SYNTHESIS OF NANOSILICA FROM PADDY HUSK ASH AND THEIR SURFACE FUNCTIONALIZATION

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ABSTRACT

Nanosilica was synthesized by a chemical precipitation process from paddy husk ash (PHA) efficiently and effectively. Surface functionalization of the silica nanoparticles was carried out with oleic acid ($C_{18}H_{34}O_2$). Scanning electron micrographs (SEM) data showed that the nanosilica particle size was in the range of 50-70 nm and they were in the agglomerate form. X-ray diffraction (XRD) analysis data revealed that synthesized nanosilica was in amorphous form showing a strong broad peak at 22.14^o (2θ). Fourier transform infrared spectroscopy (FT-IR) data supported the presence of hydrogen bonded silanol group and siloxane groups in nanosilica. Surface functionalized nanosilica with oleic acid was characterized using thermogravimetric analysis (TGA) and FT-IR methods. FT-IR experimental data showed that the modified nanosilica formed the ester bonding between silanol group in nanosilica and the carboxylic group of oleic acid with a successful functionalization.

Keywords: Nanosilica; Paddy husk ash; Oleic acid; Functionalization

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INTRODUCTION

Nanotechnology has attracted considerable scientific interest due to the new potential uses of particles in 1-100 nanometer scale (Stone *et al*. 2010). At the nanoscale, physical, chemical, and biological properties differ from the properties of individual atoms and molecules of bulk matter. Therefore, it provides opportunity to develop new classes of advanced materials which meet the demands from high-tech applications (Kharisov *et al*. 2010). Thus, industries may be able to re-engineer many existing products that function at unprecedented levels. A quickly growing range of applications of nanomaterials in many fields has been observed in recent years (Kharisov *et al*. 2010). Among them, nanosilica is a widely used nanomaterial with applications in polymer, adhesives, fiber optic strands, sealants, inks, paints, coatings, cosmetics, food additive and in cement-based building materials (Hessien *et al*. 2009). Nanosilica is one of the most common nanofillers used in the preparation of nanocomposites (Dorigato *et al*. 2012). Low valued silica bearing natural resources are converted into value added marketable types of silica by various processes (Zaky *et al*. 2008). The resulting silica products are generally classified based on their properties and include nanosilica, fumed silica, precipitated silica, colloidal silica and silica gels (Jal *et al*. 2004). The applications of nanosilica ultimately depend on the surface chemistry, molecular structure, morphology and porosities (Sun *et al*. 2004). Therefore, the modification of silica nanoparticles to enhance the surface chemical and physical properties is the key for the successful applications of the material (Guo *et al*. 2008).

Burning paddy husks as fuel to generate energy results paddy husk ash (PHA) as a waste product. PHA is rich in silica (more than 60%) and can be used as an economically viable raw material for the production of silica and nanosilica as value added products (Kalapathy *et al*. 2000). At present, nanoscale silica materials are synthesized using several methods, including precipitation from sodium silicate, sol-gel route, templated synthesis, synthesis using emulsions, and bioinspired methods (Liou *et al*. 2010). It is however unclear how these methods are suited for synthesizing nanosilica for a given application by a given silica source. Furthermore,

these synthetic methods compare with those employed industrially are required to be assessed (Kalapathy *et al*. 2000). As an agricultural country, Sri Lanka produces tones of paddy husk annually during the post harvesting process. The beneficiation of paddy husk has been used in many applications (Shelke *et al*. 2010). Therefore, the present investigation is intended to synthesize nanoslica from PHA using efficient chemical precipitation methods and characterize of nanosilica synthesized. Surface modification of nanosilica particles is carried out with oleic acid to improve the compatibility between inorganic silica nanoparticles and organic matrix for the applications in polymer engineered materials and compounds.

