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Article

Hydrophobic Coating Synthesized from Palm Oil Based Waste Ash

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Abstract: Commercial silica is widely used in coating industries to create hydrophobic surfaces. However, it involves high production costs and an unhealthy fabrication process. One of the greeners approaches to producing silica is by extracting this substance from unwanted agriculture waste. In this research, organic-based silane, stearic acid, is used to modify the hydrophilic nature of silica to be used as a hydrophobic coating at a lower cost as compared to that associated with fluoro-based silane. The main objective of this work was to investigate the effects of stearic acid silane concentration on hydrophobic properties of the silica produced upon treatment. The silica was obtained from waste palm kernel (PK), and waste palm kernel fiber (PKF) collected from local palm oil mill. In order to extract silica from the raw feedstock, these materials were thermally decomposed into ash before treated with citric acid to remove undesirable contaminants. The stearic acid modification was then conducted on the silica ash, and the mixture was then sprayed on 3M-adhesive glass slides for further analysis. Zeta-sizer, SEM, XRF, and contact angle measurements were performed on the silica ash and coating samples. The results showed that the silica ash produced is within the nano-size range (835 nm), which is favorable to create high hydrophobicity. XRF analyses on the ash samples revealed higher silica content in PKF (93.6%) than that in PK (73.4%). In the hydrophobicity test, a higher contact angle was demonstrated when higher stearic acid concentration was used. This work ultimately shows PKF ash modified with stearic acid has good potential to be an alternative for commercial silica in the hydrophobic coating industry since it is renewable, inexpensive to produce, and environmentally friendly.

Keywords: agriculture waste; hydrophobic coating; palm oil; renewable alternative.

1. Introduction

Hydrophobicity properties have gain attention recently due to its vast functionality towards various industries [1]. Thanks to its self-cleaning and anti-corrosion characteristics, it aids in the paint industry to produce a hydrophobic coating on the wall, concrete, and construction industry, which produces hydrophobic cement, which prevents ingress of water during the rainy season [2]. In nature, there are many examples of materials that exhibit excellent hydrophobicity properties. One of the best examples is lotus leaf, which demonstrated a water contact angle (WCA) of more than 150^{O} [3].

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This is due to fine branch-like nanostructures on every micro-papilla on the surface of the leaf, which can induce very high WCA.

According to a research done by De Varies et al. [2], it is found that hydrophobic treatment will be able to reduce the ingress of water into concrete up to 90%, while at the same time prevent penetration of harmful chemicals like chlorine. This is because water repellent treated concrete will reach equilibrium moisture content faster than normal concrete [2]. Other than the application of the hydrophobic coating on concrete, it can also be used in the steel industry due to its anti-corrosion property. According to Tittarelli et al. [4], steel corrosion can be prevented since water, an important prerequisite for corrosion, is prevented from penetrating the hydrophobic concrete into the reinforcing steel. Meanwhile, Marconi et al. [5] synthesized hydrophobic polyurethanes for biomedical applications. In order to create a hydrophobic coating, two major criteria have to be taken into consideration, which is low surface energy and surface roughness of coating materials [6].

Hydrophobicity can be created artificially by applying hydrophobic coating materials which exhibit low-surface energy, for example, fluoroalkyl silane (FAS) [3]. Some other examples of hydrophobic chemicals that can be applied are silane, siloxanes, and silicones [7]. It is vital in creating a rough surface to induce hydrophobicity. In this research study, green hydrophobic nanoparticles coating is a major concern. Artificial hydrophobic nanoparticles can be obtained from green materials such as agricultural wastes. In recent years, since the fabrication of commercial nanoparticles is costly [1], alternatives are preferred in producing SiO from waste materials. Many researchers have taken the initiative in utilizing waste materials to extract silica content in order to produce lower-cost silica particles and, at the same time, solving potential environmental issue [1, 8-11]. The most commonly used waste material is rice husk ash (RHA) due to its high silica content, up to 97.5wt% [1]. Other examples of waste used to generate super-hydrophobicity are waste orange peel (149.2^0) and waste paper sludge ash (PSA) (153.0^0) [10-11].

