating is presented.

Observation dealing with the application of bamboo leaf silica as a superhydrophobic coating was minimal. Therefore, the bamboo leaf silica was chosen as the raw material for a superhydrophobic coating to reinforce material durability. This paper investigates appropriate nonpolar solvent types such as n-hexane, cyclohexane, and isooctane. The appropriate solvents acted as solvent exchangers when introduced with the surface modifier, i.e., trimethylchlorosilane (TMCS), creating a solution. This solution was then mixed with the treated bamboo leaf silica to form a coating solution with the highest superhydrophobic property in response to the contact angle. This study also applied a simple method to formulate superhydrophobic coatings-based bamboo leaf silica considering only using a solvent exchange. In this paper, the surface modification agent's alkyl groups were used to modify silica particles as a coating. Then the coating was applied onto a zinc plate by using a simple and time-efficient spray coating method.
2. Materials and methods

2.1. Materials
Bamboo leaf used in this study was procured from local sources of Central Java, Indonesia. The chemicals such as hydrochloric acid (HCl, 37%, p.a.), sodium hydroxide (NaOH, 99%, p.a.), trimethylchlorosilane (TMCS, 99%, p.a.), and Whatman™ Grade 41 filter paper are provided from Merck, Germany. The zinc plates were procured from the miscellaneous metal store in Semarang, Indonesia.

2.2. Bamboo leaf silica preparation and purification
Bamboo leaf used in this study was procured from local sources of Central Java, Indonesia. The silica extraction method from a bamboo leaf in this paper followed previous research [9,10]. Bamboo leaf was grounded and immersed in 1 M hydrochloric acid (HCl, 37%, Merck) for two hours to release impurities. After following washing and drying, the leaves were put in the muffle furnace to remove its organic compound by calcination at 650 °C for two hours. Bamboo Leaf Ash (BLA) was obtained as the result of the furnace process. The BLA was continued to remove the inorganic impurity by acid leaching method using 1 N hydrochloric acids with constant stirring at 500 rpm at 70 °C for three hours. The slurry was then washed with demineralized water until the neutral condition (pH = 7) was achieved. After that, the slurry was filtered using a vacuum pump, and the cake was dried in an oven at a temperature of 110 °C. The dried silica was carried out to form sodium silicate by using 2 M sodium hydroxide (NaOH, 99%, Merck). Extraction of silica was conducted by a sol-gel method to remove its inorganic impurities besides silica itself further. BLA was immersed in 2 M sodium hydroxide (NaOH, 99%, Merck), under constant stirring and temperature of 120 °C for an hour. The solution was filtered through Whatman™ Grade 41 paper. Afterward, the solution was kept and carried out at room temperature. The solution was added 1 N HCl with constant stirring to form a gel. The formed gels were aged for 18 hours, and then, the gels were contacted with 100 ml demineralized water and centrifuged at 3000 rpm to produce a slurry. Afterward, it was introduced by filtration and washing. White powder silica as the coating material raw can be obtained after drying filtration cake at 80 °C for 12 hours.

2.3. Superhydrophobic solutions preparation
The dried product was then ball-milled using a milling instrument for 30 minutes, i.e., High Energy Milling (HEM) Ellipse 3D. The silica in different ratios and surface modification agent trimethylchlorosilane (TMCS) of 13 %-v/v concentration were homogenized by Ultrasonic Processor (FS-250N) for 15 minutes before mixed in 13 %-v/v various solvents of n-hexane, cyclohexane, or isooctane. The coating method referred to previous research [5]. The solution of the superhydrophobic coating was stirred for two hours under heating at 50 °C. The solution was applied by spraying to sample with 40 x 40 x 0.15 mm dimension to the zinc plate. The spraying to the surface of materials was conducted at room temperature and left for 15 minutes in ambient condition. Then, the coated material was cured in an oven under 150 °C for 3 hours.