MATERIALS AND METHODS

White rice paddy husk ash (PHA) collected from Kaduwela area in Sri Lanka was used in this research study. Analytical grade amorphous nanosilica (<30 nm) from Sigma-Aldrich was used as the standard nanosilica sample. Sodium hydroxide, ammonium hydroxide, sulfuric acid, oleic acid, n-heptane and ethanol used were of analytical grade. X-ray diffraction (XRD) analysis was carried out using Brucker D-8 Focus X-ray diffractometer. Scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) analyses were carried by using Hitachi SU 6600 FE-SEM to ascertain morphology and the elemental composition of samples respectively. Fourier transform infrared spectroscopy (FT-IR) data were obtained from the Diffused Reflectance mode by using Bruker Vertex80 coupled with Ram-FT module (RAM II) spectrometer. Thermogravimetric analysis (TGA) of the samples was done using TA Instruments SDTQ600 from ambient temperature to 1200 $^{\circ}$C at a rate of 10 $^{\circ}$C/min at nitrogen atmosphere.
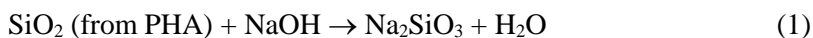
Synthesis of nanosilica

Paddy husk ash (PHA) was washed by deionized water and dried at 105 $^{\circ}$C in order to remove the moisture. Then, the dried PHA sample was burnt at 700 $^{\circ}$C for 6 hours. Ten grams (10 g) of burnt PHA was stirred in 80 mL of 3.0 M NaOH solution and the mixture was boiled for 3 hours. The solution was filtered and the residue was washed with 20 mL deionized water. The filtrate was allowed to cool down to room

temperature and 2.5 M H_2SO_4 acid was added until the pH of the solution becomes pH 2 and followed by NH_4OH until pH 8.5 at room temperature. The filtrate was then dried at 120 $^{\circ}$C for 12 hours. The resulted sample was powdered and pure silica sample was extracted by refluxing with 6 M HCl for 4 hours. Then the silica sample was washed repeatedly with deionized water until the solution become acid free. Precipitate was separated by centrifugation. The purified silica sample was dried at 105 $^{\circ}$C for 2 hours and was subjected to EDX, XRD, FTIR, and TGA analysis.

Pure silica sample extracted from PHA was then dissolved in 3.0 M NaOH by continuous stirring for 10 hours on a magnetic stirrer. Then 0.5 M H_2SO_4 was added drop-wise to adjust pH in the range of 7.5-8.5. The precipitated silica was washed repeatedly with warm deionized water until the filtrate became alkali free. Precipitate was separated by centrifugation (9000 rpm for 1 hour). The resulted sample was dried at 50 $^{\circ}$C for 48 hours in order to obtain nanosilica. Finally, the nanosilica sample prepared was subjected to EDX, SEM, XRD, TGA and FTIR analyses.

The initial step is extraction of silica from Paddy husk ash (PHA) as sodium silicate using sodium hydroxide as shown in Eq. (1).

$$SiO_2 \text{ (from PHA)} + NaOH \rightarrow Na_2SiO_3 + H_2O \qquad (1)$$

In the second step of the process, silica is precipitated from sodium silicate using sulfuric acid as given in Eq. (2).

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O \qquad (2)$$

Functionalization of nanosilica

For the functionalization of nanosilica, 4 mL of oleic acid ($C_{18}H_{34}O_2$) was mixed with 40 mL of n-heptane and was stirred for 30 minutes at 1000 rpm. Then 100 mg of silica nanoparticles was added into the solution and was stirred for another four hours at 1000 rpm at 60 $^{\circ}$C. Oleic acid modified nanosilica particles were washed using ethanol to remove excess oleic acid and the mixture was subjected to oven dry at 60 $^{\circ}$C until the ethyl alcohol was evaporated to obtain the final product. The functionalized nanosilica was characterized by using TGA and FTIR methods.