In this research, palm oil-based waste is proposed as another alternative source of silica particles in fabricating hydrophobic coating. This is because palm oil-based ash contains almost 50% of silica-based material [12]. The majority percentage of silica content in palm oil-based waste ash might be a potential alternative to the preparation of hydrophobic coating. Besides, as Malaysia is the second-largest exporter of palm oil products, hence the biomass produced from the industry has raised concern among society. In 2017, it was estimated that around 51.19 million tonnes of oil palm biomass wastes were produced from the oil palm industry, which consists of empty fruit brunches, palm kernel shells, and trunk [13]. Hence, palm oil-based waste ash can be a potential alternative source towards expensive commercial nanoparticles production. Furthermore, during the modification of silica particles from hydrophilic to hydrophobic, stearic acid (SA) is used instead of a fluoropolymer due to its lower cost and non-toxic characteristic [14]. Therefore, instead of using a fluoropolymer, SA is used to investigate its potential as an alternative towards fluoropolymer, also inevitably, aid in -hydrophobic coating industry to lower their cost of production. Different concentrations of stearic acid will be used to determine the optimum ratio of stearic acid needed and to the amount of silica input. Hence, the objective of this research is to prepare green hydrophobic coating from palm oil-based waste and to measure the effect of SA concentration on the hydrophobicity of the modified surface.

2. Materials and Methods

2.1. Materials.

Palm kernel shell (PK) and palm kernel fiber (PKF) were obtained from Sime Darby Sdn. Bhd., Pulau Carey, Selangor, Malaysia. For chemicals used, anhydrous citric acid was purchased from AnalaR, absolute ethanol, and stearic acid (99 % by GC) was bought from HmbG and MERCK Millipore Sdn. Bhd., respectively, while the 3M adhesive was obtained from 3M Ptd. Ltd.

2.2. PKF and PK Preparation and Characterization.

PKF and PK were collected and washed under running tap water for at least three times. Then, both samples were dried in the oven overnight at 110^0C. Dried PKF and PK were collected and underwent citric acid treatment at the fixed concentration of 0.5M (105.07g of citric acid in 1000ml of distilled water) for 2 hours at 50^0C.

The treated raw materials were rinsed, filtered, and dried overnight. Then, the samples were calcined in a furnace at 1100 ^{0}C for 2 hours in order to obtain the ash. The ash was ground to a smaller size since nanoscale is preferable in creating roughness, which affects the hydrophobicity. XRF (Rigaku, Rix 3000) analysis was conducted to determine the type of chemical composition that existed in the ash. Scanning Electron Microscope (SEM, Phenom ProX) analysis was carried out to study the particle size range and morphology of both samples. Zeta Sizer (Malvern, Zeta Sizer Nano Range) was done to analyze the particle size quantitatively.

2.3. Coating preparation and characterization.

SA was selected for the modification process, which introduces the carbon chain group to the silica ash in order to enhance its hydrophobicity. The concentration of SA was altered (6 mM, 16 mM, 32 mM, and 64 mM). Two grams of ash was added to the solution, which underwent modification at room temperature for 5 hrs. Sonication was conducted for 30 minutes to break the ash particles into a smaller size.

The solutions with four different SA concentrations were obtained and sprayed on the glass slide, which contains a layer of 3M adhesive. When the first spraying was done, the glass slides were left to be dried in the oven. These spraying steps were repeated for at least five times to obtain full coverage of ash particles on the glass slides. The details of the samples are listed in Table 1, as shown below:

Table 1. Details of the sample used in this research.

Sample	Description
GS	Only the glass slide
3M-GS	Coating which only contains 3M adhesive (on a glass slide)
3M-PKF-GS	Coating which contains 3M adhesive and pure palm kernel fiber ash (on glass slide)
3M-PKF-SA-6-GS	Coating which contains 3M adhesive and modified palm kernel ash with 6mM of stearic acid. (on a glass slide)
3M-PKF-SA-16-GS	Coating which contains 3M adhesive and modified palm kernel ash with 16mM of stearic acid. (on a glass slide)
3M-PKF-SA-32-GS	Coating which contains 3M adhesive and modified palm kernel ash with 32mM of stearic acid. (on a glass slide)
3M-PKF-SA-64-GS	Coating which contains 3M adhesive and modified palm kernel ash with 64mM of stearic acid. (on a glass slide)

The coatings were later characterized by Fourier Transform Infrared (FTIR, PerkinElmer, Spectrum 400) Spectroscopy, which serves the purpose of investigating the modification effect on the ash particles. Water contact angle measurement was conducted using a goniometer (Dataphysics, OCA 15EC), which captured the water droplet image together with the angle contacted to the surface.