2.4. Characterizations
The silica was analyzed for its structure, porosity, purity, and surface topography by X-Ray Diffraction (XRD, Pan Analytical Type ExpertPro), Brunauer–Emmett–Teller (BET, Nova 4200e), X-Ray Fluorescence (XRF PANalytical, Minipad 4), and Scanning Electron Microscopy (SEM, FEI Inspect S50 EDAX AMETEX with a voltage of 20kV), respectively. Finally, the coated material was analyzed in terms of contact angle (Contact Angle Meter by Laplace-Young fitting mode), the surface morphology by using SEM, and the functional groups by using FTIR (Shimadzu IRPrestige21). Contact angle measurement was conducted in Center for Isotope and Radiation Application, National Nuclear Energy Agency of Indonesia (BATAN) using Contact Angle Meter equipment (FACE 90-2-1) with repeating the measurement to different points of one sample, three measurements of sample's left side.
and three measurements of sample's right side. The result of the contact angle was denoted as the average measurements.

3. Results and discussion

3.1. Characterization of bamboo leaf silica
Bamboo leaf ash generally consists mainly of silica, while the rest are impurities substances that still take a role in influencing silica's property. Therefore, these impurities must be removed from silica in order to increase its hydrophobic characteristic. Purification sequences were started from furnace combustion, acid leaching, followed by the sol-gel method. These steps were aimed to eliminate inorganic impurities, thus, to increase the concentration of silica and to inhibit the formation of structured silica [13]. In this study, the weight reduction of a bamboo leaf after the leaching process was revealed up to 79.03 %-w from the initial weight, regarding the removal of metal oxide impurities dissolved in acid solution.

![Figure 1. Bamboo leaf silica; (a) before purification, (b) after purification](image-url)

Figure 1 shows silica before and after BLA purification, while unpurified bamboo leaf silica seems darker than that of the purified silica. It implies that impurities remained within the product. Therefore, purification was required to reduce impurities. In the beginning, the bamboo leaf ash consisted of silica, about 94.2%, with more than 5% of other impurities. Some major impurities that have been detected such as potassium, calcium, titanium, and chromium, with content about 0.25%, 2.07%, 0.21%, and 0.005%, respectively. Impurities will have an adverse effect on the desired superhydrophobic coating because metal impurities tend to provide water-attracting interactions so that it will have a negative effect on the desired superhydrophobic coating. So that the lower the impurity in the silica, the better the effect to produce superhydrophobic coating [5]. After the purification process was carried out, there was a significant increase in silica levels to 99.4% with the remaining impurity content of 0.6%. This gives a very strong indication that the purification process carried out to purify the silica from bamboo leaves ash has been successfully carried out.
Meanwhile, in Figure 2, the silica content in the bamboo leaf ash was also confirmed by SEM-EDX to ensure silica compound in bamboo leaf before purification. The composition of bamboo leaf ash was recorded with silica, oxygen, and carbon with 32.68 wt-%, 52.39 wt-%, and 14.93 wt-%, respectively. This result provides the information of the silica content in bamboo leaf silica is quite high. Based on the XRD visualized in Figure 3, it can be figured out that bamboo silica before the purification step has peaks at an angle of around 23°, 32°, and 45°, indicating its structure as amorphous silica (23°) with impurities such as titanium oxide (32°) and calcium oxide (45°), respectively [10,14].

Figure 2. The SEM-EDX profiles for bamboo leaf ash

Figure 3. The XRD result of bamboo leaf silica (a) diffractogram after the purification (b) diffractogram before the purification

Amorphous silica can be obtained as silica with an increased melting point and reduced impurities during the drying process [6]. The amorphous silica has a small and porous crystal size that facilitates mass transfer during the reaction with TMCS in nonpolar solvents [17]. Post purification, XRD result shows significantly different findings compared to prior silica purification. The final peak remains at
23° belonging to the amorphous bamboo leaf silica [10,14], while the other peaks (32° and 45°) disappeared. It is expected that the disappearance of impurities peak was resulted from the purification process by dissolving impurities in acid solution.