RESULTS AND DISCUSSION

Energy dispersive X-ray spectroscopy (EDX) analysis

Table 1: **EDX analysis of different products at different steps in nanosilica synthesis process**

Element	Weight percentage (%)				
	PHA after burnt at 700 ºC	Before reflux with HCl	After reflux with HCl	Nanosilica	Oleic acid functionalized nanosilica
C	4.64	3.55	3.40	3.41	10.53
O	55.01	43.81	56.02	55.52	50.82
Na	-	25.02	-	-	-
Mg	0.59	-	-	-	-
Al	0.77	0.71	-		-
Si	35.47	13.05	40.58	41.07	38.65
P	0.94	-	-	-	-
Cl	0.09	-	-	-	-
K	1.73	0.51	-	-	-
Ca	0.53	-	-	-	-
Fe	0.21	-	-	-	-
S	-	13.35	-	-	-

Table 1 presents the chemical composition of different products at different steps throughout the synthesis process of nanosilica from PHA. According to EDX chemical analysis data, synthesized nanosilica has high chemical purity. However, 3.4% carbon can be detected in synthesized nanosilica as impurities which had come during the sample preparation step. In addition, oleic acid functionalized nanosilica has given higher percentage of carbon (10.5%) compared to the nanosilica during

EDX analysis. The intermediate silica product, before HCl acid treatment, contained 25% of Na and 13.4% of S forming Na_2SO_4 compound (Indumathi *et al*. 2011). However, the intermediate silica product after HCl acid treatment followed by a washing cycle gave only 40.6% of silican, 56% of oxygen and 3.4% of carbon. The percentage yield of nanosilica synthesized from burnt PHA at 700 $^{\circ}$C was 64%.
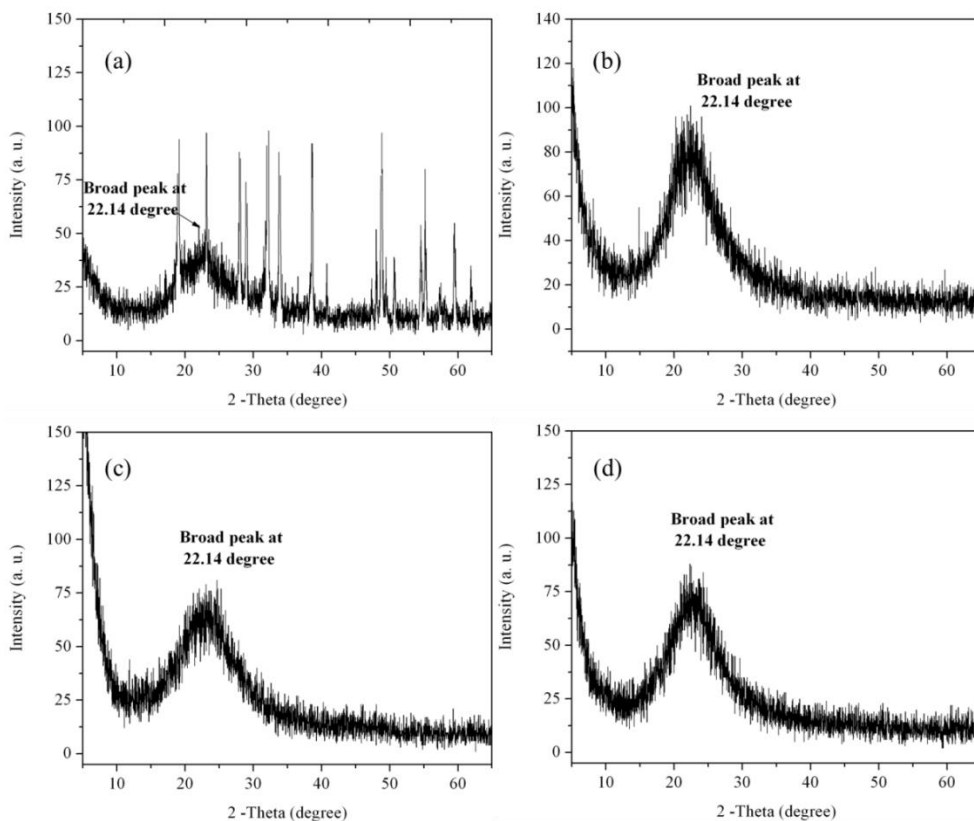
XRD analysis