3. Results and Discussion

3.1. Ash Characterization.

The first analysis conducted was the XRF analysis, which examined the chemical components in the ash obtained from calcination in the furnace. The color of the ash obtained was in a mixture of orange and white color, which indicate the presence of iron (Fe_2O_3) and silica (SiO_2) particles in it as there are two raw materials used for the purpose of ash characterization. Hence, the chemical composition was compared and tabulated in Table 2. It was observed that PKF contains higher silica content (93.6%), whereas PK contains only 73.4% of silica particles. However, the silica content in both materials is higher than the values reported in the literature [12]. The ash color of both samples can be observed from Figure 1(a) and 1(b), as shown below.

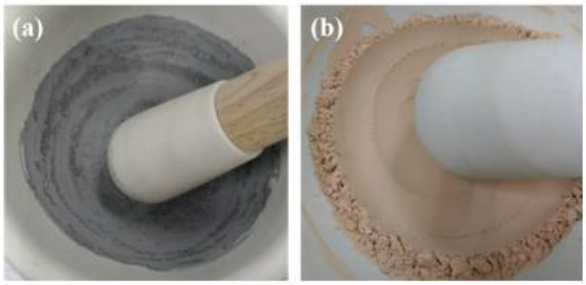

Figure 1. Ash Color: (a) PK, (b) PKF.

Table 2. XRF analysis for waste samples calcined at 1100 ºC for 2 hrs.

	Component (%)						Size (nm)
	SiO_2	Fe_2O_3	P_2O_5	Al_2O_3	K_2O	CaO	
PKF	93.60	1.91	1.79	0.91	0.72	0.60	417.70

PK	73.40	8.80	1.87	1.53	6.71	6.19	876.40

The high percentage of silica particles obtained in this research might be contributed by higher operating temperature (1100 ^{0}C) during the calcination process, whereby in the research conducted in [12], the temperature is at 600 ^{0}C. When the high temperature is used, potassium and carbon in the materials can be reduced [1]. This can be proven by the XRF analysis data in Table 2, in which the potassium content (P_2O_5) is as low as 1.8 - 1.9 % while the carbon content is not able to be detected from the XRF. The second contribution of such high purity of silica particles is due to the citric acid treatment, which aims to remove or reduce metal oxide from the raw materials (PKF and PK) [1].

Zeta-Sizer analysis was conducted to investigate the particle size quantitatively, as shown in Table 2. From the result, PKF has a smaller particle size (417.70 nm) than PK (876.40 nm), and the size of the samples is based on the average size of the ash sample, as shown in Figure 2(a) and 2(b).

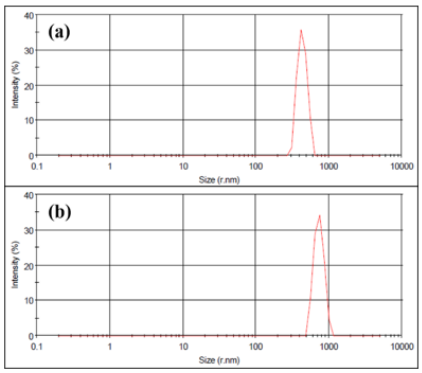

Figure 2. Zeta Sizer analysis: (a) PKF, (b) PK.

SEM was conducted to study the morphology of particle size in PKF and PK. From Figure 3(a) and 3(b), the size of PKF is smaller than PK, and hence PKF was used for the next experiment in order to obtain the highest contact angle. PK contains larger particles, which could be interpreted that a longer period of time may be needed to grind the particles as palm kernel shell is harder than palm kernel fiber and harder to break into smaller particles. It may also cause by the overheated temperature in the furnace, which induces the tendency of aggregation among particles [15].

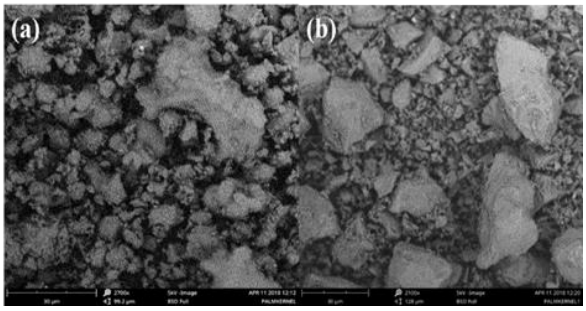

Figure 3. SEM of samples: (a) PKF, (b) PK.