Surface and texture analysis of the bamboo leaf silica were confirmed by BET analysis to measure the surface area, pore-volume, and pore radius of bamboo leaf silica. The summary of BET analysis was listed in Table 1.

| Parameter         | Value            |
|-------------------|------------------|
| Surface area      | 159.224 m²/g     |
| Pore volume       | 0.235 cc/g       |
| Pore radius       | 15.839 Å         |

The surface area of the bamboo leaf silica attained at 159.224 m²/gram. The surface was recognized as larger than that of silica sand [12]. The amorphous structure of bamboo leaf silica can also be lower in hardness than that of the silica sand. Furthermore, it eases the milling process to shrink the particle size of bamboo leaf silica, thus provides a large surface area, which may increase the reactivity and solubility of silica [18]. The bamboo leaf silica possessed a large surface area that may react completely with TMCS. Its physical property could produce transparent layers on materials with a high contact angle [19]. Regarding the pore diameter of the bamboo leaf silica (3 nm), the silica can be classified as mesoporous silica-supported by sorption isotherm data with the hysteresis [20,21,22]. It can be seen in Figure 4.

![Figure 4](image)

**Figure 4.** The sorption isotherm hysteresis of purified bamboo silica based on BJH analysis of BET classified as the type V material.

Figure 5 shows SEM images of purified silica from bamboo leaf ash. The silica particles are distributed in various sizes. However, as shown in Figure 5, most silica particles are smaller than 100 nm creating a porous structure. It may also affect the reaction rate between bamboo leaf silica and TMCS as the surface modification agent. Larger porosity provides a larger surface area to speed up the surface-modification reaction to change bamboo leaf silica characteristics into superhydrophobic [23].
3.2. Effects of solvents type and bamboo leaf silica concentration to the hydrophobicity

The coating solution was applied on a zinc plate with a TMCS of 13 %-v/v. Previous research confirmed that the solvent types and silica concentration had been revealed as a significant impact on the hydrophobicity [5]. Superhydrophobic criteria were confirmed with the contact angle up to 150° [12]. In Figure 7, higher bamboo leaf silica concentration results in a higher contact angle for all solvent types. In the beginning, with 0.1 %-w/v silica concentration, the contact angle was obtained in a similar result, around 100°. The contact angle increased sharply for n-hexane solvent by increasing silica concentration, while smoothly increased for cyclohexane and isooctane. From Figure 6, using n-hexane with 1.75 %-w/v can attain a contact angle of 180°.

Meanwhile, both other solvents achieved a maximum contact angle of 180° at a silica concentration of 3 %-w/v. Distinguished results may be due to the different dielectric constant of the used aprotic solvents. The different dielectric constant of solvents releases different power [24]. The order of high to low in dielectric constant is reflected by isooctane (2.2), cyclohexane (2.01), and n-hexane (1.9) [25]. Therefore, this study's efficient and effective method attained the formulation of 1.75 %-w/v of bamboo leaf silica, 13 %-v/v of TMCS with n-hexane as the solvent. TMCS has a polar functional group of chloride [21], which can change the polarity of modified bamboo leaf silica, thus decreasing its hydrophobicity. This phenomenon is also found in previous research, i.e., lower concentration of silica, resulting in lower hydrophobicity [5].

Due to polarity differences of n-hexane, cyclohexane, and isooctane solvents, the isooctane solvent in silica coating preparation released less hydrophobic than other solvents of n-hexane and cyclohexane. N-hexane and cyclohexane with polarity index ~0.1 and 0.2 may inhibit the solvent's interaction with various polar test solutes compared to isooctane with a 0.25 polarity index [26]. N-hexane can effectively dissolve the nonpolar silica in releasing a superhydrophobic surface. This result was complied by other surface modification process studies carried out using a mixture of TMCS and n-hexane. The mentioned studies found that these compounds may stabilize, creating a stable and robust silica structure [27,28].

Surface morphology between before and after superhydrophobic bamboo leaf silica coating onto zinc plate using the best formulation of 3% bamboo leaf silica with solvent n-hexane and TMCS 13 %-v/v can be reflected in Figure 7. Based on Figure 8, before the coating process, the material surface seems clear and has a flat surface, while the surface becomes rough and rug after coating. This result indicates that the modified bamboo leaf silica has successfully attached to the spray coating method's material surface. It may be explained by the fact that the modified bamboo leaf silica particle from the superhydrophobic solution appeared after the coating process and without loss during the curing process.
This finding further supported the idea of the previous study [5]. The rough surface of the material will prevent the droplet of water from sticking on the material surface. Because of this reason, the superhydrophobic coating could prevent and improve the material resistance by preventing the oxidation process caused by water.