Figure 1: XRD patterns of (a) silica prior to HCl acid treatment, (b) silica after HCl acid treatment, (c) nanosilica from PHA and, (d) standard nanosilica

Figure 1 shows the powder X-ray diffraction patterns of silica in the intermediate stage before refluxing with HCl (a), silica in the intermediate stage after

refluxing with HCl (b), nanosilica synthesized from PHA (c), and standard amorphous nanosilica (<30 nm) from Sigma-Aldrich (d). Figure 2(a) shows a different XRD diffractogram due to the crystalline structural peaks of sodium sulfate (Na_2SO_4), which has formed as a result of the reaction between sodium silicate and sulfuric acid. It can be removed by a simple washing process. XRD diffractograms of nanosilica synthesized from PHA in Figure 1(c) and standard nanosilica in Figure 1(d) showed strong board peaks at 22.14º (2θ) which is characteristic of amorphous silica (Singh *et al.* 2008). Therefore, nanolisica synthesized from PHA is purely amorphous type.

SEM analysis
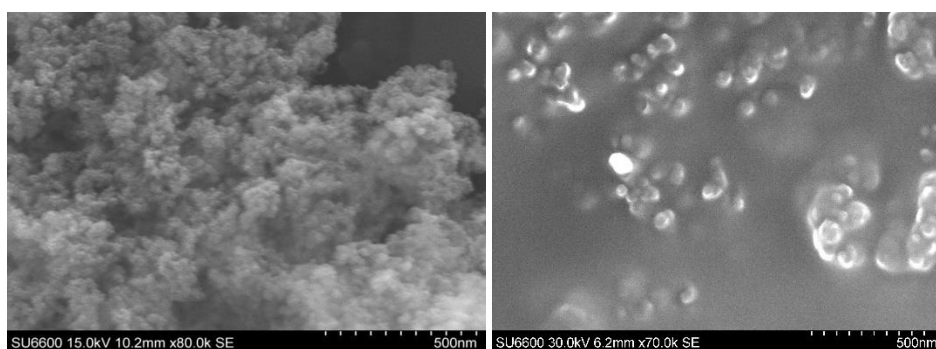
Figure 2: SEM images of the nanosilica synthesized from PHA

SEM images given in Figure 2 show the morphology and the particle size of the silica nanoparticles synthesized form PHA. According to the SEM images obtained at 15 kV and 30 kV, the particle size of the nanosilica was found to be in the range of 50-70 nm. The nanosilica particles do not show clear boundaries as they are in agglomerate and amorphous form. Therefore, SEM data confirmed that the size of the silica particles synthesized from PHA is in the nanorange (1-100 nm).

Thermogravimetric analysis

The thermogravimetric analysis (TGA) and the derivatives curves of different products at different stages in nanosilica synthesis process and the standard nanosilica (<30 nm) are shown in Figure 3. In Figure 3 (a), approximately 40% weight loss can be observed in the intermediate silica product prior to HCl acid treatment due to Na_2SO_4 formed during the reaction. However, the thermogram given in Figure 3(b) does not show a significant weight between 1100 °C-1200 °C compared to Figure3(a), as the excess Na_2SO_4 has been removed with the acid treatment followed by a washing cycles. There are two distinct mass loss steps in thomograms in Figure 3(c) and Figure 3(d). The first step (less than 130 °C) is abrupt and is most probably due to the removal of physisorbed water from the silica surface (Ek *et al*. 2001). The second step is border and is considered to correspond to slow condensation of silanols (Ek *et al*. 2001). Therefore, the TGA data showed that the synthesized nanosilica from PHA has the same characteristic properties compared to the standard amorphous nanosilica sample (<30 nm) from Sigma-Aldrich.

