Surface Modification of Nano-Biosilica Extracted from Rice Husk using A Silane Coupling Agent

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Abstract. Nano-biosilica extracted from rice husk, an abundant by-product of rice milling, has many potential applications in industry. However, the high amount of hydroxyl group in silica make it easy to adsorb moisture and form aggregates that are difficult to distribute in the hydrophobic matrices. This research aimed to modify the surface of nano-biosilica by using a coupling agent and characterize the changes in physical properties. Nano-biosilica was extracted using a sol–gel technique and treated with a silane coupling agent (bis-(triethoxy-silyl-propyl) tetrasulfide/TESPT) at concentrations of 0–20%. Characterization included colour (chromametry), weight increase (gravimetry), crystallinity (X-Ray Diffraction/XRD), microscopic structure (Scanning Electron Microscopy/SEM), functional groups (Fourier Transform–Infrared Spectroscopy/FTIR), silica content (X-Ray Fluorescence Spectroscopy/XRF), and specific pore surface area (Brunauer Emmett–Teller/BET). Crystallinity decreased with the increase in silane concentration, indicating more amorphous structures of surface-modified nano-biosilica. This was confirmed by a more porous surface structure in the silane-treated nano-biosilica as shown under SEM observation. FT-IR analysis exhibited some peaks at methylene bounds at the surface-modified nano-biosilica demonstrating its interaction with TESPT. The silica content (SiO₂) and the specific pore surface area of the treated nanobiosilica decreased, confirming the presence of TESPT on the surface. This study provides more potential applications of nano-biosilica as a filler agent.

Keywords: Nano-biosilica, surface modification, coupling agent, rice husk

1. Introduction
The high production of rice in Indonesia is accompanied by the abundance availability of husk as a rice milling by-product. However, the utilization of rice husk as high economic value products is still limited. This is due to the characteristics of rice husks which have low nutritional value, low density (volume), and relatively long time to decompose naturally. In a limited amount, rice husks are used as a plant growing medium and a source of energy (direct burning or in the form of charcoal briquettes). Furthermore, the ash from the combustion has not been fully utilized. In fact, rice husks contain high amount of silica (around 15-20%) [1-3] that can be used to produce high economic value products.

Upon complete combustion process, rice husks produce 17-20% ash [4] containing 90% - 98% silica [2,5-7]. Silica has many uses in industrial fields such as rubber filler, drug delivery agent, detergents, adhesives, electronic semiconductors, catalysts, absorbents, corrosion inhibitors, optical materials, and micro element fertilizers [1,2,8], food anti-caking, beverage purifier, and oil refining [9]. In the rubber industry, silica is widely used as a reinforcing filler which has an effect on increasing the mechanical
strength of rubber finished goods. Compared to other reinforcing fillers such as carbon black, this white silica has the advantage of being very suitable for colored rubber finished goods.

Silica from rice husk has amorphous properties, ultra fine size, and is very reactive [10]. In this paper, the silica extracted from rice husk is called as nanobiosilica for their nano size and biological origin. One of the weaknesses of nanobiosilica as a filler in rubber products is the difficulty to obtain a homogeneous distribution in the rubber matrix. This is because nanobiosilica is very polar and hydrophilic, so it is not compatible with the non-polar and hydrophobic rubber [11,12]. The hydrophilicity of nanobiosilica is contributed by the Si-OH group on the surface structure [13]. A promising approach to improve the dispersion properties of nanobiosilica and enhance its interaction with rubber polymers is by modifying the surface structure of the silica with a silane coupling agent. Bis-(triethoxysilyl) tetrasulfide (TESPT) is one of bifunctional silanes that are widely used in the process of modifying silica surfaces [12]. It has ethoxy groups and sulphur atoms that can react with hydroxyl group of nanobiosilica and with rubber matrix as vulcanizing agent, respectively [14].

Surface modification produced silica with a smaller particle size and narrower particle distribution as well as weaker silica agglomeration trends [15]. Some studies showed that surface modification of silica with TESPT prior to incorporation into rubber processing produced rubber-based product with better mechanical properties and tensile strength [16,17]). In this research, nanobiosilica was treated with TESPT to modify its surface structure. Characterization on product properties were carried out to gain a better insight into the product properties for a more optimum utilization of rice husk silica.

2. Materials and Methods

2.1. Extraction of nanobiosilica from rice husk

Nanobiosilica was extracted from rice husk using a sol-gel technique. In this technique, rice husk was transformed into rice husk ash by direct combustion at 350°C prior to extraction. The rice husk ash was mixed with sodium hydroxide solution at a ratio of 1:5 and underwent a hydrothermal extraction process at temperatures of 110-120°C, pressures of 1.5 – 2 bar for 15 mins under stirring. The mixture was filtered and the filtrate was subsequently neutralized to pH 7 by adding HCl (1 N). Upon the neutralization, gelation of the filtrate occurred. The gel was separated from the salt solution by filtration after settling down overnight. The gel was then dried at 60°C and subsequently transformed into free-flowing powder by grinding.