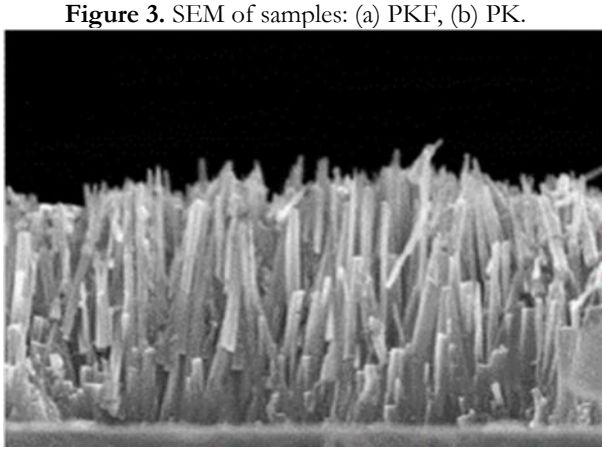

Figure 4. Cross-sectional SEM image of nanorods.

The nanoparticles size is very important in determining the surface roughness, whereby the smaller particle size will induce higher surface roughness and result in higher hydrophobicity [14]. This is because the nanorods of the particles will create roughness and entrapped air between the randomly distributed nanorods [14], as shown in Figure 4.

3.2. Characterization of Hydrophobic PKF Ash Coating.

In the modification step, PKF was treated by using SA and was sprayed onto the glass slide, which was attached with 3M adhesive in order to investigate its hydrophobicity. Before investigating its hydrophobicity, FTIR analysis was conducted to examine the type of bond that existed in the ash before modification and after the modification process. There are some important peaks observed from the FT-IR Spectra. It was observed that two constant peaks exist in both spectra, which range from 850-1200cm^{-1} and 850-950cm^{-1} [1] as observed from Figure 5(a). This peak indicates the presence of the Si-OH bond that exists in the PKF ash. As the percentage of silica found in palm kernel fiber ash was around 93% from XRF analysis, which was conducted above, hence, this further proven that palm kernel fiber contains high silica particles under appropriate acid and heat treatment.

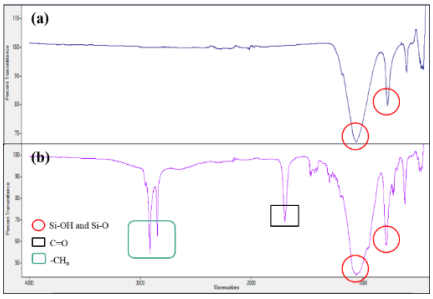

Figure 5. FTIR analysis of PKF: (a) Before SA modification, (b) After SA modification.

After SA modification, it was observed that C=O and $–CH_2$ bond exists in the ash, which indicates the success of the modification process. C=O group from SA can be observed at the range from 1600-1800cm^{-1}, while $–CH_2$ bond can be observed at the range of spectra between 2960-2850cm^{-1} [1]. These two carbon groups are originated from the long alkane chain of SA, which is believed to contribute hydrophobicity towards the modification [14]. Due to its hydrophobic characteristics, the surface energy of the modified surface can be reduced [1], and the water contact angle will be more than >90^0.

In this research, the surface wettability can be adjusted by varying the concentration of SA in the modification process. Contact angle measurement was conducted to measure the effect of SA concentration on the hydrophobicity of the modified surface, and the result is presented in Figure 6 and Figure 7.

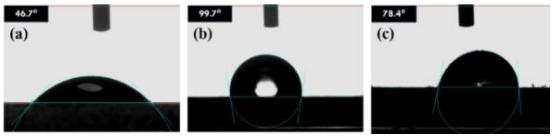

Figure 6. Water contact angle image: (a) GS, (b) 3M-GS, (c) PKF-3M-GS.