TGA and the derivative curves of nanosilica synthesized from PHA, pure oleic acid and, oleic acid functionalized nanosilica are shown in Figure 4. In Figure 4(a), the percentage weight loss of nanosilica synthesized from PHA is 16% whereas the percentage weight loss of oleic acid functionalized nanosilica is 9% in Figure 4(c) at 117 °C temperature. Those weight losses are due to the removal of moisture adsorbed on the surface hydroxyl groups of nanosilica. Therefore, TGA results showed that oleic acid functionalized nanosilica made less water absorption than the pure nanosilica sample indicating 7% weight loss difference between pure nanosilica and oleic acid functionalized nanosilica at 117 °C temperature. According to Figure 4(b) oleic acid is decomposed before 500 °C temperature. When nanosilica particles are functionalized with oleic acid, surface hydroxyl groups form ester bonds through carboxylic groups of oleic acid resulting hydrophobic surface which do not facilitate water molecules to be adsorbed on to the surface of the nanosilica. Still there are number of hydroxyl groups which are not modified by oleic acid. Therefore, water molecules can attach to those areas where free hydroxyl groups are existed.
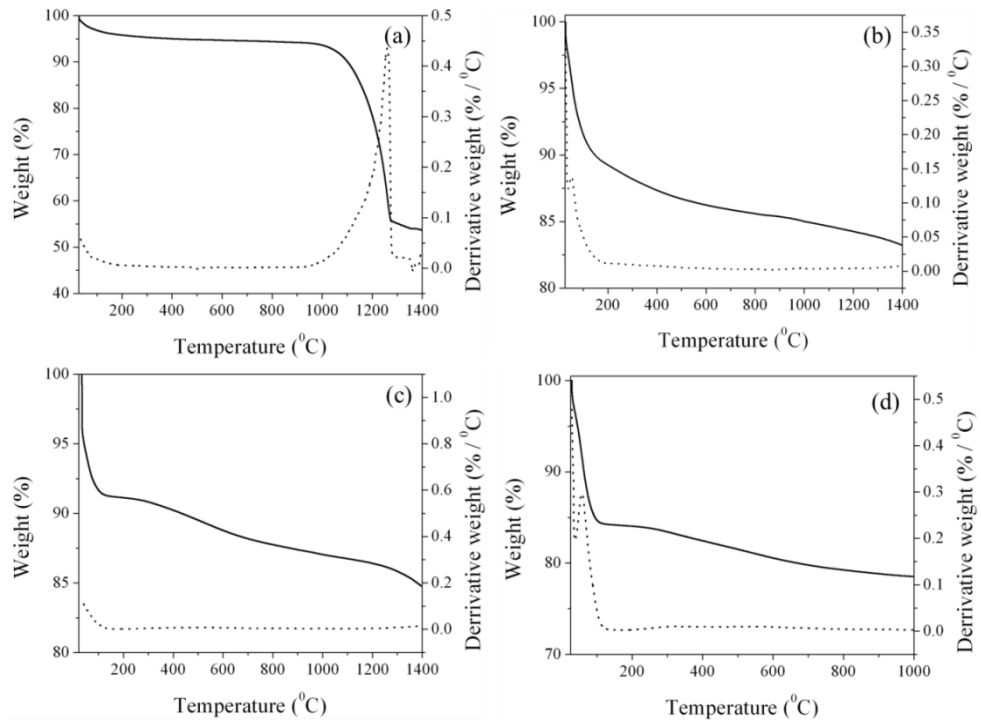
Figure 3: **TGA and the derivative curves of (a) silica prior to HCl acid treatment, (b) silica after HCl acid treatment, (c) nanosilica from PHA and, (d) standard nanosilica**