2.2. Surface modification of nanobiosilica

Surface modification was carried out according to the technique developed by Thongsang and Sombatsompop (2006)[18] with some modifications. The silane coupling agent (Bis[3-(triethoxysilyl)propyl] Tetrasulfide)/TESPT) was dissolved in ethanol at a concentration of 0-20% (w/v). Nanobiosilica was added into the ethanolic silane solution at a ratio of 1:2 (w/v) and mixed with a magnetic stirrer at a speed of 350 rpm for 30 mins. The solid part was separated by filtration and air dried at room temperature overnight. The remaining ethanol in the solid part was further removed by oven drying at 100°C. The residual solid (surface modified nanobiosilica) was then kept in a plastic bag for further uses.

2.3. Characterization

Surface modified nanobiosilica was characterized for its colour (chromametry), weight increase (gravimetry), crystallinity (X-Ray Diffraction/XRD), microscopic structure (Scanning Electron Microscopy/SEM), functional groups (Fourier Transform – Infrared Spectroscopy/FT-IR), silica content (X-Ray Fluorescence Spectroscopy/XRF), and specific pore surface area (Brunauer Emmett-Teller/BET).

3. Results and Discussion

3.1. Colour

Colour of surface modified nanobiosilica varied with the concentration of silane coupling agent. Lightness (L), redness (a) and Hue (H) slightly increased with the increase in silane concentration (Table 1). The presence of silane brought the colour of nanobiosilica from dull white towards slight reddish
white. These were contributed by the yellowish colour of the silane coupling agent. The white colour of nanobiosilica was of advantage for a more flexible choice of colour in the end product.

### Table 1. Colour properties of modified nanobiosilica at different silane concentrations

| Silane concentrations (%) | L     | a     | b     | C     | H˚    |
|---------------------------|-------|-------|-------|-------|-------|
| 0 (control)               | 92.92 | 4.19  | -7.49 | 8.59  | 299.20|
| 1                         | 92.74 | 4.23  | -7.54 | 8.65  | 299.29|
| 2                         | 93.20 | 4.41  | -7.49 | 8.70  | 300.49|
| 3                         | 93.20 | 4.48  | -7.30 | 8.56  | 301.58|
| 4                         | 93.43 | 4.53  | -7.34 | 8.62  | 301.66|
| 5                         | 94.67 | 5.13  | -8.17 | 9.65  | 302.13|
| 6                         | 94.85 | 5.07  | -7.97 | 9.45  | 302.46|
| 7                         | 94.77 | 5.14  | -7.76 | 9.32  | 303.56|
| 8                         | 95.22 | 5.42  | -7.65 | 9.39  | 305.44|
| 10                        | 94.16 | 4.68  | -5.63 | 7.32  | 309.73|
| 12                        | 95.72 | 5.34  | -6.88 | 8.71  | 308.12|
| 14                        | 95.89 | 5.49  | -6.93 | 8.84  | 308.38|
| 16                        | 96.45 | 5.61  | -7.59 | 9.43  | 306.47|
| 18                        | 96.11 | 5.52  | -7.54 | 9.34  | 306.22|
| 20                        | 96.32 | 6.36  | -8.48 | 10.62 | 306.32|

Note: L=lightness; a=redness; b=greenness; C=chroma; H=hue

#### 3.2. Weight increase

The weight of modified nanobiosilica increased with the rise in silane concentration (Figure 1). The increase in weight was proportional to the increase in silane concentration. At the highest concentration of silane, the weight increase reached 163.48%. These showed that the silane coupling agent was physically presented in the modified product and contributed to the final weight.

![Figure 1. Weight increase of nanobiosilica treated with different concentrations of silane](image)

#### 3.3. Crystallinity

The percentages of crystallinity of nanobiosilica treated with different concentration of silane are given in Figure 2. The increase in silane concentration gave slight decrease in nanobiosilica crystallinity.
particularly at silane concentration higher than 10%. Other studies found that surface modification did not change the crystalline structure of nanoparticles significantly [19,20,21]. The different results might be related to the high concentration of silane used in this study. The excess silane was in a free form and might contribute the non-crystalline part of the mixture. The diffractogram in Figure 3 showed that nanobiosilica had a broad peak at 2θ=22°. Nanobiosilica treated with TESPT exhibited a slight sharper peak than the un-treated one.