![Figure 6. The contact angle of coating applied on zinc plate](image)

**Figure 6.** The contact angle of coating applied on zinc plate

![Figure 7. SEM analysis of zinc plate surface: (a) before application of superhydrophobic bamboo leaf silica coating (b) after application of superhydrophobic leaf silica coating](image)

**Figure 7.** SEM analysis of zinc plate surface: (a) before application of superhydrophobic bamboo leaf silica coating (b) after application of superhydrophobic leaf silica coating

FTIR analysis was conducted on bamboo leaf silica before and after it was synthesized into the superhydrophobic coating to evaluate functional groups' changes in bamboo leaf silica modification. The result can be seen in Fig. 8.
Specific characteristics peaks such as hydroxyl (-OH) and silanol (Si-OH) group in Fig. 8 present on both superhydrophobic bamboo leaf silica and bamboo leaf silica. The presence of -OH groups in silanols makes the silica hydrophilic and may cause aggregates due to hydrogen bonds between two neighboring particles [29]. Meanwhile, modified bamboo leaf silica has a lower peak of -OH and Si-OH groups. With the loss of these groups, hydrogen bonds between two silica particles and water from the environment are inhibited, contributing to its superhydrophobic property. Some comparable results may be seen in other studies [30-33]. The normalization of both FTIR curves can determine the changing quantity of functional groups caused by the surface modification reaction between TMCS and bamboo leaf silica, becoming the superhydrophobic bamboo leaf silica [34]. Based on the normalized FTIR curves, it can be calculated the relative changing of the two most important functional groups caused superhydrophobic property. Si-O-Si/OH and Si-C/OH. The ratio of both functional groups in bamboo leaf silica (BLS) was lower than superhydrophobic bamboo leaf silica (SBLS) that has reacted with TMCS. It means the quantity of the Si-O-Si and Si-C group after the reaction with TMCS was increasing. The only substance that could increase this substance was expected as TMCS. Another argument, there are no other chemicals that contain Si-O-Si and Si-C except TMCS. This changing of quantity has proved that the reaction was palpable, and both FTIR spectra show the evidence. Moreover, this evidence can be seen in Table 2.

| The ratio of peak area | BLS | SBLS |
|-----------------------|-----|------|
| Si-O-Si/OH            | 1.82| 3.33 |
| Si-C/OH               | 0.55| 1.83 |

Fig. 10 (a), (b), (c) show several results of surface analyses by using SEM EDX Mapping to provide a diagnose of coating and materials compounds [34]. This paper provides the uncoated, the tested-coated, and the coated zinc plate. The result showed that there were different components between uncoated and coated zinc. The uncoated zinc consisted of O, Al, Fe, and Zn as the main compound. Further comparison can be seen that the silica percentage in the coated sample was higher than that of
the coated with an assessment. The SEM EDX Mapping results that the coating-based silica particle with TMCS was embedded in the zinc plate. Further evidence, the surface morphology of the zinc plate with silica coating was better homogenous. The detailed evidence can be seen in the following graph of SEM EDX with a magnification of 40,000 (i), and 40,000, including mapping (ii).

Figure 9-a. SEM-EDX analysis with mapping for the uncoated sample

Figure 9-b. SEM-EDX analysis with mapping for the coated sample

Figure 9-c. SEM-EDX analysis with mapping for tested coated sample

4. Conclusion
This study set out to determine utilizing bamboo leaf silica as the raw material for superhydrophobic coating. Based on the results mentioned earlier, this paper can be summed up in the following: The final characteristic of purified bamboo leaf silica was obtained 99.4% in purity with an amorphous structure and average particle size of 100 nm. It also found that the surface area achieved at 159.224 m²/gram was considered as the raw material for superhydrophobic coating and was classified as mesoporous silica concerning sorption isotherm curve. The efficient and effective formulation of the superhydrophobic coating was attained by applying n-hexane solvent, 13 %-v/v TMCS, 1.75 %-w/v of bamboo leaf silica with 180° of contact angle.

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