According to the thermogram given in Figure 4(c), there is a significant weight loss between 400 $^{\circ}$C and 500 $^{\circ}$C in oleic acid functionalized nanosilica compared to unmodified nanosilica in Figure 4(a). This is mainly due to the decomposition of oleic acid from the surface of the functionalized nanosilica. TGA data showed that the functionalization of nanosilica with oleic acid has been occurred successfully.
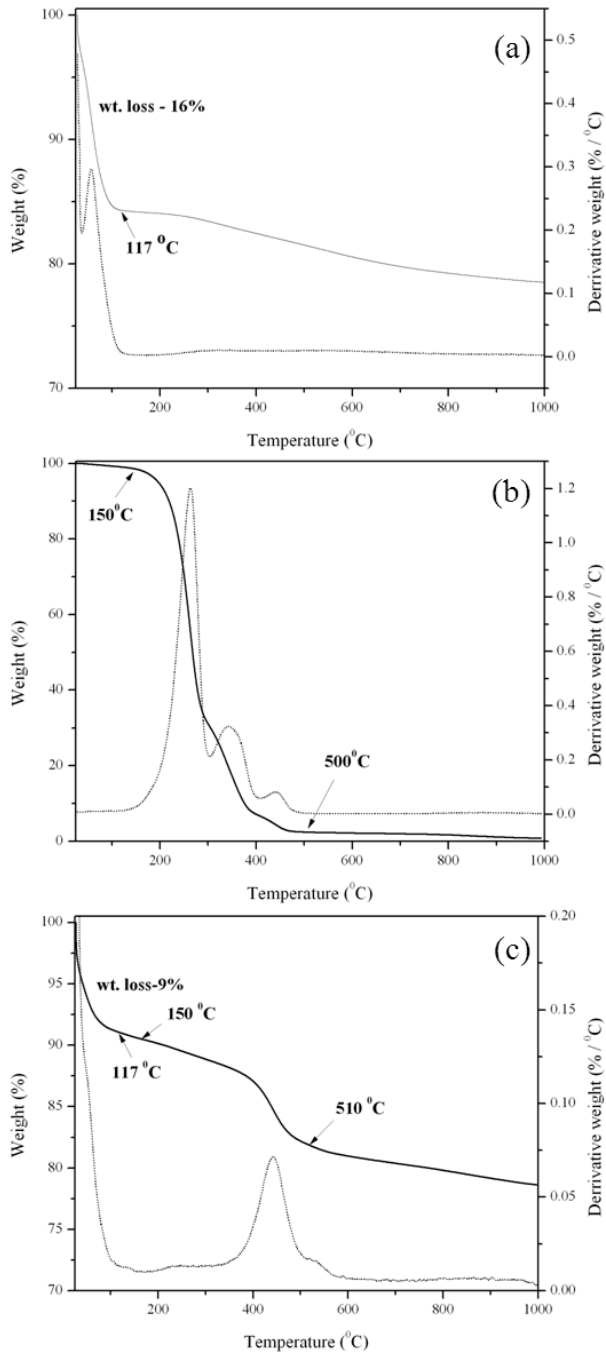
Figure 4: TGA and the derivative cures of (a) nanosilica from PHA, (b) pure oleic acid and, (c) oleic acid functionalized nanosilica
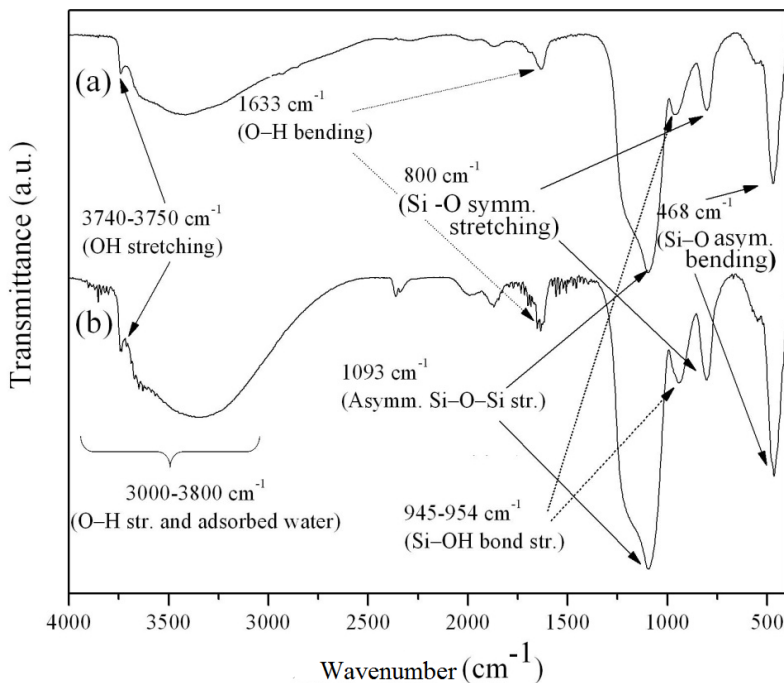
FT-IR spectroscopic analysis