![Figure 2. Crystallinity of treated nanobiosilica with different silane concentration](image2)

![Figure 3. Diffractogram of un-treated and treated nanobiosilica with TESPT 4%](image3)

3.4. Microscopic Structure
Microscopic structures of nanobiosilica, both treated and un-treated, were observed using Scanning Electron Microscope (SEM). It can be seen that nanobiosilica is in the form of aggregates in the micron size. The aggregation might be associated with very fine particle size of nanobiosilica and their corresponding large surface area to size ratio which results in its high surface free energy [22]. This is also related to the interaction among silanol groups at the surface of nanobiosilica through hydrogen
bonding [16]. SEM image shows that un-treated nanobiosilica has larger particle size (Fig. 4A) than the treated ones (Fig. 4B). The smaller particle sizes was also observed in silane surface-modified fly ash [16] and silane -treated precipitated silica [15]. The un-treated nanobiosilica had a closed surface structure because of massive aggregation (Fig. 5A). Some small aggregates with open structures were found in the treated nanobiosilica (Fig. 4B). This aggregate consists of small individual particles overlapping each other in the 357 to 418 nm range (Figure 5B). These open structures might be associated with the reaction of silanol groups of silica with TESPT which reduce the occurrence of silica aggregation.

Figure 4. SEM images of un-modified nanobiosilica (A) and modified nanobiosilica at magnification of 1000x

Figure 5. SEM image of un-modified nanobiosilica (A) and modified nanobiosilica at magnification of 20,000x

3.5. Chemical structure
The structure of nanobiosilica was characterized using Fourier Transform Infra-Red (FTIR) (Figure 6). Both treated and un-treated nanobiosilica have adsorption peaks at wave numbers 3452.86 cm\(^{-1}\), 1638.74 cm\(^{-1}\), 1100.46 cm\(^{-1}\), 798.22 cm\(^{-1}\), 564.41 cm\(^{-1}\), and 469.35 cm\(^{-1}\) (Figure 5). The adsorption peaks at wavenumbers 3440 and 1650 cm\(^{-1}\) are related to the stretching and vibration of H-O-H bonds from the adsorbed water molecules. The absorbance in the range between 1000 cm\(^{-1}\) to 1150 cm\(^{-1}\) is related to the stretching of the Si-O-Si bonds [23]. In the treated nanobiosilica, peaks around 2922 cm\(^{-1}\) was detected, while in the untreated sample, the peaks were not found. The appearance of peaks at 2850 – 2900 cm\(^{-1}\) in the treated sample was attributed to the methylene (–CH\(_2\)–) bonds of the TESPT indicating a grafting between hydroxyl groups of the silica and the hydrolyzed silanol groups of TESPT [24]. Similar results were found by Li et al. (2014) [17] who identified the peaks at 2855 cm\(^{-1}\) and 2950 cm\(^{-1}\) in the surface-
modified silica samples demonstrating a successful grafting of TESPT to the surface of silica. In the untreated sample, the (–CH–) bonds were not formed so that the peaks around 2922 cm\(^{-1}\) were not observed.

3.6. Specific surface area and content of SiO\(_2\)

The specific surface area of Brunauer–Emmett–Teller (BET) of nanobiosilica changed with treatment with TESPT. As nanobiosilica has a porous structure, its interaction with TESPT might fill and close the pores. This resulted in a decrease in the BET of treated nanobiosilica from 109.84 to 79.85 m\(^2\)/g. Similar results were also observed by Li et al. [15] in the surface modified silica. The decrease in BET was related to the presence of TESPT filling out most of silica surface pore, which was attributed to the condensation reaction between hydroxyl groups of both silica and TESPT. The purity (content of SiO\(_2\)) characterized by X-ray fluorescence (XRF) was also modified with the TESPT treatment. Interaction of nanobiosilica with TESPT resulted in reduction of SiO\(_2\) content from 90.74% to 82.80%, indicating the presence of TESPT in the treated nanobiosilica.

![FTIR spectra of untreated and treated nanobiosilica](image)

**Figure 6.** FTIR spectra of untreated and treated nanobiosilica

4. Conclusion

Nanobiosilica extracted from rice husk have been successfully modified with a silane coupling agent TESPT. The surface modification was observed by some changes in characteristics of treated nanobiosilica including colour, weight, crystallinity, microstructure, chemical structure, specific surface area BET and its purity. The tendency of nanobiosilica particles to agglomerate was reduced by the interaction of silanol group of nanobiosilica with TESPT to form siloxanes. This provided more readily use of nanobiosilica as a filler agent. This study offers more potential utilization of rice husk as a source of advanced functional material.

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