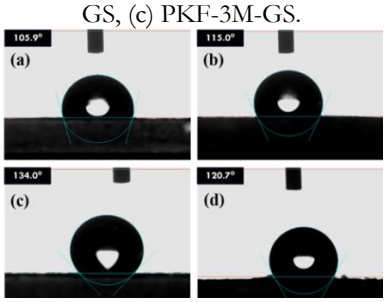

Figure 7. Water contact angle image: (a) 6mM, (b) 16mM, (c)32Mm, (d) 64Mm.

Table 3. Water contact angle on different types of samples.

Sample	Contact Angle Value (^{0})
GS	46.7
3M-GS	99.7
PKF-3M-GS	76.4
PKF-3M-SA-6mM-GS	105.9
PKF-3M-SA-16mM-GS	115.0
PKF-3M-SA-32mM-GS	134.0
PKF-3M-SA-64mM-GS	120.7

From Table 3, the PKF ash has slightly hydrophobic characteristics (<90^0) due to the presence of hydroxyl bonds (polar bond) in silica particles. Hence, modification is necessary to modify it into hydrophobic nanoparticles. The long hydrophobic alkyl chain and carboxyl group in SA reacts with the hydroxyl group from Si-OH and attached together to form hydrophobic tails which exposed to the surface. The mechanism of modification is shown below:

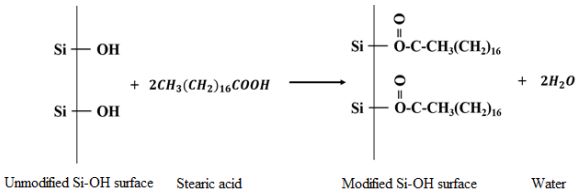

Figure 8. Modification mechanism between SA and PKF ash.

The concentration of SA was adjusted from 6 mM to 64 mM, and the water contact angle increases with the concentration. This is due to the increase in the deposition of stearate crystals on the surface, which results in higher surface roughness. Hence, the water contact angle increased. This result corresponds to the research conducted by Gurav et al., which stated that the water contact angle is affected by SA concentration [14]. Due to the accumulation of the hydroxyl group, the SiOH surface is hydrophilic in nature. With the treatment of SA on SiOH surface, the Si-stearate group will be formed and the hydrophobic tails will be exposed perpendicular to the modified surface, as shown in Figure 8. The water contact angle at 6 mM SA was only 105.9^0, as shown in Figure 7(a) due to incomplete coverage of stearate crystals on the surface. The water repellency of the surface can be increased by having a closely packed monolayer of stearate crystals whereby the hydrophobic tails are exposed to the surface [14]. Hence, the increase of SA concentration will lower the surface energy and increase the roughness of the surface layer. At 32mM, it exhibits the highest contact angle, which was 134.0^0, which can be observed from Figure

7(c). This stage can be defined as Cassie Baxter's state [16]. This is because the surface possesses low surface free energy due to full overage of stearate crystal on the surface, where the surface roughness of the nanorods entrapped the air particles, which partially support the water molecules on the surface [16].

When the SA concentration was increased further to 64 mM, the water contact angle decreased to 120.7^0, as shown in Figure 7(d). This is due to the overgrown stearic acid later, which interfere with the orientation of the hydrophobic tails, and extra hydrophilic heads are attached to the surface of the coating, which decreases the water contact angle greatly. This result hence complies with Wenzel's theory [17], which emphasizes the importance of surface roughness towards hydrophobic characteristics. Hence, the hydrophobicity of PKF ash can be adjusted by using various SA concentrations in the modification process.

4. Conclusions

PKF contains more silica particles then PK, and it exhibits hydrophobicity after SA modification. The PKF was treated by citric acid and undergo heat treatment at 1100 ^{0}C to produce 93.7% of silica particles. From the analysis conducted on the PKF ash, the size of the ash particles is determined, and the smaller particle sample was used. It is also confirmed that the modification process was successful, as seen from the FTIR result. It exhibits the successful grafting of a long alkyl group from SA onto PKF ash, as seen from the peak with a wavenumber of 1600-1800cm^{-1} and 2960-2850cm^{-1}. 3M adhesive was used to act as an interface for PKF ash to attach to the glass slide. Various concentration of SA was prepared, and the water contact angle was measured to investigate its effect on hydrophobicity. The highest water contact angle of 134^0 was obtained at a concentration of 32mM. Further increase in SA concentration, however, reduces the contact angle due to an uneven coating surface.

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Conflicts of Interest

The authors declare no conflict of interest.

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