Figure 5: FT-IR spectra of (a) nanosilica from PHA and, (b) standard nanosilica

Figure 5 shows the FT-IR spectra of nanosilica synthesized from PHA (a) and standard amorphous nanosilica sample (<30 nm) from Sigma-Aldrich (b). The broad band in the range of $3800 - 3000$ cm^{-1} region is mainly due to O-H stretching vibration of different kinds of hydroxyl (-OH) groups such as silanol hydroxyl groups. Research studies by Zhou *et al*. (2001) also indicated that -OH peak broadening can happen due to physically and chemically adsorbed water molecules on the SiO_2 surface. The moderately sharp peak at 3750-3740 cm^{-1} region is assigned to the stretching frequency of hydroxyl group and the peak at 1633 cm^{-1} is attributed to the bending vibration of the O-H bonds in adsorbed water molecule on the surface of nanosilica. The peak at 1093 cm^{-1} is assigned to Si-O-Si asymmetric stretching vibration and the band at 800 cm^{-1} is due to the symmetric stretching vibration of the Si-O-Si bond. The peak appeared at 468 cm^{-1} is related to bending vibration peak of the Si-O-Si bond (Guo *et al*. 2008). Therefore, FT-IR spectrum of nanosilica

synthesized from PHA clearly indicated that they are in amorphous form compared with the standard amorphous nanosilica sample given in Figure 5(b).
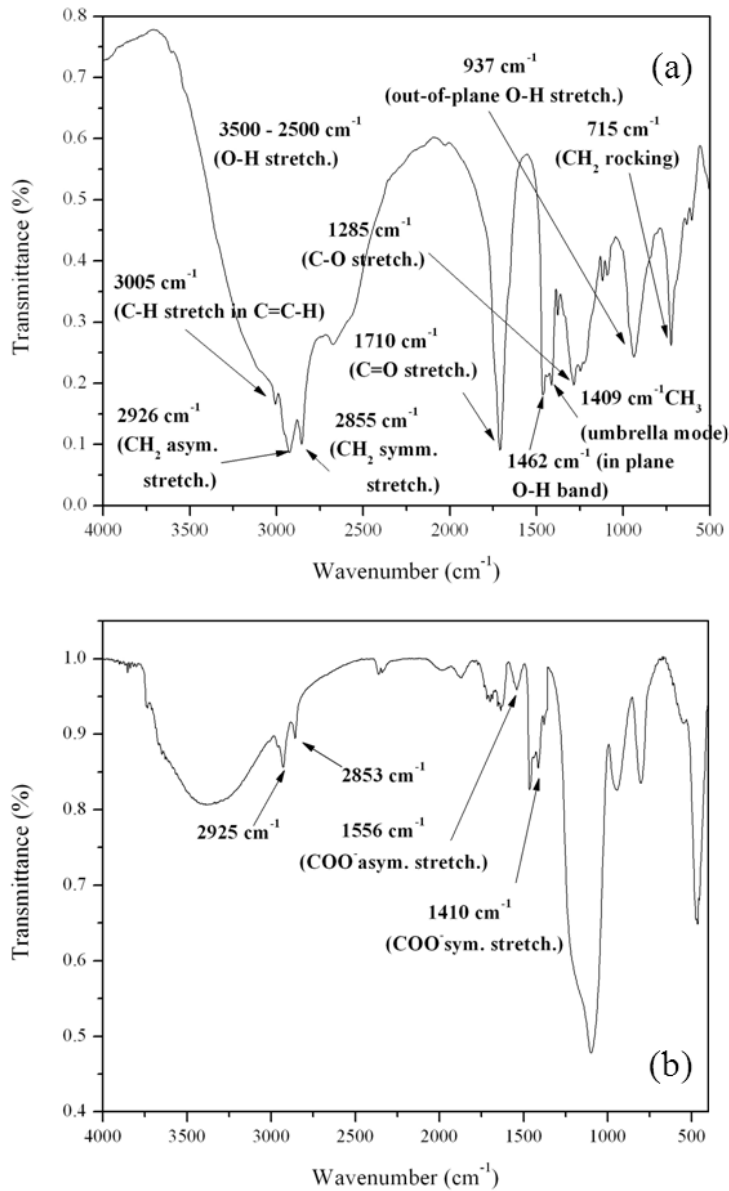

Figure 6: FTIR spectra of (a) oleic acid and, (b) oleic acid functionalized nanosilica

In order to get a better understanding of the surface functionalization of the oleic acid on the surface of silica nanoparticles, FT-IR measurements were carried

out on pure oleic acid and the nanosilica fictionalized with oleic acid. Figure 6(a) shows the FT-IR spectrum of oleic acid. The broad peak in the 3500-2500 cm^{-1} region is due to the O-H stretching of carboxylic acid groups (-COOH) (Kooter *et al*. 1997). Two sharp peaks appeared at 2855 cm^{-1} and 2926 cm^{-1} represent symmetric and asymmetric -CH$_2$ stretching vibrations respectively (Hong *et al*., 2009). The moderately sharp peak at 3005 cm^{-1}, which is superimposed with O-H stretching band, is attributed to the C-H stretching in vinyl moiety (Kooter *et al*. 1997). The sharp peak appeared at 1710 cm^{-1} is mainly due to the C=O stretching and the peak appeared at 1285 cm^{-1} is attributed to the C-O stretching of carboxylic group (Kooter *et al*. 1997).

In Figure 6(b) and Figure 5(a), both modified and unmodified nanosilica showed the bands at 1093, 800 and 468 cm^{-1} which can be assigned to –Si-O-Si- vibration modes (Guo *et al*. 2008). In Figure 6(b), two new peaks appearing at 1410 and 1556 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of COO- (Hong *et al*. 2009), while no such peaks can found in nanosilica in Figure 5(a). Oleic acid functionalized nanosilica indicated a smaller peak at 1717 cm^{-1}, which confirmed the ester bonding between silinol group and the carboxylic group of the oleic acid. Therefore, it can be concluded that the –COOH of the oleic acid has reacted with the surface –OH groups of nanosilica to form carboxylate bond (Pishvaei *et al*. 2010). In addition, the absorption peaks at 2853 and 2925cm^{-1} in Figure 6(b) are characteristic of stretching vibrations of -CH$_2$ group (Hong *et al*. 2009), which are not observed in pure nanosilica in Figure 5(a). It shows that long alkyl chains are present in the modified nanosilica with oleic acid. Therefore, FT-IR data revealed that silica nanoparticles have been successfully functionalized by oleic acid.

CONCLUSIONS

Nanosilica was synthesized from paddy husk ash (PHA) efficiently and effectively and was characterized by various analytical techniques. The percentage yield of nanosilica synthesized from burnt PHA at 700 $^{\circ}$C was 64%. SEM analysis data showed that the nanosilica particles from PHA were in the agglomerate form and the particle size was in the range of 50-70 nm. The particle shape was found to be

uniform. X-ray diffractograms showed a strong broad peak at 22.14º (2θ) indicating nanosilica synthesized from PHA was amorphous. FTIR data revealed the presence of hydrogen bonded silanol group and siloxane groups in silica. Silica nanoparticles were subjected to surface functionalization with oleic acid and characterized using TGA and FT-IR methods. TGA data indicated the thermal decomposition of oleic acid from the surface of functionalized nanosilica with a significant weight loss between 400 ºC to 500 ºC. FTIR experimental data showed that the modified nanosilica has the ester bonding between silanol group and the carboxylic group of the oleic acid. Therefore, TGA and FT-IR data revealed that silica nanoparticles have been successfully functionalized by oleic acid.

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